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CHIMIA

NEUE SCHWEIZERISCHE CHEMISCHE GESELLSCHAFT
NOUVELLE SOCIETE SUISSE DE CHIMIE
NEW SWISS CHEMICAL SOCIETY

VERLAG HELVETICA CHIMICA ACTA

Die neue Forscher**gen**eration

Molekularbiologen, Genetiker, Biotechnologen, Chemiker, Zellbiologen, Proteinchemiker, Verfahrensingenieure, Mikrobiologen, Immunologen: Das sind einige bekannte und einige weniger bekannte Berufe, die heute aus der biologischen Forschung nicht mehr wegzudenken sind. Und Berufe, die viel mit einer Technik zu tun haben, die Lösungen für bisher ungelöste Probleme möglich macht: mit Gentechnik.

SANDOZ

Forschen Entwickeln Weiterkommen

CHIMIA 48 (1994) Nr. 7/8 (Juli/August)

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CHIMIA

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für Wissenschaft, Technik und Wirtschaft im Bereich der Chemie

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Frau B. Köchli
c/o Institut für Organische Chemie der Universität Bern
Freiestrasse 3, CH–3012 Bern
Telefon 031 · 631 43 11

Geschäftsstelle der Neuen Schweizerischen Chemischen Gesellschaft
Dr. K. Gubler
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Was gibt's Neues?

EDITORIAL

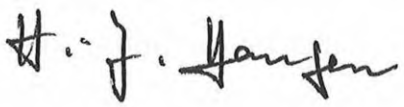
Liebe Leserin, lieber Leser,

als Wissbegierige, die sich auch – wenigstens mit halbem Blick – für das Impressum der CHIMIA interessieren, wird Ihnen nicht entgangen sein, dass sich hier etwas Wesentliches geändert hat: CHIMIA hat ein «Editorial Board» erhalten, das seit dem 1. Juli 1994 im Amte ist. Bis zu diesem Zeitpunkt war die Herausgabe der CHIMIA für die Neue Schweizerische Chemische Gesellschaft von einer kleinen Kommission wahrgenommen worden, eben der CHIMIA-Kommission, der Dr. *W. Graf, (Lonza),* Dr. *H. G. Leuenberger, (F. Hoffmann-La Roche)*, der Schreibende und *ex officio* unser Redaktor/Editor Prof. *C. Ganter* sowie zeitweise Dr. *M.V. Kisakürek* als technischer Herausgeber angehörten. Gemäss Auftrag des Präsidenten unserer Gesellschaft hatte die Kommission neben der Abwicklung der laufenden Geschäfte aber auch ein «Reglement für die Herausgabe der CHIMIA» zu verfassen und ein «Editorial Board» ins Leben zu rufen. Darüber hinaus galt es, der Tatsache Rechnung zu tragen, dass der Verlag Helvetica Chimica Acta unserer Gesellschaft in eine Aktiengesellschaft umgewandelt werden sollte, was inzwischen, am 12. Juli 1994, ja geschehen ist.

Es ist das Ziel aller, die an der Herausgabe der CHIMIA mitwirken, dass die CHIMIA umfassend über Aktivitäten und Ereignisse auf dem gesamten Gebiet der Chemie in der Schweiz berichtet und durch die Veröffentlichung attraktiver und exemplarischer Beiträge in- und ausländischer Fachkolleginnen und -kollegen ihren Leserinnen und Lesern ein aktuelles und allgemeines Bild der Chemie vermittelt. Dessenungeachtet soll CHIMIA aber auch eine Plattform der Diskussion von Wissenschafts- und Gesellschaftsfragen sein, die im Zusammenhang mit der Chemie stehen. Schliesslich sollen in der CHIMIA

vermehrt der Vorstand unserer Gesellschaft, ihre Sektionen und angeschlossenen Gesellschaften sowie ihre Kollektivmitglieder zu Worte kommen.

Es ist also ein umfangreiches Verantwortungs- und Aufgabenpaket, das dem siebenköpfigen «Editorial Board» mit auf den Weg gegeben wurde. Die Mitglieder der zurückgetretenen CHIMIA-Kommission wünschen dem jungen «Editorial Board» von ganzem Herzen alles Gute für seine Arbeit. Aber fromme Wünsche und jugendlicher Elan allein genügen nicht bei einer so vielgestaltigen und schwierigen Aufgabe wie der Herausgabe der CHIMIA, die ihre Leserinnen und Leser nicht nur postalisch erreichen soll. Deshalb bitten wir alle, nun da die Mitglieder des «Editorial Board» im Impressum erscheinen, sie in Belangen der CHIMIA anzusprechen, damit auch Sie als Leserin und Leser sich angesprochen fühlen – von unser aller Zeitschrift, der CHIMIA.



Hans-Jürgen Hansen
Vorsitzender der aufgelösten
CHIMIA-Kommission

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Neue Schweizerische Chemische Gesellschaft
Nouvelle Société Suisse de Chimie
New Swiss Chemical Society

Herbstversammlung 1994/Assemblée d'automne 1994
21. Oktober 1994/21 octobre 1994

Chemische Institute, Universität Bern/
Instituts de chimie, Université de Berne
Freiestrasse 3, 3012 Bern

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W2 *Andreas Hafner*
Konzernbereich Forschung, Ciba, Fribourg-Marly
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Anorganische Chemie und Koordinationschemie/ Chimie minérale et de coordination

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Informationen/Informations:

Keine Anmeldung erforderlich, der Eintritt ist frei.

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Pas d'inscription, l'entrée est gratuite.

Les étudiants qui sont membre de la NSSC, peuvent demander un remboursement des frais de voyage: Billet de train Berne et retour, 2e classe, 1/2 prix. Le billet doit être joint à la demande de remboursement. Veuillez indiquer l'adresse du lieu de travail et privée, le compte bancaire ou postal et joindre, si possible, un bulletin de versement. La demande est à adresser au Secrétariat de formation continue et des congrès de la NSSC, Mme *B. Köchli*, Institut de chimie organique, Université de Berne, Freiestrasse 3, CH–3012 Berne.

Sektion Chemische Forschung/Section Recherche chimique und/et Sektion Medizinische Chemie/ Section Chimie Thérapeutique

Anorganische Chemie – Koordinationschemie/ Chimie minérale et de coordination

Minisymposium:
'Inorganic Aspects of Supramolecular Chemistry'
Hörsaal/Auditoire NE 16
Chairman: ***A. Williams***
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Université de Bordeaux I
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Universität Basel
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Université de Neuchâtel
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University of Bath
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Postersession/Session des posters: Abstracts 1–75
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55 ***C. Renouard**, H. Stoeckli-Evans, G. Süss-Fink*
Institut de Chimie, Université de Neuchâtel
Dérivés cycliques de l'acide carbonimidodithioique en tant que source de carbène: fragmentation de ces ligands lors de leur coordination à un complexe trinucléaire de ruthénium

56 ***A. Neels**, H. Stoeckli-Evans, A. Escuer, R. Vicente*
Dépt. de Cristallographie, Institut de Chimie, Université de Neuchâtel
Dépt. de Quimica Inorgànica, Universitat de Barcelona
Cu^{II} Complexes of 2,5-Bis(2-pyridyl)pyrazine. – The Formation of Coordination Compounds with Interesting Magnetic Properties

57 ***R.F. Carina**, G. Bernardinelli, A.F. Williams*
Dépt. de Chimie Minérale, Analytique et Appliquée, Université de Genève
A Study of Self-Assembly About a Square Planar Pd(II) Centre

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58 ***P. Desmartin***, *G. Bernardinelli, A. F. Williams*
Dépt. de Chimie Minérale, Analytique et Appliquée, Université de Genève
Coordination Chemistry of a Functionalised Bipyridyl Ligand

59 ***L. Charbonnière***, *C. Piguet, G. Bernardinelli, A.F. Williams*
Dépt. de Chimie Minérale, Analytique et Appliquée, Université de Genève
Synthesis, Structure and Resolution of a Dicobalt(III) Triple Helix

60 *H.C.L. Abbenhuis, C. Köllner, I. Steiner,* ***A. Togni***
Laboratorium für Anorganische Chemie, ETH-Zürich
Versatile Synthesis of Optically Active Ferrocene Derivatives: Novel Chiral Modifiers for Efficient Asymmetric Hydroboration and Hydrogenation

61 *C.W. Schläpfer,* ***U. Meier***
Institut für Anorganische und Analytische Chemie, Universität Freiburg
Gegenionenkondensation von Chloridionen in Polyethyleniminlösungen pH-, $[Ni^{2+}]$- und Temperaturabhängigkeit, untersucht mit ^{35}Cl- und ^{37}Cl-NMR

62 ***P. Bonhôte***, *M.S. Wrighton*
Dept. of Chemistry, Massachusetts Institute of Technology, Cambridge, MA
Bi- and Trinuclear Ruthenium Complexes Containing Tetrapyridophenazine as a Bridging Ligand

63 *G. González,* ***N. Graeppi***, *L. Helm,* ***O. Ni Dhubhghaill, D.H. Powell, D. Pubanz***, *V. Tissières, A.E.Merbach, K. Micskei, E. Brücher*
Institut de Chimie Minérale et Analytique, Université de Lausanne
Institute of Inorganic and Analytical Chemistry, Kossuth University, Debrecen
Water Exchange on Gadolinium Based Medical MRI Contrast Agents

64 ***N. Graeppi***, *D.H. Powell, A.E. Merbach*
Institut de Chimie Minérale et Analytique, Université de Lausanne
Propylene Diamine-*N,N,N'N'*-tetraacetate (PDTA) Complexes with the Lanthanide(III) Ions: Water Exchange Kinetics Studied by ^{17}O NMR

65 ***L. Dadci***, *H. Elias,* ***U. Frey,*** *A. Hörnig, U. Kölle, A.E. Merbach, H. Paulus, J.S. Schneider*
Institut de Chimie Minérale et Analytique, Université de Lausanne
Eduard-Zintl-*Institut für Anorganische Chemie, TH Darmstadt*
Institut für Anorganische Chemie, TH Aachen
High-Pressure ^{17}O NMR Study of Water Exchange Kinetics on $[Cp^*M(H_2O)_3]^{2+}$ (M = Rh, Ir)

66 ***B. Moullet***, *G. González, M. Martinez, A.E. Merbach*
Institut de Chimie Minérale et Analytique, Université de Lausanne
Dept. de Química Inorgànica, Universitat de Barcelona
Steric Effects on Water Exchange Mechanisms of Aquapentaaminemetal(III) Complexes (M = Cr, Co, Rh). A Variable Pressure Oxygen-17 NMR Study

67 ***A. Abou-Hamdan***, *A. Roodt, J.G. Leipoldt, L. Helm, A.E. Merbach*
Institut de Chimie Minérale et Analytique, Université de Lausanne
Dept. of Chemistry, University of the Orange Free State, Bloemfontein, SA
Kinetics and Mechanism of Oxygen Exchange and Inversion Along the M=O Axis in the Diprotonated-, Monoprotonated- and Dioxotetracyanometalate Complexes of Re(V), Tc(V), W(IV), and Mo(IV)

68 ***N. Aebischer***, *G. Laurenczy, M. Ravera, D. Osella, A.E. Merbach*
Dépt. de Chimie Minérale et Analytique, Université de Lausanne
Dipt. di Chimica Inorganica, Università di Torino
Comparative Study of the Electrochemical Properties and of the Water Exchange Rate on Complexes of the Type $[Ru(H_2O)_5L]^{2+}$

69 ***Th. Kowall, F. Foglia***, *L. Helm, A.E. Merbach*
Institut de Chimie Minérale et Analytique, Université de Lausanne
Molecular Dynamics Simulation Study of Lanthanide Ions Ln(III) in Aqueous Solution Including Water Polarization – Structure and Internal Rearrangement of the First Hydration Shell

70 ***K. Bernauer***, *Ch. Nusbaumer, P. Schurmann, L. Verardo*
Institut de Chimie, Université de Neuchâtel
Laboratoire de Biologie Végétale, Université de Neuchâtel
Kinetic Stereoselectivity in the Cu^{2+} Sequestration from Native or Mutant Plastocyanins by Optically Active Ligands

71 ***C. Piguet***, *G. Hopfgartner, A.F. Williams, B. Bocquet*
Dépt. de Chimie Minérale, Analytique et Appliquée, Université de Genève
F. Hoffmann-La Roche AG, Basel
Self-Assembly of Heteronuclear Helical Complexes

72 ***P. Belser***, *Ph. Lainé*
Institut für Anorganische und Analytische Chemie, Universität Freiburg
Enantioselective Octahedral Metal Complex Formation

73 ***E.C. Plappert***, *K.-H. Dahmen, R. Hauert*
Laboratorium für Anorganische Chemie, ETH-Zürich
EMPA, Dübendorf
Growth Kinetics of TiO_2-MOCVD with Highly Volatile Ti(IV)(β-Diketonate)$_x$(OR)$_y$

74 *E.C. Plappert,* ***K.-H. Dahmen***, *H. van den Bergh, T. Stumm, R. Hauert*
Laboratorium für Anorganische Chemie, ETH-Zürich
Laboratoire de Pollution Atmosphérique et Sols, EPF-Lausanne
Laboratoire d'Optique Appliquée, EPF Lausanne
EMPA Dübendorf
Investigation and Characterization of Thin MOCVD Copper Films from Pyrazolylborato-Copper(I) Complexes

75 *F. Lang,* ***R. Frischknecht***, *K.-H. Dahmen*
Laboratorium für Anorganische Chemie, ETH Zürich
Chemical Functionalization of Surfaces by Immobilization of Organometallic Compounds

Organische Chemie und Medizinische Chemie/ Chimie organique et Chimie thérapeutique

Vorträge/Conférences: Abstracts 76–90
Hörsaal/Auditoire UG 113
10.00 Chairmen: ***R. Scheffold/P. Müller***
Institut für Organische Chemie, Universität Bern
Dépt. de Chimie Organique, Université de Genève

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15.00 Chairman: ***E. Kündig***
Dépt. de Chimie Organique, Université de Genève

76 10.00 ***U. Schwitter***, *A. Dussy, C. Elie, P. Erdmann, B. Giese*
Institut für Organische Chemie, Universität Basel
Synthese und selektive Spaltung von modifizierten Oligonucleotiden

77 10.20 ***M. Altorfer***, *Ch. Abrecht, U. Bohdal, P. Schönholzer, D. Obrecht, K. Müller*
F. Hoffmann-La Roche AG, Basel
A Novel Strategy for the Synthesis of α-Methyl(alkyl)-serines and Their Incorporation into Peptides

78 10.40 *P. Dumy, I. Ernest, J. Kapron, M. Mutter, O. Nyanguile,* ***G. Tuchscherer***
Institut de Chimie Organique, Université de Lausanne
Template Assembled Synthetic Proteins (TASP) by Chemoselective Ligation Methods

79 11.00 ***M. Thommen***, *A. Veretenov, R. Keese*
Institut für Organische Chemie, Universität Bern
Kaskadenreaktionen mit Übergangsmetallverbindungen

80 11.20 *W. Oppolzer, A.C. Spivey,* ***Ch. G. Bochet***
Dépt. de Chimie Organique, Université de Genève
Suprafacialité des cyclisations thermiques de *N*-4-alcényl-hydroxylamines: synthèses du (±)-α-lycorane et de la (+)-trianthine

81 11.40 *P. Müller,* ***P. Polleux***
Dépt. de Chimie Organique, Université de Genève
Induction asymétrique dans l'insertion intramoléculaire lors de la décomposition des diazoesters avec des catalyseurs chiraux du Rh^{II}

82 12.00 ***B. Bourdin***, *E.P. Kündig*
Dépt. de Chimie Organique, Université de Genève
Asymmetric *Diels-Alder* Reactions Catalyzed by a Chiral Iron *Lewis* Acid

83 12.20 ***G.C. Lloyd-Jones***, *A. Pfaltz*
Institut für Organische Chemie, Universität Basel
Tungsten-Catalysed Allylic Alkylation: Stereospecificity, Stereoselectivity, Mechanism

84 12.40 *M. Kägi, G. Mloston, M. Petit,* ***H. Heimgartner***
Organisch-chemisches Institut, Universität Zürich
Neue Reaktionen von Thiocarbonyl-yliden und -imiden

85 15.00 ***M.G. Wubbolts***, *J.B. van Beilen, B. Witholt*
Institut für Biotechnologie, ETH-Zürich
Enantioselective Oxidation of Unfunctionalized Olefins by Engineered Bacteria

86 15.20 ***Ch. Fehr***, *J. Galindo*
Firmenich SA, Genève
Katalytische enantioselektive Protonierung von Enolaten

87 15.40 ***J.C. Muller***, *P.H. Williams, D. Loyaux, M. Fontecave, J.L. Decout, B. Roy*
SYNTHELABO Recherche, Bagneux
Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité, Grenoble
FK 409: An Unusual Way to Store and Release Nitric Oxide

88 16.00 *F.A. Merckling,* ***P. Rüedi***
Organisch-chemisches Institut, Universität Zürich
Konfigurativ und konformativ fixierte Organophosphate als Inhibitoren der Acetylcholinesterase

89 16.20 ***A. Lendlein***, *P. Neuenschwander, U.W. Suter*
Institut für Polymere, ETH-Zürich
Synthese neuer biokompatibler und biodegradierbarer Blockcopolymere für die medizinische Anwendung

90 16.40 ***M. Reist***, *P.-A. Carrupt, B. Testa, S. Lehmann, J.-J. Hansen*
Inst. de Chimie Thérapeutique, Ecole de Pharmacie, Lausanne
Dept. of Medicinal Chemistry, Royal Danish School of Pharmacy, Copenhagen
Hydantoins as Models for Non-enzymatic Racemization of Chiral Drugs

Postersession/Session des posters: Abstracts 91–124
13.00–15.00: *1. und 2. Stock/1er et 2e étage*

91 ***A. Fretzen***, *E.P. Kündig*
Dépt. de Chimie Organique, Université de Genève
Planar chirale Aren Chromtricarbonylkomplexe *via* Alkylierung/Arylierung und Hydrid Abstraktion

92 ***A. Quattropani***, *E.P. Kündig*
Dépt. de Chimie Organique, Université de Genève
Planar Chiral Arene Tricarbonylchromium Complexes *via* Enantioselective Deprotonation/Electrophile Addition Reactions

93 ***P. Jeger***, *E.P. Kündig*
Dépt. de Chimie Organique, Université de Genève
New Aspects of C-Nucleophile Additions to Cationic $[(Arene)(Cyclopentadienyl)Fe(II)]^+$ Complexes

94 ***L.-H. Xu***, *E.P. Kündig*
Dépt. de Chimie Organique, Université de Genève
Diastereoselective Synthesis of β-Aminoacid Derivatives by Alkyl Radical Addition to α-Aminoacrylates

95 ***O. Loiseleur***, *P. Meier, A. Pfaltz*
Institut für Organische Chemie, Universität Basel
Palladium-Catalyzed Enantioselective Alkenylation of Olefins

96 *P. Müller,* ***D. Ené***
Dépt. de Chimie Organique, Université de Genève
Cyclopropanations et cyclopropénations intermoléculaires asymétriques

97 ***B. Minder***, *T. Mallat, A. Baiker,* ***T. Heinz***, *G. Wang, A. Pfaltz*
Laboratorium für Technische Chemie, ETH-Zürich
Institut für Organische Chemie, Universität Basel
Enantioselective Hydrogenation of Ethyl Pyruvate Over PT/Alumina with Novel Chiral Modifier

98 *S. Bienz,* ***S. Bratovanov***, *A. Chapeaurouge,* ***P. Huber***, *C. Syldatk*
Organisch-chemisches Institut, Universität Zürich
Institut für Bioverfahrenstechnik, Stuttgart
Synthese optisch aktiver alkoxymethyl-substituierter Silane durch Biotransformation mit der Hefe *Tigonopsis variabilis*

99 *C.W. Jefford, D. Misra, A.P. Dishington, J.C. Rossier, G. Bernardinelli,* ***G. Timári***
Dépt. de Chimie Organique, Université de Genève
Asymmetric Dihydroxylation of *cis*-Fused Cyclopenteno-1,2,4-trioxanes

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100 ***M. Gerster***, *N. Moufid, P. Renaud*
Institut de Chimie Organique, Université de Fribourg
Reactivity and Stereochemical Study of 1-(Alkoxy) and 2-(Alkoxy)alkyl Radicals Complexed with *Lewis* Acids

101 ***A. Boiron***, *Th. Tschamber, J. Streith*
Ecole Nationale Supérieure de Chimie, Université de Haute Alsace, Mulhouse
A Simple Asymmetric Synthesis of 2-Methyl-1,2-dihydropyridine and the Ensuing (D)-1,5,6-Trideoxy-5-aminoaltrose

102 ***J. Zhuo***, *H. Wyler*
Institut de Chimie Organique, Université de Lausanne
A Synthesis of 2-Ethoxy-2*H*-pyranes *via* Hetero-*Diels-Alder* Cycloaddition and their Reactivity

103 ***B. Diab***, *H. Jolibois, B. Laude, L. Ouahab, A. Chambaudet*
Laboratoire de Microanalyses Nucléaires, Université de Franche-Comté, Besançon
Nouvelle classe de composés heptacycliques préparés en une seule étape à partir de sels de flavylium

104 ***A. Franz***, *Y. Rubin. R. Neier*
Institut de Chimie, Université de Neuchâtel
Tandemreaktion von *N*-Butadienyl-*N*-Alkylketen-*N,O*-Silylacetalen

105 ***M. Schreiber***, *J. Anthony, F. Diederich, C. Boudon, J.P. Gisselbrecht, M. Gross*
Laboratorium für Organische Chemie, ETH-Zürich
Nanoscale Carbon-Rich Rods

106 ***R. Hannak***, *T. Derer, W. Mühlecker, R. Konrat, B. Kräutler*
Institut für Organische Chemie, Universität Innsbruck
An Organometallic Rotaxane

107 ***S. Hemamalini***, *R. Scheffold*
Institut für Organische Chemie, Universität Bern
Synthesis of (+)-Multifidene

108 ***A. Baudat***, *P. Vogel*
Section de Chimie, Université de Lausanne
Total Asymmetric Synthesis of (11*R*,12*S*,13*S*)-Trihydroxy-9(Z),15(Z)-octadecadienoic Acid, a Self-Defensive Agent Against Rice Blast Disease

109 *H. Bertschy,* ***A. Chaperon***, *R. Neier*
Institut de Chimie, Université de Neuchâtel
Eine neue, 6-stufige Synthese von Porphobilinogen – Realisierung eines biomimetischen Konzeptes

110 ***S. Abazi***, *J.P. Vionnet, P. Renaud*
Institut de Chimie Organique, Université de Fribourg
Use of O,Se-Acetals for Radical Mediated Phenylselenenyl Group Transfer Reactions

111 ***M. Mayor***, *A. Hagfeldt, M. Grätzel, L. Walder*
Institut für Organische Chemie, Universität Bern
Institut de Chimie Physique II, EPF-Lausanne
Photo-Electrosynthesis on Nanocrystalline TiO_2-Electrodes Modified with Vitamin B_{12}

112 ***N. Burki***, *R. Tabacchi*
Institut de Chimie, Université de Neuchâtel
Isolation of Phytotoxic Metabolites from Culture Medium of *Ceratocystis fimbriata* f.sp. *platani*

113 *W.-G. Ma,* ***N. Fuzzati***, *J.-L. Wolfender, K. Hostettmann, C.-R. Yang*
Institut de Pharmacognosie et Phytochimie, Université de Lausanne
Kunming Institute of Botany, Chinese Academy of Science, Kunming
A New Type of Acylated Secoiridoid Glycoside from *Gentiana rhodentha*

114 *A. Hädener,* ***A. Niemann-Leibundgut***
Institut für Organische Chemie, Universität Basel
A Kinetic Analysis of the Reaction Catalysed by Porphobilinogen Deaminase (PBGD) from *Escherichia coli*

115 ***A. Nefzi***, *T. Wöhr, T. Haack, D. Ryan, M. Mutter*
Institut de Chimie Organique, Université de Lausanne
Pseudo-Prolines in Peptide Synthesis

116 ***B. Hinzen***, *F. Diederich*
Laboratorium für Organische Chemie, ETH-Zentrum
De Novo Design of Macrocyclic Amino Acid Receptors as Synthetic Vancomycin-Analogs

117 ***Ch. Bisang***, *Ch. Weber, J.A. Robinson*
Organisch-chemisches Institut, Universität Zürich
Stabilization of β-Turn Conformations in the NPNA-Repeat Motif of a Synthetic Malaria Vaccine

118 ***K. Burkhardt***, *N. Philippon, A. Birch, A. Leiser, J.A. Robinson*
Organisch-chemisches Institut, Universität Zürich
Coenzyme B_{12}-Dependent Methylmalonyl-CoA Mutase from *Streptomyces cinnamonensis*. Isolation of the Enzyme and Cloning and Sequencing of Its Structural Gene

119 ***P. Strazewski***, *A. Amantea, M. Walser*
Institut für Organische Chemie, Universität Basel
Calculating the Thermodynamics of Weakly Interacting H-Bonded Complexes from ^{15}N-NMR Spectroscopical Data

120 ***Ch. de Haën***, *E. Felder, F. Uggeri, A. Gallotti*
Bracco SpA, Milano
Synthesis, Atropisomerism, Crystal Structure and Albumin Binding of the Gadolinium Chelate Gd-BOPTA/Dimeg, a Liver-Specific Contrast Agent for Magnetic Resonance Imaging

121 **R. *Breckenridge***, ***I. Lewis***, *C. Bruns*
Sandoz Pharma AG, Basel
Molecular Modelling of Somatostatin Analogues Incorporating Nucleo Amino Acids

122 ***G. Sabbioni***
Institut für Toxikologie, Universität Würzburg
Prediction of Hemoglobin Binding, Carcinogenicity and Mutagenicity of Arylamines and Nitroarenes

123 ***F. Billois***, *P.-A. Carrupt, P.G. Strange, B. Testa*
Institut de Chimie Thérapeutique, Ecole de Pharmacie, Université de Lausanne
Biological Laboratory, University, Canterbury, Kent
Molecular Modelling of D_2-Like Dopamine Receptors

124 ***P. Weber***, *P.-A. Carrupt, J. Paris, D. Gerlier, Ch. Rabourdin-Combe, L. Ettouati, B. Testa*
Institut de Chimie Thérapeutique, Ecole de Pharmacie, Université de Lausanne
Laboratoire de Chimie Thérapeutique, Faculté de Pharmacie, Université de Lyon I
Immunité et Infections Virales, CNRS-UCBL, Lyon
Immunologie Moléculaire, CNRS-ENS, Lyon
Molecular Modelling and QSAR Study of the Binding of HEL (52–61) and Related Peptides by I-A^k Class II Mhc Molecule

Physikalische Chemie/Chimie physique

Vorträge/Communications: Abstracts 125–133
Hörsaal/Auditoire S 481, 4. Stock Süd/4e étage sud

125 10.00 ***M.-A. Thelen***, *P. Felder*
Physikalisch-chemisches Institut, Universität Zürich
Photodissociation of CF_3Br Studied in the First UV-Band

126 10.20 ***E. Kades***, *M. Rösslein, J.R. Huber*
Physikalisch-chemisches Institut, Universität Zürich
From Monomers to Clusters: Photodissociation of RONO and $[RONO]_n$

127 10.40 ***W. Mohr***, *S. Leutwyler*
Inst. für Anorg., Analyt. und Physikal. Chemie, Universität Bern
Large Amplitude Motions of the Phenol · $(NH_3)_n$ $n = 1, 2$ Clusters

128 11.00 *F. Arnaud*, ***S. Fanni***, *M.J. Schwing*
EHICS, Laboratoire de Chimie Physique, Strasbourg
A Study of the Cs^+/Na^+ Selectivity in Calixcrowns

129 11.20 ***S.H. Bossmann***, *I. Koptyug, N.J. Turro, A.M. Braun*
Lehrstuhl für Umweltmesstechnik, Universität Karlsruhe
Columbia University in the City of New York
FT-ESR Studien in mikroheterogenen Systemen

130 11.40 ***C. Blättler***, *H. Paul*
Physikalisch-chemisches Institut, Universität Zürich
ESR Messung der Reaktionskinetik spinpolarisierter Radikale in Konkurrenz zur Relaxation

131 12.00 ***H. Dilger***, *E. Roduner, M. Schwager, I.D. Reid, D.G. Fleming*
Physikalisch-chemisches Institut, Universität Zürich
Paul Scherrer Institut, Villigen PSI
TRIUMF and Dept. of Chemistry, University of British Columbia, Vancouver
Chemische Reaktion und Spinaustausch zwischen dem Ethylradikal und Sauerstoff in der Gasphase

132 12.20 ***O. Haas***, *Ch. Velasquez, Z. Porat, R.W. Murray*
Paul Scherrer Institut, Villigen PSI
Kenan *Laboratories of Chemistry, Univ. of N. Carolina, Chapel Hill, NC*
Electrochemical Measurements of Diffusion Coefficients of Redox-Labelled Poly(ether) Dissolved in Poly(ether) Electrolyte Melts

133 12.40 ***P. Bonhôte***, *M. Grätzel, M. Jirousek, P. Liska, N. Pappas, N. Vlachopoulos, L. Walder*
Institut de Chimie Physique II, EPF-Lausanne
Redox Mediators for Electrochemical Photovoltaic Cells Based on Dye-sensitized TiO_2 Electrodes

Postersession/Session des posters: Abstracts 134–143
14.30–17.00: *4. Stock/4e étage*

134 ***P. Voumard***, *R. Zenobi, Q. Zhan*
LPAS, EPF-Lausanne
The Surface Science Aspect of Laser Desorption Mass Spectrometry

135 ***F. Atamny***, *A. Baiker, H.-J. Muhr, R. Nesper*
Laboratorium für Technische Chemie, ETH-Zürich
Laboratorium für Anorganische Chemie, ETH-Zürich
AFM and XRD Investigation of Crystalline Vapor-Deposited C_{60} Films

136 ***M. Becht***, *K.-H. Dahmen, F. Atamny, A. Baiker*
Laboratorium für Anorganische Chemie, ETH-Zürich
Laboratorium für Technische Chemie, ETH-Zürich
Surface Morphology and Electrical Properties of Copper Thin Films Prepared by MOCVD

137 ***T. Fässler***, *R. Nesper*
Laboratorium für Anorganische Chemie, ETH-Zürich
The Interpretation of STM Images Using Tight Binding Calculations – Electronic Structure on the Si(100) Surface

138 ***A. Henseler***, *E. Vauthey*
Institut für Physikalische Chemie, Universität Freiburg
Rotational Relaxation Time of Ruthenium(II)-bis(2,2'-bipyridine) (2,2'-biquinoleine) Measured by Transient Grating Holography

139 *F. Binder, G. Calzaferri*, ***N. Gfeller***
Institut für Anorg., Analyt. und Physikal. Chemie, Universität Bern
Dye Molecules in Zeolites as Artificial Antenna System

140 *M. Bärtsch*, ***P. Bornhauser***, *G. Calzaferri, R. Imhof*
Institut für Anorg., Analyt. und Physikal. Chemie, Universität Bern
Correlation of the Vibrational Structure of $H_8Si_8O_{12}$ and $H_{10}Si_{10}O_{15}$

141 *C. Barbero, O. Haas*, ***R. Kötz***
Paul Scherrer Institut, Villigen PSI
Electrochemical Formation of a Conductive Polymer in Absence of Supporting Electrolyte. A Copolymer of *o*-Aminosulfonic Acid and Aniline

142 *S. Müller*, ***F. Holzer***
Paul Scherrer Institut, Villigen PSI
Alkaline Secondary Zn/O_2 Battery Using Pasted Zn-Electrodes

143 *D. Weber*, ***H.P. Brack***
EMPA Dübendorf
Paul Scherrer Institut, Villigen PSI
Surface Energies and Surface Reconstruction of Ion-Containing Polymers – A Dynamic Contact Angle Study

Computerunterstützte Chemie/Chimie computationnelle

Vorträge/Communications: Abstracts 144–149
Hörsaal/Auditoire S 481, 4. Stock Süd/4e étage sud

14.00 –17.00 Chairman: ***J. Weber***
Dépt. de Chimie Physique, Université de Genève
Hörsaal/Auditoire S 481, 4. Stock Süd/4e étage sud

144 14.00 ***M. Bühl***, *W. Thiel*
Organisch-chemisches Institut, Universität Zürich
Helium and Lithium NMR Chemical Shifts of Endohedral Fullerene Compounds – An *ab initio* Study

145 14.20 ***M. Brändle***, *G. Calzaferri*, ***M. Lanz***
Institut für Anorg., Analyt. und Physikal. Chemie, Universität Bern
Size Quantization and Surface States of Molybdenum Sulfide Clusters

146 14.40 ***L. Campana***, *A. Selloni, J. Weber, A. Pasquarello, I. Papai, A. Goursot*
Dépt. de Chimie Physique, Université de Genève
Institute IRRMA, EPF-Lausanne
Ecole Nationale de Chimie, Montpellier

First Principles Molecular Dynamics Calculation of the Structure and Acidity of a Bulk Zeolite

147 15.00 ***A.C. Stückl***, *C.A. Daul, H.U. Güdel*
Institut de Chimie Inorganique et Analytique, Université de Fribourg
Institut für Anorg., Analyt. und Physikal. Chemie, Universität Bern
Excited State Properties of d^0 Tetroxo Ions – a Density Functional Study

148 15.20 ***O. Schafer***, *C. Daul*
Institut de Chimie Inorganique et Analytique, Université de Fribourg
Modeling of the Coordination Sphere of Hydrated Lanthanide Ions with DFT Methods

149 15.40 ***P. Gaillard***, *P.-A. Carrupt, B. Testa*
Institut de Chimie Thérapeutique, Ecole de Pharmacie, Lausanne
Benefits of the MLP, an Empirical Molecular Field, in 3D-QSAR

Postersession/Session des posters: Abstracts 150–155
13.00–17.00: *4. Stock/4e étage*

150 *G. Calzaferri*, ***R. Rytz***
Institut für Anorg., Analyt. und Physikal. Chemie, Universität Bern
Calculation of Electronic CT Transition Oscillator Strength

151 *P. Bützer*, ***I. Silvestri***
Bützer + Silvestri, Altstätten
Die grossräumige Wirkung von toxischen Gasgemischen

152 ***B. Flückiger***, *L. Walder*
Institut für Organische Chemie, Universität Bern
Cyclic Voltammetry Equipment Tuning – CV Data Handling Under WINDOWS

153 ***U. Häussermann***, *St. Wengert, R. Nesper*
Laboratorium für Anorganische Chemie, ETH-Zürich
Die Elektronenlokalisierung in intermetallischen Aluminiden

154 ***U. Häussermann***, *St. Wengert, R. Nesper*
Laboratorium für Anorganische Chemie, ETH-Zürich
Eindeutige Wirkungsbereiche in Kristallstrukturen intermetallischer Aluminide

155 ***T. Brodmeier***, *E. Pretsch*
Laboratorium für Organische Chemie, ETH-Zürich
Application of Genetic Algorithms in Molecular Modeling

156 ***S. Stoll***, *J. Buffle*
Dépt. de Chimie Minérale, Analytique et Appliquée, Université de Genève
Computer Simulation of Bridging Flocculation

Sektion Analytische Chemie/Section Chimie analytique

10.00–10.30 Jahresversammlung der Sektion analytische Chemie
Assemblée générale de la Section Chimie analytique
Aula Sekundarlehramt, Gertrud Woker Strasse 5

Vorträge/Conférences: Abstracts 157–158, 196–197
Aula Sekundarlehramt, Gertrud Woker Strasse 5

196 10.30 ***Fred E. Regnier***
Dept. of Chemistry, Purdue University, Lafayette
Electrophoretically Mediated Microanalysis (EMMA) of Biological Extracts

11.30 ***W. Thormann***
Institut für Klinische Pharmakologie, Universität Bern
Capillary Electrophoresis of Drugs in Body Fluids

157 12.10 ***G. Fóti***, *P. Hajós, G. Révész, E. sz. Kováts*
Laboratoire de Chimie Technique, EPF Lausanne
System Peaks and Retention Mechanism in Ion Chromatography

158 12.30 ***J.-L. Wolfender***, *K. Hostettmann*
Institut de Pharmacognosie et Phytochimie, Ecole de Pharmacie, Université de Lausanne
Combined Use of Thermospray and Continuous Flow-FAB Liquid Chromatography-Mass Spectrometry for the Analysis of Glycosides in Crude Plant Extracts

Postersession/Session des posters: Abstracts 159–195
14.00–16.00: *Chemische Institute/Instituts de chimie 2., 3., 4. Stock/2e, 3e, 4e étage*

159 ***K.O. Börnsen***, *E. Gassmann, H.M. Widmer*
Ciba-Geigy AG, Basel
Matrix Molecules: The Key for MALDI-MS Applications

160 ***S. Schuerch***, *U.P. Schlunegger*
Institut für Organische Chemie, Universität Bern
Determination of Oligosaccharides in Soil Samples by Matrix-assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

161 ***J. Krause***, *U.P. Schlunegger*
Institut für Organische Chemie, Universität Bern
New Matrix Compounds for Matrix Assisted Laser Desorption Ionization Mass Spectrometry

162 *O. Plaut*, ***Ch. Staub***
Institut Universitaire de Médecine Légale, Genève
Analysis of Drugs and Drugs of Abuse by Micellar Electrokinetic Capillary Chromatography

163 ***M. Howald***, *U.P. Schlunegger*
Institut für Organische Chemie, Universität Bern
Capillary Electrophoresis – a Fast and Universal Tool in Soil Analysis

164 ***N. Burggraf***, *A. Manz, N.F. de Rooij, H.M. Widmer*
Ciba-Geigy AG, Basel
Institute of Microtechnology, Université de Neuchâtel
Synchronized Cyclic Capillary Electrophoresis (SCCE)

165 ***G.J.M. Bruin***, *I. Barmé, D. Hüsken, H.M. Widmer, A. Paulus*
Ciba-Geigy AG, Basel
Antisense Oligonucleotides and the Analytical Challenges for Capillary Gel Electrophoresis

166 ***A. Klockow***, *R. Amadò, H.M. Widmer, A. Paulus*
Ciba-Geigy AG, Basel
Institut für Lebensmittelwissenschaften, ETH-Zürich
Capillary Electrophoresis of ANTS Labeled Oligosaccharide Ladders Complex Carbohydrates

167 ***M.P. Vivarat-Perrin***, *S.G. Claude, R. Tabacchi*
Institut de Chimie, Université de Neuchâtel
Synthèse de phases stationnaires HPLC pour séparations chirales

168 ***M. Przybylski***, *M.O. Glocker, C. Maier, C. Borchers, E. Dürr, W. Fiedler, H. Wendt, H.R. Bosshard*
Fakultät für Chemie, Universität Konstanz
Biochemisches Institut, Universität Zürich
Direct Characterization of Supramolecular Complexes of Polypeptides and Proteins by Electrospray Mass Spectrometry

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169 ***S. Rodriguez***, *J.-L. Wolfender, K. Hostettmann*
Institut de Pharmacognosie et Phytochimie, Ecole de Pharmacie, Université de Lausanne
Systematic Search for New Xanthones in *Gentianaceae* species by LC-UV and LC-TSP-MS Analysis

170 ***M. Monzione***, *S.G. Claude, R. Tabacchi*
Institut de Chimie, Université de Neuchâtel
Methoxyphenylpolysiloxanes. Polarizable Stationary Phases for Capillary Chromatography

171 ***L. Jelinek***, *R. Ohmacht, A. Pfenninger, E. sz. Kováts*
Laboratoire de Chimie Technique, EPF-Lausanne, Chemie Uetikon, Uetikon
Monosized, Silica Based Microspheres for Chromatographic Separations

172 ***S.G. Claude***, *R. Tabacchi, A. Saxer*
Institut de Chimie, Université de Neuchâtel
Institut für Organische Chemie, Universität Bern
Analyse par chromatographie gazeuse de racémates au moyen de cyclodextrines peralkylées

173 *T. Schenk,* ***B. Schmidt***
Biologie V, RWTH Aachen
Development of a New HPLC Method for Monitoring Rhamnolipid Biosurfactants Excreted by *Pseudomonas* Species

174 *H. Lacalle,* ***Ch. Staub***
Institut Universitaire de Médecine Légale, Genève
Analysis of Cannabinoids by High Performance Liquid Chromatography with Electrochemical Detection (HPLC/ED)

175 ***F. Sadeghipour***, *D. Bertin, J.-L. Veuthey*
Laboratoire de Chimie Analytique Pharmaceutique, Université de Genève
Dialyse, enrichissement et séparation par HPLC des amphétamines contenues dans le sérum après dérivatisation par FMOC-Cl

176 ***H. Gfeller***, *U.P. Schlunegger, U. Schaffner, J.L. Boevé, I. Ujvary*
Institut für Organische Chemie, Universität Bern
Zoologisches Institut, Universität Bern
Screening for a Defence System in a Caterpillar by Tandem MS

177 ***M. Wilkinson***
Sandoz AG, Basel
The Investigation of 'Single Event'. Quality Deviation as a Contribution to Pharmaceutical Quality Assurance

178 ***P. Edder***, *W. Haerdi, J.L. Veuthey, C. Staub*
Dépt. de Chimie Minérale, Analytique et Appliquée, Université de Genève
I. Extraction en phase subcritique d'opiacés contenus dans une matrice liquide – Application à l'urine

179 ***P. Edder***, *W. Haerdi, J.L. Veuthey, C. Staub*
Dépt. de Chimie Minérale, Analytique et Appliquée, Université de Genève
II. Extraction en phase subcritique d'opiacés contenus dans une matrice solide – Application aux analyses des cheveux

180 ***S. Rudaz***, *J.L. Veuthey*
Laboratoire de Chimie Analytique Pharmaceutique, Université de Genève
Séparation chirale de la méthadone contenue dans le sérum

181 *P. Fontannaz, M. Salanon,* ***D. Sallin***
Zyma SA, 1260 Nyon
Determination of the Enantiomers of Zy 17617B in Plasma by Two-dimensional Liquid Chromatography with Automated Solid-Phase Extraction and Column-Switching

182 ***A. Ritter***
EMPA, St. Gallen
Spurenanalyse von chlorierten Phenolen in komplexen Matrices

183 ***D.E. Raymond***, *A. Manz, H.M. Widmer*
Ciba-Geigy AG, Basel
Continuous Sample Pretreatment Using a Silicon Free Flow Electrophoresis Device

184 ***N. Parthasarathy***, *R. Agraz, E. Haseroth, O. Keller, J. Buffle*
Dépt. de Chimie Minérale, Analytique et Appliquée, Université de Genève
Application of Supported Liquid Membrane to Trace Metal Speciation Studies

185 ***M.-L. Tercier***, *J. Buffle*
Dépt. de Chimie Minérale, Analytique et Appliquée, Université de Genève
Development of Sensors for *in situ* Measurements in Natural Waters

186 ***D. Citterio, C. Demuth***, *M. Linnhoff, S. Rasònyi, U.E. Spichiger*
Centre of Chemical Sensors/Biosensors and (Bio-)Analytical Chemistry, ETH-Zürich
Quality Assessment of Magnesium-Selective Potentiometric Electrodes

187 ***U.E. Spichiger***, *D. Citterio, M. Nägele*
Centre of Chemical Sensors/Biosensors and (Bio-)Analytical Chemistry, ETH Zürich
Quantitative Structure-Selectivity Relationship (QASSER) of 'Magnesium-Selective' Neutral Carriers Incorporated in Solvent Polymeric Membranes

188 ***N.A. Corfù***, *U. Kettenring, M. Zehringer*
Gewässerschutzamt Basel-Stadt, Basel
Representative Sampling of Inhomogeneous Riverwater

189 ***V.R. Meyer***
Institut für Organische Chemie, Universität Bern
Quantitation of Second Eluted Small Chromatographic Peaks

190 ***S. König***, *P. Kofel, U.P. Schlunegger*
Institut für Organische Chemie, Universität Bern
Ion-Molecule Reactions with HCN in a Quadrupole-Quistor-Quadrupole Tandem Mass Spectrometer

191 ***B. Pellascio***, *B. Aebi, U.P. Schlunegger*
Institut für Organische Chemie, Universität Bern
Collision-Induced Fragmentation Studies of 1-R-1,2,3,4-Tetrahydroisochinolines and Benzaldehydoxime-O-(n)-R'-ethers

192 ***D. Giron***
Sandoz-Pharma AG, Basel
Use of Thermal Analysis for Design of the Solid State

193 ***J. Müller***, *J. Korell, U. E. Spichiger*
Centre of Chemical Sensors/Biosensors and (Bio-)Analytical Chemistry, ETH-Zürich, Sandoz Pharma AG, Basel
Amperometric Biosensors for Redox-Active Substrates

194 ***Q. Zhan***, *P. Voumard, R. Zenobi*
LPAS, EPF-Lausanne
Automated Wavelength Scanning in Two-Step Laser Mass Spectrometry: Application to Environmental Contaminants

195 ***D. Giron***, *P. Piéchon, S. Pfeffer*
Sandoz-Pharma AG, Basel
Analytical Methods for Quantitative Determination of Polymorphs

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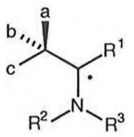
Organic Chemistry **W1**

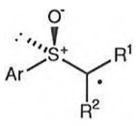
Control of the Stereoselectivity of Radical Reactions

Philippe Renaud
Université de Fribourg, Institut de Chimie Organique, Pérolles,
CH-1700 Fribourg

During the last decade, radical reactions have been intensively investigated by synthetic organic chemists. The new synthetic methods which arise from this work are characterized by mild reaction conditions and by their nature complementary to ionic processes. Moreover, the possibility of executing "cascade" or "tandem" reactions provides a unique way of shortening complex reaction sequences. Recently, a great effort has been devoted to the control of the stereoselectivity of radical reactions and we report here our contribution to this topic. For instance, we have investigated the 1,2-asymmetric induction of amino (**A**) and arenesulfinyl (**B**) substituted radicals. Depending on the substitution pattern of the radicals, different models based on allylic strain, dipole-dipole interactions and stereoelectronic effects have been developed. External factors such as the nature of the solvent and the presence of additives have also been investigated. High degree of stereocontrol have been reached with sulfinylated radicals in the presence of very bulky Lewis acids.



A



B

W2

Transition Metal Complexes, Useful Substrates in Enantioselective Synthesis and Photocatalysis

Dr. A. Hafner
Ciba-Geigy Limited, Materials Research, CH-1723-Marly(1)

Titanium reagents have been successfully applied by chemical industries to increase selectivity in carbanion chemistry. Ecological and economical criterias are very well met by this particular metal. Chiral monocyclopentadienyl-dialkoxy titanium reagents introduced by us (with formal 12 valence electrons) are especially suited for the enantio- and stereoselective addition of allyl groups[1] and ester enolates[2] to aldehydes. Such complexes serve also as catalysts for the enantioselective addition of achiral alkoxy-alkyl titanium complexes to aldehydes. In many cases, these reagents are currently the best choice for medium to large scale preparation of optically active compounds. Ti-NMR measurements, crystal structure analyses and systematic variation of the complex geometry revealed an **interligand interaction** between the Cp-ligand and the chiral alkoxy ligands; it is responsible for the observed high enantioface selection inducing a distortion of the coordinating geometry on titanium.

First results in the newly discovered field of **P**hotoinduced **R**ing-**O**pening-**M**etathesis-**P**olymerisation (**PROMP**) of strained bicyclic olefins are also presented. Photogenerated Ru(II)-aquo-complexes are efficient catalysts yielding polymers with interesting mechanical and electrical properties.

1) Hafner A.; Duthaler R.O.; Marti R.; Rihs G.; Rothe-Streit P.; Schwarzenbach F. *J. Am. Chem. Soc.* **1992**, *114*, 2321. 2) Duthaler R.O.; Hafner A. *Chem. Rev.* **1992**, *92*, 807.

1

Anorganische Chemie

Electrochemical Insertion of Small Cations in MoO_3

Michael E. Spahr[a], Petr Novák[a], Otto Haas[a], and Reinhard Nesper[b]

[a]Paul Scherrer Institut, Sektion Elektrochemie, CH-5232 Villigen PSI
[b]Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

Unlike the cases of lithium and sodium, the chemical and electrochemical insertion of small divalent cations in transition metal oxides and sulfides has been studied only in a limited number of investigations. Especially the insertion of magnesium is of particular theoretical and practical interest, both because of the similar ion size of monovalent lithium and divalent magnesium cations, which may lead, from a steric point of view, to an analogous insertion electrochemistry, and because of a prospective application in ion-transfer battery systems.

In this study, the electrochemical insertion of divalent magnesium cations into orthorhombic molybdenum(VI) oxide has been compared to the insertion of Li^+ and Na^+. Specific charges of up to 300 Ah kg^{-1} and 240 Ah kg^{-1} were obtained in organic, propylene carbonate-based electrolytes for the lithium and sodium insertion, respectively, in the first reduction half-cycle. Reversible Mg^{2+} insertion could be demonstrated in a room temperature molten salt electrolyte consisting of 3 wt.% $MgCl_2$, 41 wt.% 1-ethyl-3-methylimidazolium chloride, and 56 wt.% $AlCl_3$. Specific charges of up to 160 Ah kg^{-1} were obtained with MoO_3 in the first reduction half-cycle. The Mg^{2+} insertion process can be enhanced using an organic electrolyte with traces of H_2O. In 1*M* $Mg(ClO_4)_2$/acetonitrile with 3 mol% of H_2O, specific charges of up to 210 Ah kg^{-1} were measured in the first reduction.

Acknowledgement: We would like to thank the "Bundesamt für Energiewirtschaft" for financial support (Grant No. EF-PROCC(91)18).

2

Anorganische Chemie

Modelling of Electronic Effects in Molecular Mechanics Calculations of Transition Metal Complexes.

Peter Comba[a], Marc Ströhle[a] and Marc Zimmer[b]

a) Anorganisch-Chemisches Institut, Universität Heidelberg
69120 Heidelberg, Germany
b) Chemistry Department, Connecticut College, New London, CT06320, United States.

Serious problems encountered in inorganic molecular mechanics that are not found in molecular mechanics of organic molecules, are the electronic effects associated with the presence of partially filled d orbitals in transition metals. This leads to variable geometries (octahedral, square planar, tetrahedral etc.), the trans effect and the Jahn-Teller effect.

Our calculations with transition metal complexes have shown that the ligand-metal-ligand angles depend not only on a metal independent 1,3-non bonded repulsion of the ligand atoms, but also on an additional metal dependent angle force constant, which we model with a $\sin^2$ function.

We also present a new method to calculate the structure of Jahn-Teller distorted metal centers. The procedure is straightforward, it requires a ligand field spectrum of the complex and a molecular mechanics program. Advantages are that the metal-ligand distances of dynamically Jahn-Teller distorted complexes or of complexes which have not been crystallographically characterised can be obtained, as can the direction of the distortion.

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3

Anorganische Chemie

Approaches to Include Entropy and Solvation in Molecular Mechanics Calculations of Transition Metal Complexes

Peter Comba, Wolfgang Goll, and Achim Sickmüller

Anorganisch-Chemisches Institut der Universität Heidelberg, 69120 Heidelberg, Germany

Molecular mechanics calculations are often used to calculate conformer and isomer distributions. Usually entropy effects other than statistical terms and solvation energies are neglected in these computations.

Solvation effects are usually neglected since the minimization of the large solvent cage requires excessive amounts of memory and CPU time. We have adapted an elegant method to calculate the solvation energy analytically via the computation of the solvent accessible surface [1] and charges which are calculated via atomic parameters [2].

Entropy effects are calculated via standard thermodynamic functions. The required vibrational frequencies and moments of inertia are obtained from the force field calculations.

[1] W. Still, A. Tempszyk, R. C. Hawley, and T.Hendrickson, *J. Am. Chem. Soc.* **1990**, *112*, 6127-6129
[2] A. K. Rappé, and W.A. Goddard III, *J. Phys. Chem.*, **1991**, *95*, 3358-3363

4

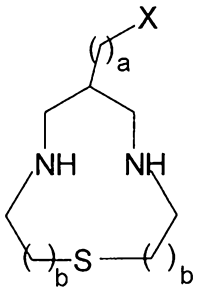
Anorganische Chemie

A new class of model systems for blue copper proteins

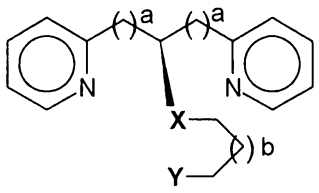
Peter Comba, Martin Rozumek, and Sandra Stebler

Anorganisch-Chemisches Institut der Universität Heidelberg 69120 Heidelberg, Germany

Two new classes of ligands (see Figure), which are used to mimick the spectroscopic (EPR, UV-vis) and redox properties of blue copper proteins, are presented. The experimentally determined properties of the corresponding transition metal compounds are used to develop the parameters for molecular mechanics and angular overlap model calculations, which then will be used for the design of modified blue copper protein model systems.



a = 0, 1
b = 1, 2
X = N, S, O



a = 0, 1
b = 0, 1, 2
X, Y = N, S, O

5

Anorganische Chemie

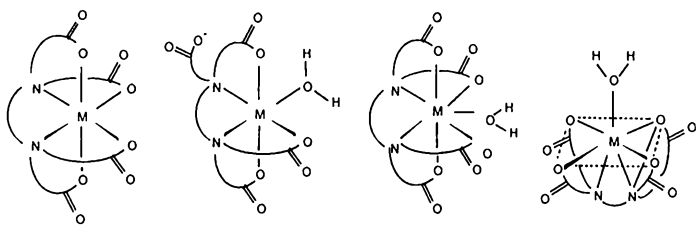
Molecular Mechanics as an Approach to Predict Solution Structures of Transition Metal Complexes with EDTA-Type Ligands

Martin Boddin[a], Peter Comba[b], Holger Jakob[b] and Roland Meier[a]

a) HTWK (FH) Leipzig, FbIMN, Fachgruppe Chemie, 04105 Leipzig, Germany
b) Anorganisch-Chemisches Institut der Universität Heidelberg, 69120 Heidelberg, Germany

Four different coordination modes of transition metal complexes with EDTA-type ligands have been reported based on crystal structural analyses (Scheme). The X-ray structures are in many cases not in agreement with the reactivity of the complexes in solution. One possible reason for the resulting controverses is that different species can coexist in solution. Based on force field calculations the individual strain energies can be calculated. These may then be used to predict the relative abundances. A correlation of the calculated equilibrium constants with appropriate redox potentials and stability constants demonstrates the validity of our approach.

Scheme



pentagonal bipyramidal

monocapped trigonal prismatic

Anorganische Chemie

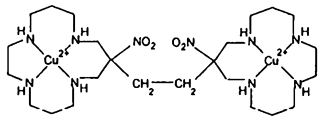
6

Comparision of Solution Structures of two Bismacrocyclic Copper(II) Complexes

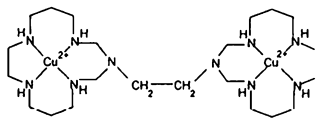
Peter Comba and Peter Hilfenhaus

Anorganisch-Chemisches Institut der Universität Heidelberg, 69120 Heidelberg, Germany

The dinuclear copper(II) complexes **1** and **2** are synthesized by template reactions of cis-coordinated primary amines with formaldehyde and aliphatic dinitrocompounds or diamines. Despite of the similarity of the two compounds their solution structures are completely different.



1



2

Whereas in **1** the EPR-spectrum indicates the presence of two identical uncoupled chromophores, the EPR-spectrum of **2** exhibits two weakly coupled Cu(II) centers. The solution structures of **1** and **2** are determined via the combination of molecular mechanics calculations with the simulation of the EPR-spectra based on the relative orientation of the Cu(II) chromophores of the calculated conformers [1]. The determined solution structures revealed that **1** exists in a streched and **2** in a folded conformation. The Cu-Cu separation of **2** is 7.2Å and about 2Å smaller than that of **1**.

[1] P.V. Bernhardt, P. Comba, T.W. Hambley, S.S. Massoud, and S. Stebler, *Inorg. Chem.* **1992**, *31*, 2644

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Anorganische Chemie **7**

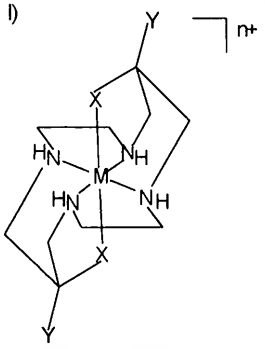
Metal Ion Selectivity

Peter Comba, Achim Lienke, and Stephan Luther

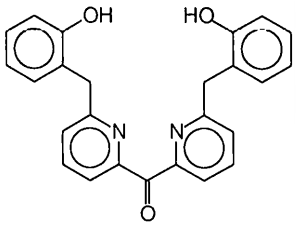
Anorganisch-Chemisches Institut der Universität Heidelberg
69120 Heidelberg, Germany

Metal ion selective ligands may be used as extractants in the recovery of metals or to separate and recycle metal bearing wastes. The selectivity of a ligand is mainly based upon the ease with which it can adopt the metal preferred bond distances and coordination geometries.
We are interested in two design principles. Starting from a given hexadentate macrocycle the donor atoms and chelate ring sizes may be changed (I). The donor atom disposition in (II) discriminates in favour of tetrahedral. Molecular mechanics calculations are used in both cases to predict the corresponding coordination geometries.

I)



II)



X= OH, SR, NH_2, Py
Y= H, CH_3, NO_2, COOEt

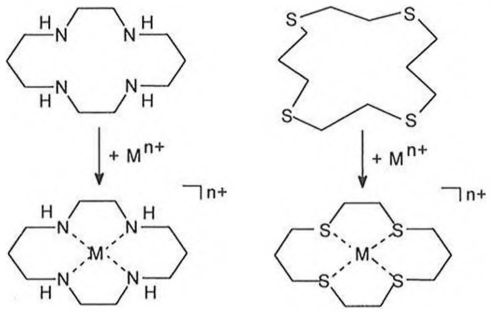
Anorganische Chemie **8**

Highly Preorganized Tetrathiamacrocycles

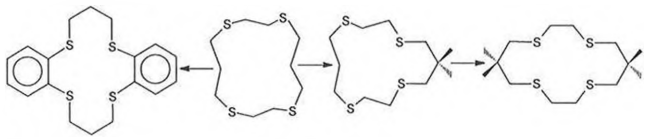
Peter Comba, Andreas Fath and Andreas Kühner

Anorganisch-Chemisches Institut der Universität Heidelberg,
69120 Heidelberg, Germany

Tetrathiamacrocyclic ligands have, in contrast to tetraaza analogues a pronounced tendency to exist as free ligands in an "exodentate" conformation. Extensive conformational change upon coordination to metal ions is therefore part of the reason for a considerably smaller macrocyclic effect and relatively small stabilities as compared to tetraaza- and crownether complexes.



A higher degree of preorganisation of S_4-macrocycles may be achieved via substitution of the ligand backbone.

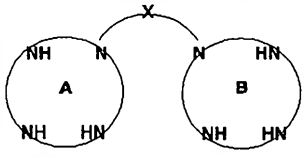


Koordinationschemie **9**

Kinetics of Cu^{2+} Incorporation into Homo- and Heteroditopic Bis-Macrocycles studied by the Stopped-Flow/Photodiode-Array Technique

Liselotte Siegfried and Thomas A. Kaden
Institute of Inorganic Chemistry, Spitalstr. 51, CH-4056 Basel, Switzerland

Having observed that the sequential addition of two metal ions to homo- (**A** = **B** = [12]aneN$_4$ **1**, or [14]aneN$_4$ **2**) and heteroditopic bis-macrocycles (**A** = [14]aneN$_4$, **B** = [12]aneN$_4$ **3**, or Me$_3$[14]aneN$_4$ **4**) can produce heterobinuclear complexes [1], we became interested, whether this is due to thermodynamical or kinetical factors. We thus have measured the kinetics of complex formation between Cu^{2+} and the bis-macrocycles **1-4** by the stopped-flow technique using a photodiode array detector, which allows to identify intermediates.



1 A=B=[12]aneN$_4$
2 A=B=[14]aneN$_4$
3 A=[12]aneN$_4$ B=[14]aneN$_4$
4 A=[14]aneN$_4$ B=Me$_3$[14]aneN$_4$
X= -CH_2-CH_2-

The kinetics of the Cu^{2+} complexation with **1** and **2** is biphasic and can be fitted with two rate constants differing by about a factor 4. This indicates that besides statistical factors the two metal ions are incorporated into the two rings more or less at the same rate. Especially interesting are the heteroditopic ligand **3** and **4**, for which a more complicated reaction scheme with two intermediates has been found. These are isomeric species containing one Cu^{2+} per bis-macrocycle. We were able to calculate all the rate constants with the program KINFIT [2], when the spectra of the intermediates were included as an additional piece of information.

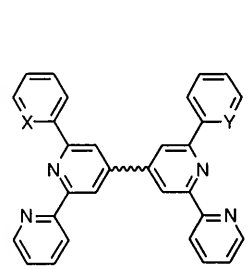
[1] A. Urfer, Th. A. Kaden, *Helv. Chim. Acta* **1994**, *77*, 23
[2] B. Jung, Ph.D. Thesis, Basel 1994

Anorganische Chemie/Koordinations Chemie **10**

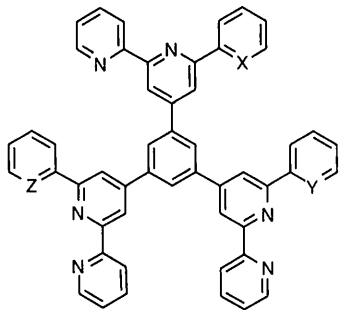
Metallated and Non-metallated Coordination Oligomers

E.C. Constable, P. Harverson, and A.M.W. Cargill Thompson
Institut für Anorganische Chemie, Universität Basel, CH-4056 Basel

Coordination oligomers may be assembled simply and efficiently from the interaction of multi-domain ligands with appropriate metal centres. The overall topology and topography of the resultant metallosupramolecular assemblies are dictated by the number and denticity of the metal-binding domains and the coordination requirements of the metal centre [1]



1



2

The design of ligands incorporating specific metallation sites and a variety of spacer functionalities and topographies will be discussed. The assembly and electronic properties of Group 8 complexes of ligands such as **1** and **2** (X, Y, Z = N or CH) will be demonstrated. The introduction of the cyclometallated site allows a subtle control over the redox and photophysical properties of the metal centres.

[1] E.C. Constable, A.M.W. Cargill Thompson and D.A. Tocher, *Supramolecular Chemistry*, Eds V. Balzani and L. De Cola, Klewer Academic Press, Dordrecht (1992) 219

CHIMIA 48 (1994) Nr. 7/8 (Juli/August)

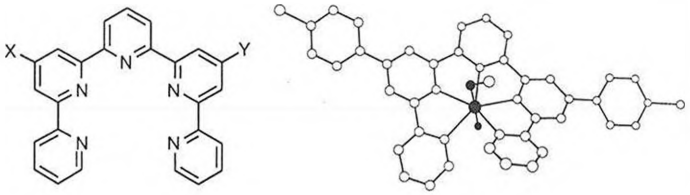
Anorganische Chemie/Koordinations Chemie **11**

Ligand Substitution Patterns Control Helicate Nuclearity

E.C. Constable, D.R. Smith, and L.A. Whall

Institut für Anorganische Chemie, Universität Basel, CH-4056 Basel

The metallosupramolecular coding for helicate self-assembly with oligopyridine ligands is now relatively well-understood [1]. A question remains, however, over the solution nuclearity of cobalt(II) complexes with 2,2':6',2":6",2"':6"',2""-quinquepyridines. We have shown that *mononuclear* but helical solution species **1** are formed from the interaction of cobalt(II) with a wide range of X_2qpy ligands (X = Y = H, alkyl, aryl, SMe). However, with X = Y = SPr, both mononuclear and double-helical solution species are present [2].



1

We have now prepared a number of ligands bearing hydrophobic substituents (X = Y = 4-^{t}BuC$_6$H$_4$, SC$_{10}$H$_{21}$) and have demonstrated that these ligands give double-helical solution species. The use of ^{1}H NMR methods for the characterisation of these paramagnetic solution species will be demonstrated. We believe that the arrangement of the hydrophobic groups in the double-helical structure drives the nuclearity change. It is significant that the asymmetric complex with X = 4-ClC$_6$H$_4$, Y = 4-^{t}BuC$_6$H$_4$) gives only a mononuclear solution species.

[1] E.C. Constable, A.J. Edwards, P.R. Raithby and J.V. Walker, *Angew. Chem.* **1993**, *105*, 1486

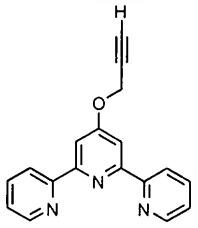
Anorganische Chemie/Koordinations Chemie **12**

Functionalised 2,2':6',2"-Terpyridines for Cluster Incorporation into Metallosupramolecules

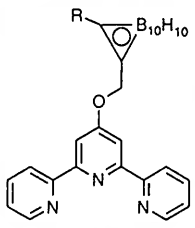
D. Armspach, E.C. Constable, and C.E. Housecroft

Institut für Anorganische Chemie, Universität Basel, CH-4056 Basel

Main group and transition metal cluster chemistry has been intensively studied for several decades. The bonding and structural aspects of such compounds are relatively well understood, but applications to date are relatively modest. In part this reflects the sensitivity of some compounds to aerobic or aqueous media. Clusters are attractive candidates for imaging (transition metals) or biomedical (boranes) applications. In order to address these topics we have embarked upon the synthesis of metallosupramolecular oligomers and dendrimers [1] incorporating cluster functionality.



1



2

Our first generation molecules are based upon alkyne-functionalised 2,2':6',2"-terpyridine **1**, which has been prepared in high yield. This is a bifurcated ligand with a chelating N_3 donor end which is designed for oligomer assembly at octahedral transition metal centres and a reactive alkyne group. The alkyne group may be used as a *C* donor to transition metals, or as a C_2 unit for the preparation of carboranyl-substituted ligand **2**

[1] E.C. Constable and A.M.W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, **1994**, 1409

13

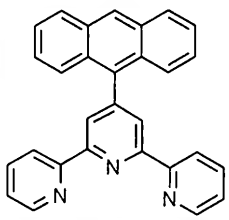
Anorganische Chemie/Koordinations Chemie

Photoactive Spectator Ligands for Metallosupramolecular Assemblies

E.C. Constable and D.R. Smith

Institut für Anorganische Chemie, Universität Basel, CH-4056 Basel

There is intense current interest in the design of photoaddressable supramolecular systems which might allow controlled and directional energy or electron transfer processes [1]. This concept has been behind the design of a ligand containing a tridentate metal-binding domain and a pendant photoactive anthracene group, **1**.



1

Attachment of the anthracene group to the 2,2':6',2"-terpyridinyl unit does not affect its photophysical properties. The metal complexes [M(**1**)$_2$][PF$_6$]$_2$ (M = Fe, Ru or Os) have also been investigated. Whereas the free ligand is intensely luminescent, the iron(II) complex is non-emissive with complete quenching of the anthracene luminescence. In contrast, the ruthenium and osmium complexes show anthracene-based emission.

[1] G. Denti, S. Serroni, S. Campagna, A. Juris, M. Ciano and V. Balzani, in *Perspectives in Coordination Chemistry*, (A.F. Williams, C. Floriani and A.E. Merbach, eds), VCHA, Basel, 1992

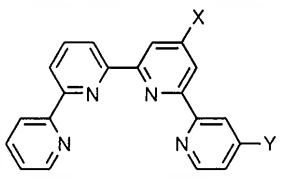
Anorganische Chemie/Koordinations Chemie **14**

Helicate Assembly with Asymmetric Ligands

E.C. Constable, F.R. Heirtzler, and A. Schneider

Institut für Anorganische Chemie, Universität Basel, CH-4056 Basel

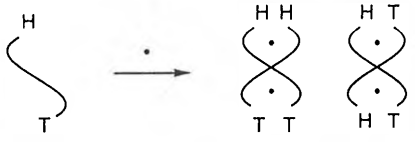
Various methods may be used to introduce asymmetry into dinuclear double-helicates. We have previously shown that heterodinuclear complexes containing different metals *but* the same ligand strands could be systematically assembled [1]. Attempts to form double-helicates with two different ligand strands were unsuccessful. We now report a new strategy, and describe the synthesis of a first generation of *asymmetrically substituted* ligand strands such as **1** and **2**.



1 X = SEt, Y = Me

2 X = Ph, Y = H

These strands may be viewed as having a head (H) and a tail (T) end. The interaction of such an asymmetrical strand with a single type of metal ion could give rise to two different double helicates. The formation of double-helicates with copper(I) and silver(I) will be described, and approaches to more selective systems discussed.



[1] E.C. Constable, A.J. Edwards, P.R. Raithby and J.V. Walker, *Angew. Chem.* **1993**, *105*, 1486

Anorganische/Koordinationschemie **15**

Proton- and Metal-Ion-Binding Properties of Cytosine-Nucleotide Derivatives

Bin Song,[a] Matthias Bastian,[a] Gerda Feldmann,[b] Bernhard Lippert,[b] and Helmut Sigel [a]

[a] Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland; [b] Department of Chemistry, University of Dortmund, Otto-Hahn-Strasse 6, D-44227 Dortmund, Germany

The biological activity of nucleotides depends in general on the presence of metal ions; this and the advent of the anticancer *cis*-$(NH_3)_2Pt^{2+}$ drug has initiated comprehensive studies on their metal-ion-binding properties [1,2]. Via potentiometric pH titrations we determined in aqueous solution (I = 0.1 M, $NaNO_3$; 25°C) several acidity and complex stability constants of cytidine 5'-monophosphate (CMP^{2-}) and 2'-deoxycytidine 5'-monophosphate ($dCMP^{2-}$) as well as of the compound resulting from the coordination of two $H(dCMP)^-$ ions via N-3 of the cytosine residue to *cis*-$(NH_3)_2Pt^{2+}$, which gives $H_2[cis\text{-}(NH_3)_2Pt(dCMP)_2]$, abbreviated as $H_2{\cdot}Pt(dC)_2$.

The acidity constants for $H_2(CMP)^{\pm}$ are $pK_{a/1} = 4.33 \pm 0.04$ [deprotonation of H^+(N-3)] and $pK_{a/2} = 6.19 \pm 0.02$ [deprot. of $-P(O)_2(OH)^-$]; for $H_2(dCMP)^{\pm}$ $pK_{a/1} = 4.46 \pm 0.01$ and $pK_{a/2} = 6.24 \pm 0.01$. Hence, removal of 2'-OH makes dCMP slightly more hydrophobic and thus somewhat less accessible to solvation by water leading to deprotonation of $H_2(dCMP)^{\pm}$ at slightly higher pH compared to that of $H_2(CMP)^{\pm}$. Deprotonation of the two $-P(O)_2(OH)^-$ residues in $H_2{\cdot}Pt(dC)_2$ occurs with $pK_{a/1} = 5.73 \pm 0.02$ and $pK_{a/2} = 6.47 \pm 0.02$. Comparison of the average of these two values with the above $pK_{a/2}$ indicates that the Pt^{2+} at N-3 has a small acidifying effect.

The stability constants of the Mg^{2+}, Cu^{2+}, and Zn^{2+} complexes of CMP^{2-} and $dCMP^{2-}$ are within the error limits identical with values calculated on the basis of the acidity constants and log $K^{M}_{M(R\text{-}PO_3)}$ *vs* $pK^{H}_{H(R\text{-}PO_3)}$ plots [1]; i.e., in these M(CMP) and M(dCMP) complexes the nucleic base does not participate in M^{2+} binding. This contrasts with purine-nucleoside 5'-monophosphate complexes [1]. The stability of the $M[H{\cdot}Pt(dC)_2]^+$ and $M[Pt(dC)_2]$ complexes is slightly affected by the Pt^{2+} and also the other PO_3^{2-} group.

Supported by the Swiss Nat. Sci. Foundation (H.S.), the 'Deutsche Forschungsgemein.' (B.L.), and the HCM programme (Brussels/Berne).

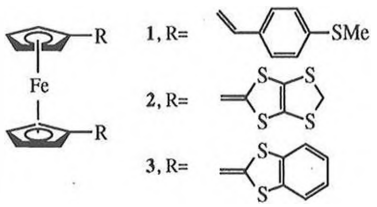
[1] H. Sigel, S. S. Massoud & N. A. Corfù, *JACS 116*, 2958 (1994).
[2] B. Lippert, *Prog. Inorg. Chem. 37*, 1 (1989).

Anorganische Chemie/Koordinationschemie **16**

1,1'-Disubstituted Ferrocenes as Donors for Charge-Transfer Complexes. Synthesis, Structures, Magnetic Properties and Conductivities.

Stefan Zürcher, Markus Hobi, Antonio Togni
Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

The 1,1'-disubstituted ferrocenes (**1**, **2**, **3**) [1] easily form 1:1 charge-transfer complexes with the known electron-acceptor $Ni(mnt)^-$ (**4**) [2].



In the complex [**1+4**] donor- and acceptor-molecules are in separated stacks. [**1+4**] and [**2+4**] show paramagnetic behaviour but do not obey the normal Curie-law and they are semiconductors with rather moderate room-temperature conductivity.

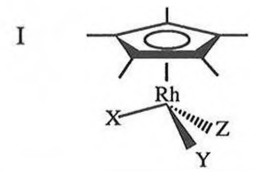
[1] A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech, H. Keller, Organometallics, 1994, 13, 1224
[2] A. Davison, R.H. Holm, Inorg. Synth., 1967, 10, 9

Koordinationschemie **17**

Direct and Inverse ^{103}Rh NMR for Half-Sandwich Complexes

V. Tedesco and W. von Philipsborn,
Organisch-chemisches Institut der Universität Zürich,
Winterthurerstrasse 190, CH-8057 Zürich.

^{103}Rh NMR shielding has proven to be a versatile probe for the study of reactivity in stoichiometric [1] and catalytic [2] reactions. We are currently investigating the rhodium chemical shifts and (Rh,P) and (Rh,C) coupling constants in a series of half-sandwich complexes of Type I [3,4]:



X,Y,Z = alkyl, aryl, halide, CO, phosphine

with a view to correlating the rhodium NMR parameters with the rates of CO insertion into a Rh-C σ-bond for compounds where X=I, Y=aryl and Z=CO [4]. Ligand X, Y and Z effects on ^{103}Rh shielding will also be discussed.

The ^{103}Rh NMR spectra were measured by direct observation at 18.9MHz (B_o=14.1 Tesla) and inverse 2D detection at 12.6MHz (B_o=9.4 Tesla) using (^{1}H,^{103}Rh) and (^{31}P,^{103}Rh){^{1}H} experiments.

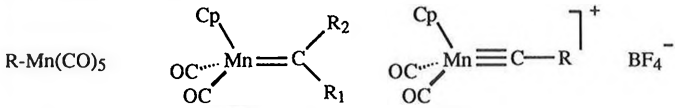
1. M. Koller and W. von Philipsborn, *Organometallics*, **11** (1992) 467.
2. B. R. Bender, M. Koller, D. Nanz and W. von Philipsborn, *J. Am. Chem. Soc.*, **115** (1993) 5889.
3. W. D. Jones and F. J. Feher, *Inorg. Chem.*, **23** (1984) 2376.
4. M. Bassetti, G. J. Sunley, F. P. Fanizzi and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, (1990) 1799.

Koordinationschemie **18**

^{55}Mn,^{13}C Coupling Constants of Manganese-Carbon Single and Multiple Bonds

D. Rentsch and W. von Philipsborn
Organisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich
D. Hörndler, J. Schleu and H. Fischer
Universität Konstanz, Fakultät für Chemie, Postfach 5560 M727, D-78434 Konstanz

The synthesis and ^{55}Mn NMR parameters of manganese carbene and carbyne complexes of type II and III will be described.



I II III

The spin-spin coupling constants of the quadrupolar ^{55}Mn nucleus and the spin 1/2 nucleus ^{13}C are not resolved in the ^{13}C NMR spectra. They can, however, be determined by lineshape analysis of the broadened signals using the iterative lineshape fitting programme QUADR [1]. Data will be presented for the Mn,C (10-40 Hz) and Mn,CO bonds (30-55 Hz).
A comparison of the ^{1}J(Mn,C) coupling constants obtained for the three types of Mn,C bonds in I, II and III indicates a correlation with bond order.

[1] V. Torocheshnikov, D. Rentsch and W. von Philipsborn, *Magn. Reson. Chem.* 1994, in press.

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Koordinationschemie **19**

^{57}Fe NMR and Steric Effects in Cyclopentadienyliron Complexes

E. J. M. Meier and W. von Philipsborn

Organisch-chemisches Institut der Universität Zürich,
Winterthurerstrasse 190, CH - 8057 Zürich

Transition metal chemical shifts are known to be a sensitive probe for steric effects in metal-ligand coordination [1]. We have synthesised a series of half-sandwich complexes of type **I** and **II** to investigate electronic and steric effects.

The ^{57}Fe NMR spectra were measured in natural isotope abundance using direct detection at 19.4 MHz (B_0= 14.1Tesla) for **I** and inverse triple resonance (^{31}P,^{57}Fe)-{^{1}H} 2D detection at 12.9 MHz (B_0= 9.4Tesla) for **II**. ^{57}Fe shielding decreases with increasing bulkiness of the alkyl group. Furthermore, shielding decreases with electron acceptor ligands R and increases with donor substituents at the Cp ring. A correlation of $\partial(^{57}Fe)$ with the reactivity of the Fe-C σ-bond is under investigation.

[1] C. Tavagnacco, G. Balducci, G. Costa, K. Täschler, W. v. Philipsborn, *Helv. Chim. Acta* **1990**, *73*, 1469.

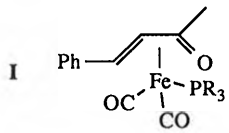
Koordinationschemie **20**

2D (^{31}P, ^{57}Fe) NMR Studies of $Fe(CO)_2L$ Transfer Reagents

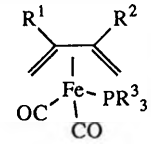
G. Hopp, D. Nanz, R. Stefanova and W. von Philipsborn

Organisch-chemisches Institut der Universität Zürich,
Winterthurerstrasse 190, CH-8057 Zürich

(η^4-Enone)$Fe(CO)_2L$ complexes (L= CO, PR_3) are known sources for the $Fe(CO)_2L$ moiety that can be transferred to other diene ligands under mild conditions [1]. Using inverse two-dimensional (^{31}P, ^{57}Fe)-{^{1}H} triple resonance NMR spectroscopy, developed by Benn and Brevard [2], we have determined the ^{57}Fe chemical shifts and $^1J(^{57}Fe, ^{31}P)$ coupling constants for the two related types of complexes **I** and **II**:



R = alkyl, phenyl, Oalkyl, Ophenyl



R^1, R^2 = H, Me; R^3 = alkyl, Oalkyl

For the first time, 2D (^{31}P, ^{57}Fe) NMR spectroscopy has been used at low temperatures (233- 179K) to provide detailed information about the structure, the electronic environment of the metal center and the reactivity of iron complexes. In both series, two conformers were observed, with characteristic differences in ^{57}Fe shielding and $^1J(^{57}Fe, ^{31}P)$ spin coupling, that could be assigned to isomers with apical and basal phosphorus ligands.

[1] J.A.S. Howell, B.F.G. Johnson and J. Lewis, J. Organomet. Chem. (1972), *39*, 329.

[2] R. Benn and C. Brevard, J. Am. Chem. Soc. (1986), *108*, 5622.

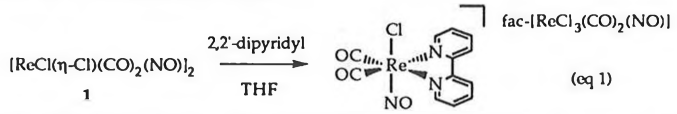
21

Inorganic Chemistry

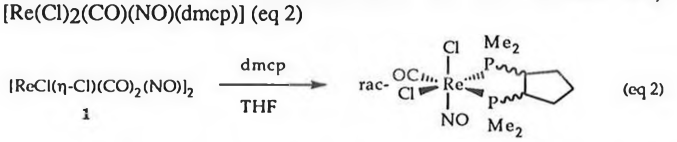
The Trans Effect as a Tool for Product Differentiation. Synthesis of Nitrosyl Containing Re(I) Complexes Bearing Chelating Ligands.

D. Veghini, H. Berke. Institute of Inorganic Chemistry, University of Zürich, Winterthurerstr. 190, 8057 Zürich, Switzerland.

The chemistry of nitrosyl containing transition metal complexes has recently attracted considerable interest, because of the capability of the nitrosyl to stabilize Lewis acidic transition metal centers. However the synthetic access to [M(NO)]-species is sometimes rather problematic and limited to some classes of compounds. In the case of d^6 Re(I) metal center, the [Re(NO)] fragment is, with only some exceptions, combined with P donors or cyclopentadienyl derivatives. In order to extend this field to bidentate P and N donors, we reinvestigated the reactivity of the halide bridged $[(CO)_2(NO)(Cl)Re(\mu\text{-}Cl)_2Re(Cl)(CO)_2(NO)$ dimeric complex **1**. **1** reacts with 2,2'-dipyridyl in boiling THF affording a cationic Re(I) complex with η^2 coordination of this moiety in moderate yield (eq1)



On the other hand the reaction of **1** under the same conditions as in eq 1 with the rigid trans 1,2-bis(dimethylphosphin)cyclopentan (dmcp) ligand yielded a racemic mixture of diastereomeres of the neutral cis,cis-$[Re(Cl)_2(CO)(NO)(dmcp)]$ (eq 2)



he proposed pathways for these reactions are in accord with the predictions from the trans effect of the 2,2'-dipyridyl and of the dmcp ligand. The configurations of all prepared compounds were determined by X ray measurement.

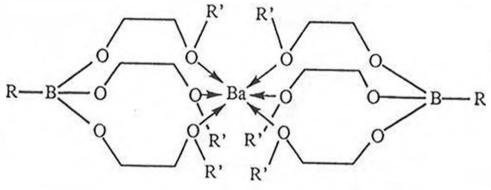
Anorganische / Koordinationschemie **22**

Novel Barium- and Copper Precursors for Depositon of Oxide Thin Films in High Vacuum

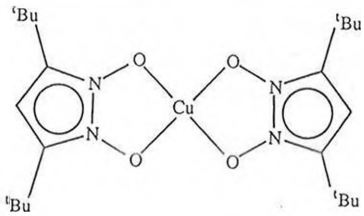
E. Fritsch[a], D. Veghini[a], S. Nefedov[a], H. Berke[a]
P. Willmott[b], M. Lingenauer[b], P. Felder[b], J.R. Huber[b]

a) Anorganisch-Chem. Institut, Universität Zürich, CH-8057 Zürich
b) Physikalisch-Chem. Institut, Universität Zürich, CH-8057 Zürich

We have started a search for new precursors suitable for the preparation of superconducting thin films by CBE (Chemical Beam Epitaxy). Novel complexes with Cu and Ba centers which sublime without decomposition at moderate temperatures (120 - 160 °C / 10 $^{-6}$ torr) have been synthesized. Two examples are shown below:



R = ^{t}Bu, Ph, Me, R' = Me. Et, ^{i}Pr



They are expected to decompose on heated surfaces more effectively to produce copper and barium films than the frequently used β-diketonate based systems. Comparative mass spectroscopic and decomposi–tion studies have been carried out.

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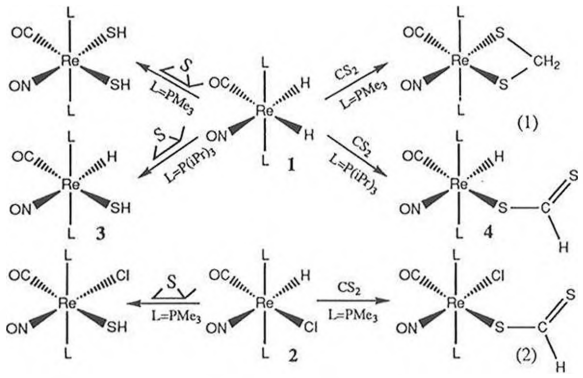
Inorganic Chemistry **23**

Reactivity of Rhenium Nitrosyl Mono- and Dihydrides and their Reactions with Sulfur Containing Substrates

S. Feracin, S. Nefedov, I. Eremenko, D. Veghini and H. Berke
Institute of Inorganic Chemistry, University of Zurich, CH-8057 Zurich

Insertions of organic substrates into transition metal bonds represent important initial steps for the further functionalization of these molecules. In this regard the ancillary ligand sphere has also a decisive influence. In our group we have recently studied the chemistry of nitrosyl hydrides and their potential to undergo insertion reactions. With the aim of extending these investigations to sulfur containing substrates we reacted the rhenium hydrides **1** and **2** with CS_2 and propylensulfide according to eq 1 and 2.



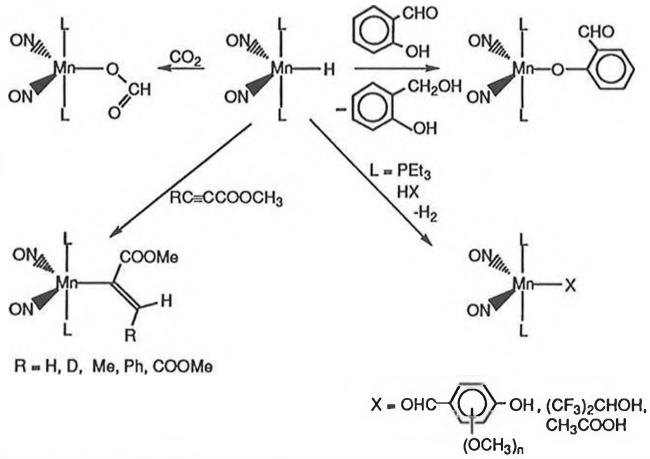
The reactions of **1** to **3** and **4** show high regioselectivity discriminating the diastereomeric hydride position of **1**. The preference for the S donor in trans position to CO may have a kinetic reason, but could also be driven by thermodynamics, as indicated by the reactions of **2**. These latter processes occur at a hydride ligand located trans to the nitrosyl group and end with a product with the newly formed sulfur ligand trans to CO. This change in stereochemistry may involve $[Re\text{-}SH]^+$ and $[Re(\eta^2\text{-}S_2CH]^+$ species as intermediates and apparently leads to the thermodynamic products.

Inorganic Chemistry **24**

A Comparative Study on the Reactivity of $Mn(NO)_2L_2$ and $Mn(CO)_3L_2H$ Complexes (L = Phosphorus Donor)

D. Nietlispach, H.-W. Bosch, H.-U. Hund and Heinz Berke
Institute of Inorganic Chemistry, University of Zurich, CH-8057 Zürich

$Mn(NO)_2L_2H$ and $Mn(CO)_3L_2H$ complexes L = phosphorus donor differing by the isoelectronic replacement of 3CO with 2NO groups are expected to show different reaction behaviour. Due to a "nitrosyl effect" the $Mn(NO)_2L_2H$ species are thought to bear an activated Mn-H bond with a quite hydridic bond polarization and a relatively high propensity to undergo insertion reactions. These reaction properties are indeed documented for $Mn(NO)_2L_2H$ compounds as can be seen from the scheme below.



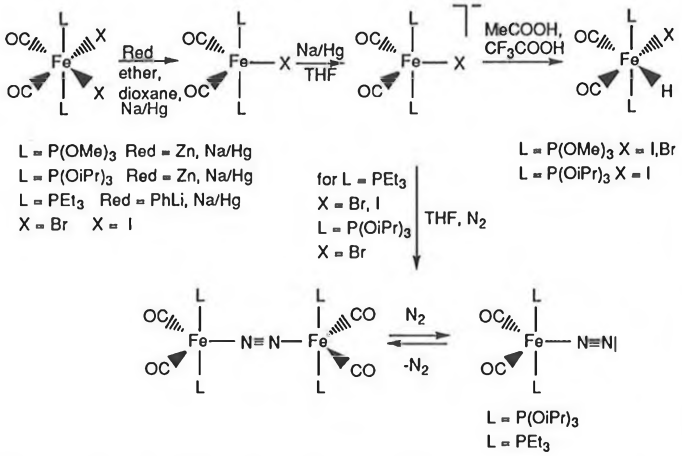
In contrast to this $Mn(CO)_3L_2H$ complexes L = PMe_3, PEt_3 react only with RC≡CCOOMe, R = H, COOMe and none of the other reagents shown in the scheme of $Mn(NO)_2L_2H$ complexes. These acetylene insertion processes proceed for both types of compounds with α metallation regio- and trans addition stereochemistry. In the case of $Mn(CO)_3L_2H$ complexes enforced reaction conditions are needed.

Inorganic Chemistry **25**

The Reduction of $Fe(CO)_2L_2X_2$ Compounds, L = $P(OMe)_3$, $P(OiPr)_3$, PEt_3, X = Br, I. From Iron(II) to Iron(0) via Stable Iron(I) Intermediates.

H. Kandler, Ch. Gauss, D. Veghini, I. L. Eremenko,
S. Rosenberger and Heinz Berke
Institute of Inorganic Chemistry, University of Zurich, CH-8057 Zürich

The reduction of $Fe(CO)_2L_2X_2$ complexes yields isolable blue or blue green oxygen-sensitive $Fe(CO)_2L_2X$ intermediates. These iron(I) radicals were characterized by IR, EPR and an exemplary X-ray structure determination.



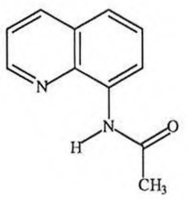
Further reduction affords $[Fe(CO)_2L_2X]^-$ anions, which for L = $P(OiPr)_3$, X = Br and L = PEt_3, X = Br, I react in the presence of N_2 to give N_2 complexes. For L = PEt_3 an equilibrium in solution between a μ-N_2 and an end-on N_2 species was found, manifested by $^{15}N/^{31}P$ NMR and IR studies. For L = $P(OiPr)_3$ only the end-on species exists. The anions $[Fe(CO)_2L_2X]^-$ L = $P(OMe_3)_3$, X = Br, I; L = $P(OiPr)_3$, X = I; were characterized chemically by protonation affording hydrido halo complexes.

Anorganische Chemie **26**

NEUE N-H AGOSTISCHE WECHSELWIRKUNGEN

P.S. Pregosin, B. Müller
Laboratorium für anorg. Chemie, ETH Zürich, CH-8092 Zürich

Mittels 2D -^1H ,^{15}N-NMR-Spektroskopie und röntgenographischen Messungen wurden eine Reihe von verschiedenen Verbindungen [1,2] untersucht, welche N-H···M Wechselwirkungen beinhalten. Die Charakterisierung und Natur dieser Interaktionen werden erläutert. zum Beispiel:



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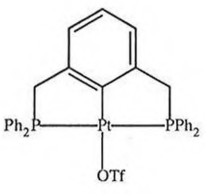
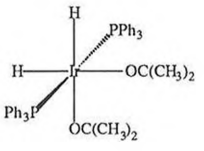


und



[1] Lee J.C., Rheingold A.L., Müller B., Pregosin P.S. and Crabtree R.H., J. Chem. Soc., Chem. Commun., 1994, p.1021-2.

[2] Albinati A., Lianza F., Müller B., Pregosin P.S., Organometallics, in print

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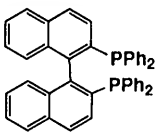
Anorganische Chemie **27**

Strukturanalyse von Pd(II) BINAP η^3-Allyl-Komplexen. Multinukleare NMR- und röntgenkristallographische Untersuchungen von Exo-Methylen-Cyclopenten und β–Pinen Allyl Komplexen.

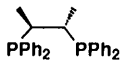
P.S. Pregosin, R. Salzmann
Laboratorium für anorganische Chemie, ETH Zürich, CH-8092 Zürich

Kristallographische Strukturdaten für S(-) BINAP (β)Pinen-allyl [Pd(η^3-$C_{10}H_{15}$){ S(-) BINAP }] CF_3SO_3, und den R(+) BINAP exo-Methylen Cyclopenten-allyl Komplex [Pd(η^3-C_6H_9){ R(+) BINAP }] CF_3SO_3, verbunden mit multidimensionalen ^1H, ^{13}C and ^{31}P NMR-Resultaten für diese beiden, sowie den neuen chiralen Allyl-Komplex [Pd(η^3-C_6H_9)(S,S-CHIRAPHOS)] CF_3SO_3, werden vorgestellt. Sie dienen zur Interpretation der Merkmale und Unterschiede in den "chiralen Taschen" von BINAP und S,S-CHIRAPHOS. In BINAP-Komplexen sind die Phenylringe eher axial und equatorial angeordnet und zeigen zudem mehr in Richtung des Allyls, womit sie stärker in diese Sphäre einzudringen vermögen. Dabei scheinen die equatorialen Phenylgruppen eine stärkere Wirkung zu haben als die axialen. Einige neue NMR-Hilfsmittel, basierend auf NOE's, helfen bei der Untersuchung der Strukturmerkmale.

Pd-(η3-$C_{10}H_{15}$)



BINAP



S,S- CHIRAPHOS

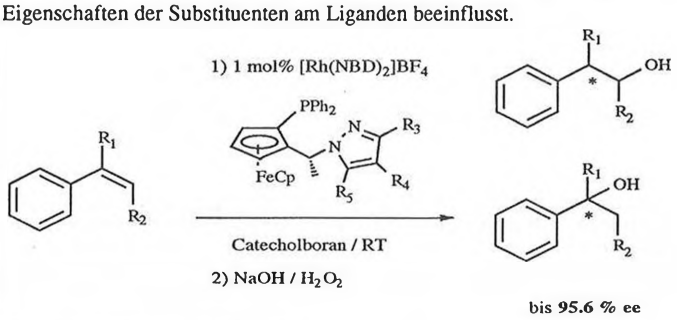
Pd-(η3-C_6H_9)

Anorganische und Koordinationschemie **28**

Hohe Enantioselektivitäten in der asymmetrischen Katalyse mit neuen chiralen Ferrocenyl–PN–Liganden

A. Schnyder, L. Hintermann und A. Togni
Laboratorium für anorganische Chemie, ETH-Z, Zürich

Der Einsatz von Josiphos in verschiedenen asymmetrischen Katalysen wurde intensiv untersucht [1]. Aufgrund dieser guten Resultate synthetisierte man neue, Josiphos-analoge PN-Liganden. Diese Liganden setzte man bei der Hydroborierung mit verschiedenen Substraten ein.
Bei der Hydroborierung von Styrol mit Catecholboran und PN-Ligand/ Rhodium als Katalysator erhielt man Enantioselektivitäten von 95% ee. Dabei wurden aber nur Regioselektivitäten von max. 50% erreicht. Die Enantio- wie auch die Regioselektivität werden stark von den elektronischen ($R_3 = R_5 = CF_3$ vs. CH_3) bzw. sterischen ($R_3 = R_5 = CH_3$ vs. Isopropyl) Eigenschaften der Substituenten am Liganden beeinflusst.



[1] C. Breutel, H. Landert, A. Schnyder, F. Spindler*, A. Tijani, A. Togni*, J. Am. Chem. Soc. **1994**, *116*, 4062.

Chimie minérale et de coordination **29**

Elucidation of an Organometallic Reaction Pathway through Principal Component Analysis of Structural Data.

Edgar Müller, 28 av. de Florimont, 1006 Lausanne

Principal Component Analysis (PCA) is an efficient tool for the search of correlation in multidimensional data clusters and has been applied successfully to structure correlation problems [1]. Major drawbacks of PCA are still: i) the rationalization of the results in terms of the underlying chemistry, and ii) the difficulty of its simultaneous application to physically inhomogeneous input data (e.g. bond lengths and bond angles at the time). The here presented method circumvents these problems:

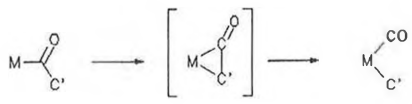
The variance-covariance matrix **V** is transformed from physical to statistical space to obtain a dimensionless correlation matrix **C**:

$$C = (S^{-1})^t V (S^{-1}); \quad s(i,i) = \sqrt{v(i,i)} \qquad (1)$$

PCA and backtransformation yields the physical displacement vectors **stw**:

$$W^t W = D = T^t (S^{-1})^t V (S^{-1}) T \qquad (2)$$

$$V = S T W W^t T^t S^t = (STW)(STW)^t \qquad (3)$$



Application of the method to the geometry of manganese, iron and other transition metal acyl complexes yields directly the **decarbonylation pathway** as the major component of the structural variance, indicating a triangular 3-center transition state for this reaction.

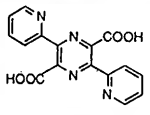
[1] **Structure Correlation**; H.-B. Bürgi and J. D. Dunitz (eds.), VCH, **1994**; T. Auf der Heyde, Angew. Chem. Int. Ed. Engl. **1994**, 33, 823–839.

Chimie minérale et de coordination **30**

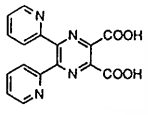
Design, Synthesis, and Crystal Structures of Two Cu(II) Coordination Polymers with a Helical Structure

Y. Wang and H. Stoeckli-Evans
Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51
CH-2000 Neuchâtel

Two new ligands, *L1* and *L2*, have been designed with the idea of forming coordination polymers. They have a very good chelating ability and a great diversity of coordination compounds have been synthesized with 3d metals.

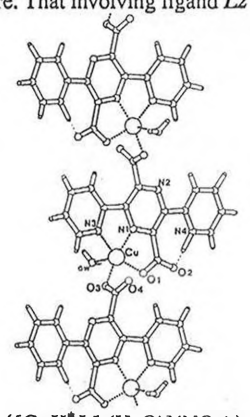


H_2L1

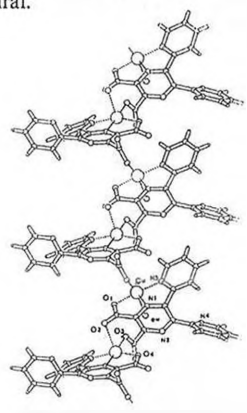


H_2L2

We will report on the synthesis, crystal structures and related assembly-processes of two Cu(II) coordination polymers with a helical structure. That involving ligand *L2* is chiral.



{[CuH^*L1(H2O)](NO3)}n



{[Cu*L2* (H2O)](H2O)3}n

Chimie minérale et de coordination **31**

Complexes gazeux du Co(tmhd)2 avec du bipyridil

Pascal Chassot, Franzpeter Emmenegger
Institut de Chimie Inorganique, Université de Fribourg, CH-1700 Fribourg

Le tmhd (2,2,6,6-tetramethyl-3,5-heptandionate) utilisé dans cette étude comme ligand est un β-dicétonate, qui contrairement à l'acétonylacétonate ne forme pas de complexes métalliques polymères (tétramère) en solution. Ceci facilitera la comparaison des réactions en solution et en phase gazeuse. Les spectres du complexe dans les deux phases sont, en effet, très semblables. En ajoutant du bipy (2,2'-bipyridyl) au $Co(tmhd)_2$, on passe d'un complexe tétracoordonné à un complexe hexacoordonné.

$$Co(tmhd)_2 + bipy = Co(tmhd)_2\ bipy$$

Les équilibres sont étudiés en phase gazeuse par spectroscopie UV-Vis entre 100 et 350 °C. Par le traitement numérique de la matrice des spectres optiques obtenus, il est possible de calculer à l'aide de modèles thermodynamiques et de la loi de Beer Lambert les constantes d'équilibre, les valeurs d'enthalpie et d'entropie ainsi que les coefficients d'extinction molaire des espèces du système. Dans un premier temps, une analyse optique du $Co(tmhd)_2$ entre 180 et 250 °C (le point de fusion étant à 149°C) permet de déterminer la valeur de l'enthalpie et de l'entropie d'évaporation de ce complexe. Ces résultats sont comparés avec les mesures de pression de vapeur obtenues par la méthode du 'modified entrainment'. Dans un deuxième temps, les spectres du $Co(tmhd)_2$bipy (avec ou sans excès de ligand) sont analysés. Entre 200 et 260 °C (le point de fusion étant à 269°C), les paramètres thermodynamiques de la sublimation du $Co(tmhd)_2$bipy sont déterminés. Entre 260 °C et 350 °C, on observe la dissociation du complexe. Par la décomposition de la matrice en composantes principales, il est possible d'affirmer la présence de deux espèces absorbantes le $Co(tmhd)_2$bipy et le $Co(tmhd)_2$. Puis il est possible de déterminer l'enthalpie et l'entropie de cette dissociation et de trouver les coefficients d'extinction molaire du $Co(tmhd)_2$bipy. La comparaison des valeurs thermodynamiques de l'équilibre en solution et en phase gazeuse permettent de quantifier les effets de solvatation.

Chimie minérale et de coordination **32**

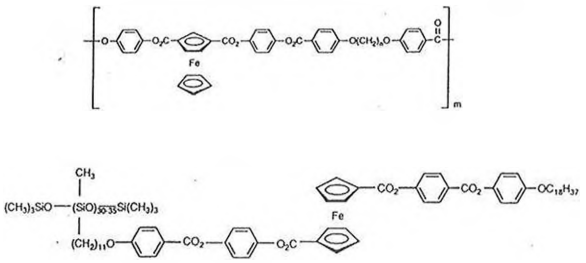
Polymères Organométalliques. Propriétés Mésomorphes de Polymères du Ferrocène

R. Deschenaux,[a] I. Kosztics,[a] J.-L. Marendaz,[a] U. Scholten,[a] D. Guillon,[b] et M. Ibn-Elhaj,[b]

[a] Université de Neuchâtel, Institut de Chimie, Avenue de Bellevaux 51, CH- 2000 Neuchâtel

[b] Institut de Physique et Chimie des Matériaux de Strassbourg, Groupe des Matériaux Organiques, 67 Rue du Loess, 67037 Strassbourg Cedex, France

A ce jour, les polymères organométalliques cristaux liquides ont été très peu étudiés. Ces composés sont intéressants car ils pourraient conduire au développement de matériaux présentant des propriétés électrochimiques, magnétiqes et optiques nouvelles.
Nous avons synthétisé et étudié des polymères cristaux liquides incorporant le ferrocène dans la chaine principale ou dans la chaine latérale du polymère.



Une étude détaillée (microscopie à lumière polarisée, calorimétrie à balayage differentiel et rayons -X) a montré que des polymères du ferrocène présentant un caractère mésomorphe important, une haute stabilité thermique et une bonne solubilité dans les solvants organiques classiques peuvent être obtenus.

33

Anorganische/Koordinationschemie

New Compounds Containing A=B=C^{x-} 16-Electron Species

M. Wörle, R. Nesper, H.-J. Muhr, H. Meyer zu Altenschildesche
Laboratorium für Anorganische Chemie, ETH Zürich, and
M. Somer, Max-Planck-Institut für Festkörperforschung, Stuttgart

Three new compounds containing linear CBN^{4-}-anions were prepared and characterized by means of X-ray diffraction and IR-, Raman- and NMR-spectroscopy.

$\mathbf{Ca_{9+0.5x}(BN_2)_{6-x}(CBN)_x}$ **(I)** (for x=0 to 2) crystallizes in space group $Im\bar{3}m$ with a=7.3224(3) (x=0) to a=7.3982(8) Å(x=2). The compound $Ca_9(BN_2)_6$ **(I)** shows a defect on one cation position, which can be filled up consecutively, followed by replacement of BN_2^{3-} by CBN^{4-}-anions .
$\mathbf{Ca_{15}(CBN)_6(C_2)_2O}$ **(II)** crystallizes in the cubic space group $Ia\bar{3}d$ with a=16.568(1) Å. It contains CBN^{4-}, C_2^{2-} and O^{2-}-anions. The fairly complicated structure can be partioned by the Gyroid nodal surface [1] for a clearer representation.

The exact composition of $\mathbf{Ca_5(XYZ)_2A}$ **(III)** (P4/ncc, a=8.1923(7), c=10.844(4) Å) is not yet clear, but we expect this phase to contain CBN^{4-}-anions, too.

I is a colorless transparent insulator which, according to preliminary doping experiments by a large number of metals and semimetals, seems to be dopable up to semimetallic behaviour. The heteroatomic cummulene systems are anions of new acids which have not been described before.

[1] von Schnering,H.G., Nesper,R.: Nodal surfaces of Fourier series: fundamental invariants of structured matter, Z. Phys. B 83 (1991)407-412

Anorganische/Koordinationschemie **34**

$Li_6B_{18}{\cdot}LiBH_4$ – Preparation, Crystal Structure, and NMR–Spectroscopic Properties

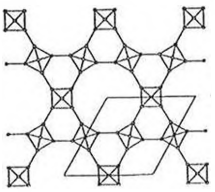
M. Wörle, H. Meyer zu Altenschildesche, R. Nesper
Laboratorium für Anorganische Chemie, ETH Zürich, 8092 Zürich

$\mathbf{Li_6B_{18}{\cdot}LiBH_4}$, initially found as a by-product during investigation of the Li–B phase system [1], is now characterized by means of X-ray diffraction and NMR-spectroscopy.

The pure compound is obtained by reacting a mixture of Li (excess), B, and $LiBH_4$ at 1270 K and subsequent removal of excess lithium by sublimation.

The crystal structure (P6/mmm, $a = 8.2386, c = 4.1614$ Å) consists of a new open framework of B_6 - octahedra forming channels of two different sizes (cf. Fig.1). The channels are occupied by Lithium and/or isolated BH_4^-–units. These anions show a high degree of orientational disorder. Lithium can partially be replaced by aluminium.

The compound was also investigated by means of ^{7}Li, ^{11}B, and ^{1}H MAS–NMR–spectroscopy. On the basis of our results, the observed disorder is discussed in detail.



Boron framework of $\mathbf{Li_6B_{18}{\cdot}LiBH_4}$ projected along [001]. Li–atoms and BH_4^-–anions are not shown.

[1] G. Mair, 'Über das System Lithium – Bor', PhD Thesis, Universität Stuttgart and Max–Planck–Institut für Festkörperforschung, 1984

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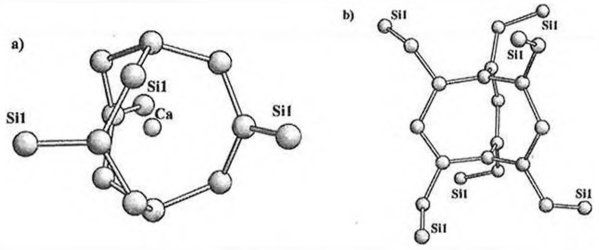
Anorganische/Koordinations Chemie **35**

$Ca_{14}Si_{19}$ und $Ca_{(3-x)}Mg_xSi_4$: Zwei neue Zintlphasen im System Ca/Mg/Si

Reinhard Nesper, Antonio Currao
Laboratorium für Anorganische Chemie, ETH Zürich, CH-8092 Zürich

Im ternären System Ca/Mg/Si ist neben CaMgSi [1] noch eine weitere ternäre Phase der Zusammensetzung $Ca_7Mg_{7.25}Si_{14}$ [2] bekannt. Bei weiteren Untersuchungen in diesem System konnten eine weitere neue ternäre Phase $Ca_{(3-x)}Mg_xSi_4$ (x=0.08) [3] und eine neue binäre Phase $Ca_{14}Si_{19}$ [4] synthetisiert und strukturell charakterisiert werden.
Bei $Ca_{(3-x)}Mg_xSi_4$ handelt es sich um eine stets verzwillingte Phase. Die zentrale Einheit besteht aus einer 11er Koordination aus Si-Atomen um eine Ca-Lage (Abb. a). Drei solche Einheiten sind über Si1 zu Schichten miteinander verknüpft. In Abb. b ist die zentrale Einheit von $Ca_{14}Si_{19}$ zu sehen, welche aus 17 Si-Atomen besteht (Ca-Atome fehlen). Drei solche Einheiten sind auch in dieser Phase über Si1 zu Schichten verknüpft. Beide Polyanionen $[Si_4]^{6-}$ und $[Si_{19}]^{28-}$ sind neuartige zweidimensionale Schichtstrukturen von Silicium.



[1] H. Axel, B. Eisenmann, H. Schäfer, A. Weiss, Z. für Naturforschung 24b, 815 (1969)
[2] R. Nesper, A. Currao, S. Wengert, ETH Zürich, J. Curda, MPI Stuttgart, Publikation in Vorbereitung
[3] R. Nesper, A. Currao, Publikation in Vorbereitung
[4]R. Nesper, A. Currao, ETH Zürich, J. Curda, H. Hillebrecht MPI Stuttgart, Publikation in Vorbereitung

Anorganische Chemie **36**

The Boron-Heterofullerenes $C_{59}B$ and $C_{69}B$: Synthesis, Enrichment and Endohedral Complexes with Alkaline Earth Metals - A Mass Spectrometric Study

H.-J. Muhr and R. Nesper
Laboratorium für anorganische Chemie, ETH Zürich, Switzerland

The substitution of carbon with neighbour elements like boron or nitrogen is a promising method to change the molecular and bulk properties of such clusters. In 1991 R.E. Smalley and co-workers succeeded in the generation of boron-heterofullerenes $C_{60-x}B_x$ (x=1-6) by laser-vaporization of boron-nitride/graphite mixtures [1,2,3]. Here, we present a possibility for the large-scale production and isolation of boron-heterofullerenes [4].
Fullerene soot is generated in a modified reactor by arc evaporation of doped graphite rods. Suitable doping materials found until now are boron nitride, boron, and boron carbide. The fullerenes are obtained out of the soot through soxhlet extraction with dry CS_2 or THF. The analysis of the extracts is carried out with LD-TOF (laser desorption time of flight) mass spectrometry, NMR and elemental analysis via ICP-MS. Negative-ion mass spectra show the presence of $C_{59}B$, $C_{69}B$ and probably higher boron-heterofullerenes with strong enhanced intensities only in the THF-extracts of the soot.
The evaporation of graphite rods doped with $M_3[BN_2]_2$ (M=Ca, Sr, Ba) generated endohedral complexes of undoped fullerenes and especially in the case of Ca the endohedral complexes $Ca@C_{59}B$ and $Ca@C_{58}B_2$ proven as THF adducts in the mass spectra of the THF extracts of the soot.

[1] R.E. Smalley in *ACS Symposium Series, Vol.481* (Eds. : G.S. Hammond, V.J. Kuck) American Chemical Society, Washington DC, **1992**, 141.
[2] T. Guo, Ch. Jin, R.E. Smalley, *J. Phys. Chem.*, **1991**, *95*, 4984.
[3] Y. Cahi et al., *J. Phys. Chem.*, **1991**, *95*, 7564.
[4] H.-J. Muhr, R. Moeri and R. Nesper, eingereicht an *Angewandte Chemie*, **1994**.

Anorganische Chemie **37**

Iron Chalcogenide Carbonyl Clusters as Precursors for Thin Film Preparation

T. Fässler, G. Mullen, K.-H. Dahmen, and E. Lang
Laboratorium für Anorganische Chemie, ETH Zürich, CH-8092 Zürich

Thin films of iron chalcogenides are of interest because of their application in thin film solar cells (FeS_2) and their magnetic properties.
In order to make metal atoms volatile, organometallic precursors are used with a big variety of organic ligands. Even though the class of carbonyl complexes is well studied in molecular chemistry, they are not often used for MOCVD film preparations.

In order to produce iron chalcogenide films on glass and silicon we started from the readily available iron chalcogenide carbonyl cluster compounds $Fe_3X_2(CO)_9$ (X = S, Se, Te).

For X = Te we successfully prepared Fe_3Te_2 - films under very mild conditions.

$$Fe_3Te_2(CO)_9 \xrightarrow{300°C} "Fe_3Te_2"$$

The films show semiconducting behaviour with a remarkable low resistance.
The film growth and the properties of the films are discussed.

38

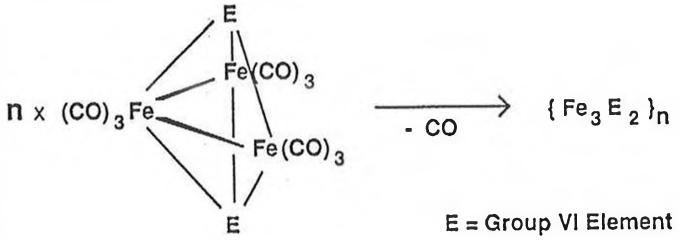
Anorganische Chemie

Iron Chalcogenide Carbonyl Clusters as Precursors for New Solid State Phases

T. Fässler and G. Mullen
Laboratorium für Anorganische Chemie, ETH Zürich, CH-8092 Zürich

The synthesis of inorganic solid state compounds using molecular starting materials offers a valuable complement to the synthesis from solid elements. This principle is well developed for the growth of thin films by thermal decomposition of volatile organometallic complexes (MOCVD), but is less used for the synthesis of new bulk materials.
Whereas typically solid state reactions mostly start from the elements by using high temperatures for the interdiffusion, the use of molecular precursors give opportunities to prepare known or metastable materials under milder conditions (< 300°C).

Here we show how thermolysis of iron chalcogenide carbonyl clusters leads to new crystalline iron chalgenide phases, not found by synthesis from the elements. The magnetic and conductive properties are discussed.
The tellurium containing cluster can also be used as starting materials to produce thin films of the composition Fe_3Te_2 on quartz and silicon at low temperatures [1]. The films show semiconducting behaviour with a remarkable low resistance.
The properties of the bulk materials are discussed using X-ray diffraction, conductivity and magnetic measurements.
[1] T. Fässler, G. Mullen and K.-H. Dahmen



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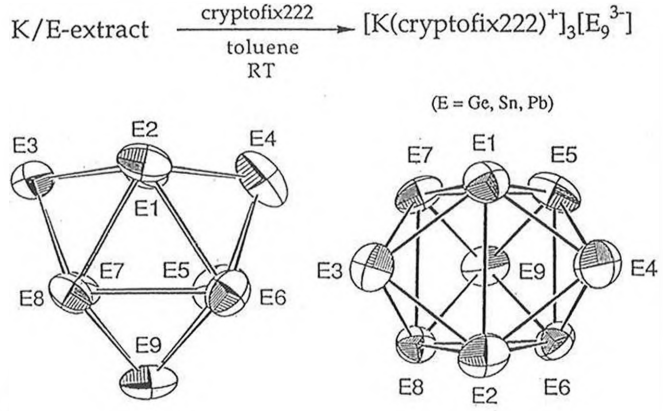
Anorganische Chemie **39**

The Largest By X-ray Diffraction Characterized, Naked Lead-Cluster Pb_9^{3-} And The Homologues Ge_9^{3-} And Sn_9^{3-}

Thomas Fässler and Markus Hunziker
Laboratorium für Anorganische Chemie, ETH Zürich, 8092 Zürich

We present here a systematic and simple pathway for the synthesis of the radical Zintlanions Ge_9^{3-}, Sn_9^{3-}, Pb_9^{3-} as well as for the diamagnetic Ge_9^{2-} starting from the binary alloys of potassium with the corresponding metal of the nominal melt "K_4E_9" (E = Ge, Sn, Pb). We report structural and physical features of these anions, which are obtained in good yields and isolated as their potassium-salt with the stabilizing help of cryptofix222*:



* cryptofix222 = 4,7,13,16,21,24-Hexaoxa-1,10-diazatricyclo[8.8.8]hexacosane

Chimie minérale et de coordination **40**

SITE EXCHANGES IN BIS(DIPHENYLPHOSPHINO)ETHENE TETRAIRIDIUM CARBONYL CLUSTERS

G. Laurenczy, G. Bondietti, R. Ros and R. Roulet
Institut de Chimie Minérale et Analytique, Université de Lausanne
3, Place du Château, 1005 Lausanne

The intramolecular processes responsible for carbonyl site exchanges in tertiary phosphine and phosphite derivatives of $Ir_4(CO)_{12}$ have been examined in the last few years [1]. Recently, phosphine migration on the metal core has been shown to occur in $[Ir_2Rh_2(CO)_{11}PPh_3]$ [2].

In the present study the intramolecular rearrangements in $[Ir_4(CO)_7(\mu_3\text{-}CO)_3(dppet)]$ (**1**) (dppet: *cis*-$PPh_2CH{=}CHPPh_2$) and $[Ir_4(CO)_5(\mu_3\text{-}CO)_3(\mu_2\text{-}dppet)_2]$ (**2**) have been investigated using variable temperature ^{13}C and ^{31}P NMR.

In solution, cluster **1** exists as an equilibrium mixture of two isomers, one with a chelating dppet (**1a**) and the other with an edge-bridging dppet in diaxial position (**1b**). The interconversion of **1a** and **1b** is due to an intramolecular P-atom migration to a site left vacant by faster CO-scrambling processes. The latter are the change of basal face for **1a** and the merry-go-round for **1b**.

In **2**, the bidentate dppet ligands are both in edge-bridging positions. CO scrambling leads by two parallel changes of basal face to a pairwise exchange of the P-atoms. At higher temperatures a second process, probably the restricted rotation at the apical Ir atom, averages the remaining two ^{31}P resonances.

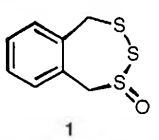
[1] B. E. Mann, B. T. Pickup, A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 889 (1989); A. Strawczynski, G. Suardi, R. Ros, R. Roulet, F. Grepioni, D. Braga, *Helv. Chim. Acta*, 76, 2210 (1993); K. Bcsançon, G. Laurenczy, T. Lumini, R. Roulet, G. Gervasio, *Helv. Chim. Acta*, 76, 2926 (1993).
[2] G. Laurenczy, G. Bondictti, A. Merbach, B. Moulet, R. Roulet, *Helv. Chim. Acta*, 77, 547 (1994).

Koordinationschemie **41**

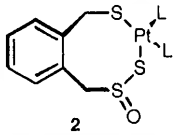
Reaktionen von Tri- und Tetrasulfan-S-oxiden mit Platin(0)-Komplexen

R. Wünsch, K. Polborn, W. Weigand*
Institut für Anorganische Chemie, Ludwig-Maximilians-Universität München, D-80333 München, Meiserstraße 1, Deutschland.

Metallkomplexe, die Anionen der bisher unbekannten Thiosulfinsäure R-S(O)-SH enthalten, sind sehr selten. Man erhält sie bei Reaktionen von Metallhydrogensulfiden des Typs $CpRu(L)(PPh_3)(SH)$ (L = CO, PPh_3) mit *N*-Sulfinylphthalimiden [1] oder durch oxidative Addition von *N*-Thiosulfinylphthalimiden phthN-S-S(O)-R (phthN = Phthalimid) an Platin(0)-Reagenzien [2]. Wir berichten hier über einen neuen Syntheseweg, der zu Platin(II)-thiosulfinato-Komplexen führt.
1,5-Dihydro-2,3,4-benzotrithiepin-2-oxid **1**, deren Struktur durch eine Röntgenstrukturanalyse gesichert ist, addiert sich oxidativ an $L_2Pt(\eta^2\text{-}C_2H_4)$ [L = PPh_3, 1/2 (-)-DIOP, 1/2 $(Ph_2P\text{-}C_5H_4)_2Fe$]. Dabei inseriert das $L_2Pt(0)$-Fragment in die Disulfid-Bindung, und es entstehen die Thiolato-thiosulfinato-Komplexe **2**:



1



2

Das entsprechende 3-Oxid und *o*-Benzotrithiolon-1 bzw. -2 spalten dagegen bei Reaktionen mit Platin(0)-Verbindungen formal das Schwefeloxid SO ab; man isoliert Dithiolato-Komplexe. Ähnliche Beobachtungen werden auch bei Reaktionen mit Tetrasulfan-S-oxiden gemacht.

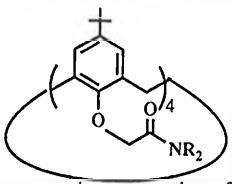
[1] W. Weigand, G. Bosl, C. Robl, *Z. Naturforsch.* **1992**, *47b*, 39; A. Shaver, P.-Y. Plouffe, *J. Am. Chem. Soc.* **1991**, *113*, 7780.
[2] W. Weigand, R. Wünsch, C. Robl, W. Amrein, *Chem. Ber.* **1994**, *127*, 97.

Chimie de coordination **42**

Extraction and Solution Thermodynamics of Complexation of Alkali and Alkaline-Earth Cations by Calix[4]arene amides

F. Arnaud, S. Fanni, W.McGregor and M.J.Schwing
EHICS, Laboratoire de Chimie-Physique, 1, rue Blaise Pascal, 67000 Strasbourg

Of the many calix[4]arenes chemically modified at the lower rim, esters , ketones and amides have attracted particular attention because they display strong extracting and complexing properties towards alkali cations, with a marked preference for Na^+ [1]. Their ease to discriminate selectively amongst these cations has been ascribed to their preorganized cone conformation . The two calix[4]arene amides already studied [2] also show a high affinity for alkaline earth cations, with a high selectivity for Ca^{2+}or Sr^{2+} over Mg^{2+}.



We now report the extracting properties of nine new calix[4]arene tetraamides towards alkali and alkaline-earth cations The enthalpies and entropies of complexation by the diethyl and pyrrolidinyl tetraamides in methanol and in acetonitrile have been determined for the first time, from calorimetric measurements. The data are compared with data for calixarene esters and solvent effects are discussed in the light of earlier results.

Acknowledgments : The work presented has been done in collaboration with the Queen's University of Belfast (Pr. M.A. McKervey) and was financially supported by the EEC in the frame of the Program "Treatment of Radioactive Wastes"

[1] F. Arnaud-Neu, E.M. Collins, M. Deasy, G. Ferguson, S.J. Harris, B. Kaitner, A.J. Lough, M.A. McKervey, E. Marques, B.L. Ruhl, M.J. Schwing-Weill and E.M. Sewart, *J. Am. Chem. Soc.*, **1989**, *111*, 8681
[2] F. Arnaud-Neu, M.J.Schwing, K. Ziat, S. Cremin, S.J. Harris and M.A. McKervey, *New J. Chem.*, **1991**, *15*, 33

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Inorganic and Coordination Chemistry **43**

Synthesis of tetranuclear complexes of Ruthenium and Osmium with a definite chirality

M.Riklin, P. Belser, A. von Zelewsky
Institute of Inorganic and Analytic Chemistry, University of Fribourg

The reaction of $[Ru(bym)_3]Cl_2$ (bym: 2,2'-bipyrimidine) with $[Ru(by)_2Cl_2]$ (by: 2,2'-bipyridine) leads to the formation of the tetranuclear complex $[Ru(Ru(bym)(by)_2)_3](PF_6)_8$ [1][2]. This product has 4 centres of chirality, and consists of 8 isomers (4 pairs of diastereomers).

Our interest is the construction of a well-defined chiral tetranuclear Ruthenium complex. To solve the problem of isomerism, we have used in a first step the chiral block $[Ru(by)_2(py)_2][(-)$-dibenzoyl-L-tartrate$]\cdot 12H_2O$ [3], in order to synthesize complexes with a external sphere composed of 3 Ruthenium having a definite chirality: the [rac-Ru(Λ-Ru(bym)$(by)_2)_3](PF_6)_8$ and the [rac-Os(Λ-Ru(bym)$(by)_2)_3](PF_6)_8$. Theoretically both complexes should then be a couple of diastereomers.

However we have noted with surprise that in both cases the ^{1}H-NMR spectrum of the products only indicated the presence of a single diastereomer. Is it an asymmetrical induction? Only the measurements of ^{1}H-NMR spectra of the separated [Δ-Ru(Λ-Ru(bym)$(by)_2)_3](PF_6)_8$ and [Λ-Ru(Λ-Ru(bym)$(by)_2)_3](PF_6)_8$ should allow to solve this enigma.

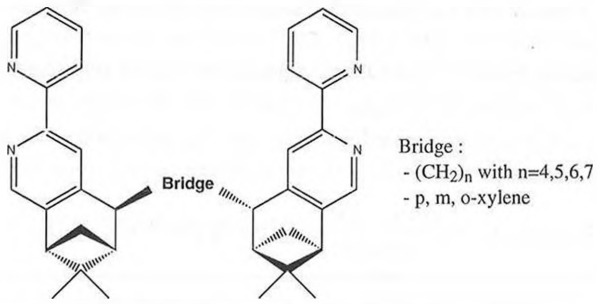
[1] A. Ludi, M. Hunziker, *J. Am. Chem. Soc.* **1977**, *99*, 7370-7371.
[2] P. Rillema, R. Sahai, L. Morgan, *Inorg. Chem.* **1988**, *27*, 3495-3500.
[3] X. Hua, thesis Nr. 1047, **1993**, University of Fribourg.

Anorganische Chemie / Komplexchemie **44**

Stereoselectively linked bipyridine units: Influence of the bridgelength upon coordination with Fe(II), Ru(II) and Os(II).

A. von Zelewsky and H.-R. Mürner
Departement of Inorganic Chemistry, University of Fribourg

Stable, enantiomerical pure mononuclear building blocks are a necessity in the preparation of well defined polynuclear species. To obtain such building blocks, the approach of P. Hayoz [1] with two stereo selectively bridged 4,5-Pinenbipyridine - units was further exploited.



Ligands with aliphatic chains were described by P. Hayoz [1]. Para-, meta- and ortho - xylene bridged ligands were newly synthesised and fully characterised.

Complex formation with Iron (II), Ruthenium(II) and Osmium(II) revealed the importance for metal centre adjusted length of the bridge. The bridge has to be sufficiently long to reach the backside of the same metal centre but with extensive chain length the formation of polymeric material is dominating. The best results were obtained with 5 and 6 CH_2 - groups in the Ru (II)-case, whereas Os(II) preferred 6 and 7 CH_2 - groups [2]. With xylenebridged ligands, yields dropped drastically by changing from ortho and meta to the para-isomer in Ru(II) complexes.

Evidence for the stereo selective formation of dinuclear trippelhelixes with Fe(II) and xylenebridged ligands are presented.

[1] P. Hayoz, A. von Zelewsky J. Am. Chem. Soc. (1993), **115** , 5111-5114.
[2] E. Jandrasics, University of Fribourg, private communication.

Anorganische Chemie/Koordinationschemie **45**

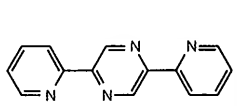
New chiral building blocks of Ru(II) and Os(II) for the synthesis of polynuclear homo- and mixed-metal -complexes

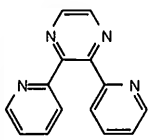
A. von Zelewsky, P. Belser and E. Jandrasics
Institut für Anorganische und Analytische Chemie, Universität Freiburg i. Ue., Pérolles, 1700 Freiburg

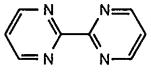
Δ-$[Ru(CG[5])(L)](PF_6)_2$ (L:bpym; 2,3dpp; 2,5 dpp; 4,6 dppm) and Δ-$[Os(CG[n])(dmso)_2](PF_6)_2$ have been developped in order to synthesize dinuclear chiral complexes.

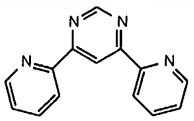
The ability of CG[n] [1] to build up directly enantiomerically pure metal complexes facilitates the synthesis of optically active, higher nuclear complexes. No resolution was necessary.

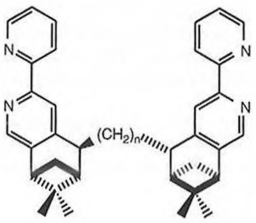
It was possible to synthesize an optical active Os(II) complex as precursor. ^{1}H n.m.r spectra and CD spectra are shown.


2,5 dpp


2,3 dpp


bpym


4,6 dppm



CG[n]

[1] Alex von Zelewsky, P. Hayoz, Helen Stoeckli Evans, *J. Am. Chem. Soc.*, **1993**, 115, 5111-5114

Inorganic and Coordination Chemistry **46**

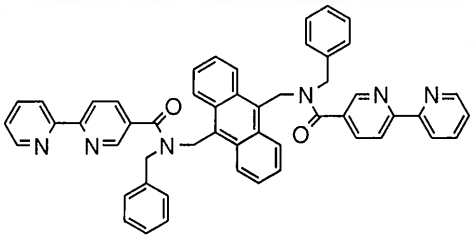
Supramolecular Ru- and/or Os-complexes of a amide-linked bis-bipyridine ligand

A. von Zelewsky, P. Belser and M. Baak

Institut für Anorganische und Analytische Chemie, Universität Fribourg, CH-1700 Fribourg

Supramolecular systems in which photoinduced energy- or electron transfer can take place are the basis of new photochemical systems, which will eventually be capable of performing well-defined light-induced functions as e.g. switching in electronic devices.

We synthesized in this context the dinuclear Ru(II)/Os(II)- resp. Ru(II)/Ru(II)- complexes with a bridging amide-linked bis-bipyridine ligand **1** [1], containing a central anthracen unit.



1

The excited state of the Ru/Ru-complex sensitizes the formation of $^1O_2$, which in turn oxidizes the central anthracen unit to the corresponding endo-peroxide. This chemical transformation blocks the energy-transfer in the molecule (self-poisening system).

[1] R. Dux, Thesis Nr. 1036, University of Fribourg, **1993**.

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Anorganische Chemie / Koordinationschemie

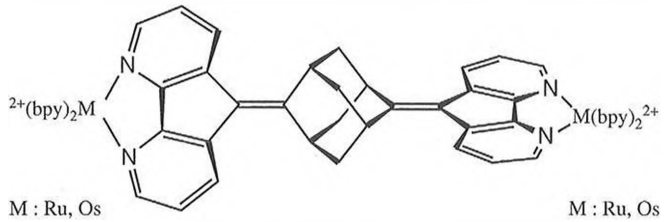
47

Starre dinukleare Metallkomplexe (Ru^{2+}, Os^{2+}), welche einen Elektronen- resp. Energietransfer über grosse Distanz zeigen.

P. Belser und St. Bernhard
Institut für Anorganische Chemie, CH-1700 Universität Fribourg

Supramolekulare Systeme, in denen photoinduzierter Elektronen- oder Energietransfer über grosse Distanz stattfinden kann, sind die Basis für die in diesem Poster vorgestellten "molecular devices", welche vielfältige Anwendungsmöglichkeiten z.B. in der künstlichen Photosynthese und in der Datenverarbeitung haben. Um Aussagen über die Bedingungen des vektorellen Energie- resp. Elektronentransfers zu machen, müssen die aktiven Zentren durch starre, nicht koppelnde Abstandhalter (Spacer) verbunden sein.

Wegen ihrer ausgezeichneten Eigenschaften (Redox- und Emissionsverhalten) sind Ru(II)- und Os(II)-bpy-Komplexe (bpy : 2,2'-Bipyridin) geeignete Bausteine für den Aufbau solcher supramolekularer Systeme.



DAD-Ligand

Es wurde ein aus zwei Diazafluorenyliden-Einheiten und einer Adamantan-Einheit bestehender Brückenligand (DAD) synthetisiert und vollständig charakterisiert. Die entsprechenden Ru(II)- und Os(II)-Komplexe wurden hergestellt und ihre photochemischen Eigenschaften gemessen.

Weitere Arbeiten zielen darauf hin, die Spacereinheit auf zwei resp. vier Einheiten zu erweitern, um den Einfluss der Distanz zwischen den Metallzentren auf den Elektronen- resp. Energietransfer zu untersuchen.

Anorganische Chemie

48

Silica-Titania Low-temperature Aerogels as Selective Epoxidation Catalysts

D.Dutoit, R.Hutter und A.Baiker
Laboratorium für Technische Chemie, Eidgenössisch Technische Hochschule Zürich, ETH Zentrum, CH-8092 Zürich

Titanium substituted silicalite zeolites with MFI (TS-1) and MEL (TS-2) structures have been shown to be good catalysts for the selective epoxidation of organic reactants. However the steric restrictions imposed by the pore size (ca. 5.5 Å) limit their use to the oxidation of relatively small organic molecules. Thus highly porous silica-titania aerogels with high dispersion of titanium in the silica matrix were synthesized by the sol-gel process. An acidic hydrolysant was added to a solution of tetraisopropoxytitanium(IV) modified by acetylacetonate and tetramethoxysilicon(IV) in isopropanol. The resulting titania-silica gels were subsequently dried by different methods, including conventional drying, high-temperature supercritical drying, and semicontinuous extraction with supercritical CO_2 (low-temperature aerogel).

The influence of the drying method applied and of the Ti content on the morphological and chemical properties of the solids were studied. The solids were characterized by means of nitrogen physisorption, X-ray diffraction, vibrational spectroscopy and thermal analysis (TG, DTA), and tested for the epoxidation of cyclohexene with alkylhydroperoxide.

The conventionally dried xerogels possess titanium well-dispersed in the silica matrix and predominantly micropores. Consequently, they do not show any catalytic activity in the epoxidation reaction. High-temperature supercritical drying leads to mesoporous aerogels with an undesired formation of anatase, which results in low activity. With the low-temperature aerogels, increasing Ti-content leads to lower microporosity, higher BET surface area (up to ca. 700 m^2/g) and enhanced catalytic activity. All these aerogels with up to 20 wt% titania show no indication for longe-range-ordered titania agglomerates, as judged by XRD.

This material is the basis of novel very active and selective catalysts for the epoxidation of small and large organic compounds with alkylhydroperoxides as oxidizing agent. The aerogels with 20 wt% TiO_2 show the highest reaction rate per gram of catalyst. Using the oxidation of cyclohexene as test reaction, 95 % conversion after 20 min with a selectivity of nearly 100% towards the epoxide (based on the olefine) was obtained.

Anorganische Chemie

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Vanadia-Titania Aerogels: Preparation, Morphological Properties and Activity for the Selective Catalytic Reduction of NO by NH_3

M. Schneider, M. Maciejewski, S. Tschudin, A. Wokaun, and A. Baiker

Laboratorium für Technische Chemie, ETH-Zentrum, CH-8092 Zürich

Highly dispersed vanadia-titania aerogels with high surface area have been synthesized by a two-stage sol-gel process with ensuing high-temperature supercritical drying. A titania gel was prepared by the addition of an acidic hydrolysant to tetrabutoxytitanium(IV) in methanolic solution. The vanadium alkoxide precursor was added after redispersing the titania gel. The influences of different preparation conditions, i. e. in terms of the sol-gel and supercritical-drying stage, on the morphological and chemical properties of the aerogels were studied. The aerogels were characterized by means of nitrogen physisorption, X-ray diffraction, transmission electron microscopy and thermal analysis (TG, DTA) coupled with mass spectrometry.

The meso- to macroporous vanadia-titania aerogels possess BET surface areas of 140–220 $m^2\ g^{-1}$ after calcination at ≤ 673 K, and contain well-developed anatase crystallites of ca. 10 nm mean size. Crystalline V_2O_5 was only detected for samples calcined at 723 K. All other aerogel catalysts, calcined at lower temperatures, showed no indication for long-range-ordered vanadia domains. Thermal analysis revealed that even calcination at 723 K was not sufficient for complete removal of organic residues, which were entrapped during supercritical drying.

The catalytic properties of the aerogels were tested for the selective catalytic reduction of NO by NH_3.

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$$

An increase of the vanadia loading from 5 to 30 wt% 'V_2O_5' resulted in a marked increase of the overall as well as specific activity, while the apparent activation energy decreased from 66 to 55 kJ mol^{-1}. An increase of the calcination temperature from 573 to 673 K led to a significant rise in the activity of the vanadia-titania aerogels. The aerogel with 30 wt% 'V_2O_5' showed a reaction rate, referred to the vanadium content ('TOF'), similar to that of multiply grafted well-dispersed vanadia/titania catalysts. Among all catalysts studied, this aerogel exhibited the highest reaction rate per gram of catalyst.

Anorganische Chemie

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Incorporation of Carbon into Palladium during CO Disproportionation over Pd / Titania

M.Maciejewski, C.Ruedin, M.Schneider and A.Baiker
Laboratorium für Technische Chemie, ETH-Zentrum, CH-8092 Zürich

In a previous study [1], we have shown that upon exposure of Pd/ZrO_2 catalysts to CO atmosphere at elevated temperature, disproportionation of CO (Boudouard reaction) occurs with subsequent incorporation of carbon into palladium. In the present work we have extended this studies to Pd/TiO_2 catalysts prepared by impregnation and the sol-gel route.

After heating the catalysts under pure CO atmosphere and subsequent quenching, the carbon incorporation was investigated by thermal analysis combined with mass spectroscopy and X-ray diffraction. Carbon was incorporated into the Pd-lattice already at 250°C. The interstitial solid solution of carbon in palladium, with a maximal carbon concentration of 15 at%, was stable in the range 330-470°C under the conditions used (heating rate 10K/min). Above 600°C the solubility of C in Pd/TiO_2 was negligible.

During incorporation of carbon into Pd, two solid solutions with different amounts of carbon were formed. The ratio of "carbon-rich" to "carbon-poor" phases depended on the catalysts preparation. For the aerogel sample, where Pd-particles are in intimate contact with TiO_2, only the "carbon-rich" phase was formed. For the impregnated Pd/TiO_2 catalysts with low Pd content, preferential formation of the "carbon-rich" Pd phase was observed. Increasing the amount of Pd deposited on the support led to the "carbon-poor" phase. Furthermore, the incorporation of carbon into the Pd-lattice occurred at much higher temperature, as observed for pure palladium powder.

The results indicate that the strength of the metal-support interaction greatly influences the formation of the interstitial solid solution Pd-C. With Pd/TiO_2 the carbon incorporation begins at significantly higher temperature (ca 50°C) compared to that observed previously with Pd/ZrO_2. However, the temperatures of decomposition of Pd-C solutions were the same, independent of the support material used.

[1] M.Maciejewski and A.Baiker, J.Phys.Chem., 1994,*98*,285.

CHIMIA 48 (1994) Nr. 7/8 (Juli/August)

Anorganische Chemie

51

$La_{0.8}Sr_{0.2}MnO_{3+x}$ Supported on $LaAlO_3$ and $LaAl_{11}O_{18}$ Prepared by Different Methods: Influence of Preparation Method on Morphological and Catalytic Properties in Methane Combustion

P.E. Marti[1], M. Maciejewski[2] and A. Baiker[2]

[1] Department of Combustion Technology, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
[2] Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092 Zürich, Switzerland.

$LaAlO_3$ and $LaAl_{11}O_{18}$ as supports for $La_{0.8}Sr_{0.2}MnO_{3+x}$ catalysts have been prepared by conventional coprecipitation and by a complexation method (citrate method). Samples prepared by the citrate method contained traces of carbon, even after calcination at 1370 K for 8 h, as revealed by thermal analysis (TA). X-ray diffraction patterns (XRD) of the two $LaAlO_3$ samples showed well-defined sharp reflections after calcination at 1370 K, while for the crystallization of both $LaAl_{11}O_{18}$ temperatures above 1500 K were required. The supported $La_{0.8}Sr_{0.2}MnO_{3+x}$ catalysts were prepared by impregnation of the supports with an adequate amount of an aqueous solution of the corresponding metal nitrates resulting in a loading of 20 wt% $La_{0.8}Sr_{0.2}MnO_{3+x}$. The formation of $La_{0.8}Sr_{0.2}MnO_{3+x}$ on the supports was confirmed by XRD. The mean crystallite size as estimated by XRD line broadening was larger for the perovskite supported on $LaAl_{11}O_{18}$ than on $LaAlO_3$. $La_{0.8}Sr_{0.2}MnO_{3+x}$ on both differently prepared $LaAlO_3$ supports was much more stable towards thermal decomposition than on $LaAl_{11}O_{18}$, as confirmed by oxygen evolution and TA.

Kinetic studies of methane combustion were carried out in a fixed-bed microreactor in the range 600 - 1220 K and at atmospheric pressure using a reactant mixture with a ratio CH_4:O_2 = 1:4. For the $LaAlO_3$-supported catalysts the reaction rates, referred to the weight of $La_{0.8}Sr_{0.2}MnO_{3+x}$, were about three times higher at 770 than corresponding rates of the unsupported $La_{0.8}Sr_{0.2}MnO_{3+x}$. In contrast, the $LaAl_{11}O_{18}$-supported catalysts showed similar activities as unsupported $La_{0.8}Sr_{0.2}MnO_{3+x}$.

Anorganische/Koordinations Chemie

52

Formation of Harmful by-Products in Selective Catalytic Reduction of Nitrogen Oxides over Cu/ZSM-5 and Alumina

Frank Radtke, René A. Koeppel and Alfons Baiker
Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich (Switzerland).

The selective reduction of nitrogen oxides by hydrocarbons in the presence of excess oxygen has attracted considerable attention for the catalytic removal of NO_x in the exhaust gas of diesel or lean-burn gasoline engines. Several aspects of lean NO_x reduction have been investigated. Regarding the formation of by-products, hydrogen cyanide and ammonia were recently reported to be formed [1].

In this study we report the formation of harmful by-products such as hydrogen cyanide, ammonia and nitrous oxide in the selective catalytic reduction of NO_x by either ethene or propene over γ-alumina and Cu/ZSM-5. The effects of the type of alumina, the nitrogen oxide (NO or NO_2), and of the hydrocarbon employed as a reducing agent (C_2H_4 or C_3H_6), on the formation of the by-products and on the overall catalytic performance were examined.

Catalytic tests using γ-alumina showed that the reduction of nitrogen dioxide to nitrogen proceeds more efficiently than the corresponding reaction with nitrogen monoxide. NO_2 conversions up to 90% were obtained as compared to maximum NO conversions of 34%. Similar results were obtained with either ethene or propene as reductants. On the contrary, a marked influence of the type of reductant was observed by employing Cu/ZSM-5 as a catalyst. With ethene, a maximal conversion of nearly 100% was reached, whereas with propene the NO_x conversion remained lower than 50% for both, NO and NO_2.

Substantial amounts of hydrogen cyanide (up to 70 ppm) and ammonia (up to 30 ppm) were found as by-products, while the formation of nitrous oxide remained low (< 10 ppm). A strong influence of the catalyst, the hydrocarbon used as a reductant and, to a lesser extent, the use of either NO or NO_2 in the reactant gas was observed.

[1] F. Radtke, R. Koeppel and A. Baiker, Appl. Catal. A, 107 (1994) L125.

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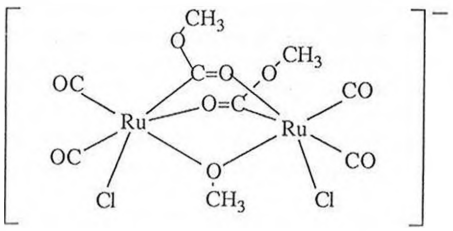
Chimie minérale et de coordination

Hydrocondensation du dioxyde de carbone avec le méthanol catalysée par des complexes anioniques du ruthénium : Synthèse et caractérisation de $[N(PPh_3)_2][Ru_2(CO)_4(OCOCH_3)_2(OCH_3)Cl_2]$

J.-M. Soulié, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink*
Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel

Des complexes anioniques du ruthénium, tel que $[Ru(CO)_3Cl_3]^-$, catalyse la formation du formiate de méthyle à partir du dioxyde de carbone, de l'hydrogène et du méthanol, en présence du méthylate de potassium comme promoteur.

$$CO_2 + H_2 + CH_3OH \longrightarrow HCOOCH_3$$



Le complexe formé lors de la réaction du catalyseur $[Ru(CO)_3Cl_3]^-$ avec le promoteur $[OCH_3]^-$ a été isolé et caractérisé par analyse aux rayons-X. L'anion $[Ru_2(CO)_4(OCOCH_3)_2(OCH_3)Cl_2]^-$ représente vraisemblablement un intermédiaire de la réaction catalytique.

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Anorganische und Koordinationschemie

$(\mu_2\text{-H})Ru_3(CO)_9[\mu_3\text{-NS(O)MePh}]$ - Ein elektronisch ungesättigter Dreikerncluster mit einer chiralen Sulfoximinkappe.

G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink*
Institut de Chimie, Université de Neuchâtel, CH-2000 Neuchâtel
C. Bolm, D. Kaufmann
Fachbereich Chemie, Phillips-Universität Marburg, D-35032 Marburg

Die thermische Umsetzung von $Ru_3(CO)_{12}$ mit *(R-)*-Methylphenylsulfoximin liefert unter Erhalt der Konfiguration am chiralen Schwefelatom den Dreikerncluster *(R-)*-$(\mu_2\text{-H})Ru_3(CO)_9[\mu_3\text{-NS(O)MePh}]$, (**1**) der mit einer Elektronenbilanz von 46e ein ungesättigtes Ru_3-System darstellt.

$$Ru_3(CO)_{12} + HNS(O)MePh \longrightarrow HRu_3(CO)_9[NS(O)MePh] + 3CO$$
(**1**)

Entsprechend seinem elektronisch ungesättigten Charakter lässt sich **1** mit Kohlenmonoxid in die gesättigte 48e-Spezies $HRu_3(CO)_{10}[\mu_2\text{-NS(O)MePh}]$ (**2**) überführen.

$$HRu_3(CO)_9[NS(O)MePh] + CO \rightleftharpoons HRu_3(CO)_{10}[NS(O)MePh]$$
(**1**) (**2**)

Beide Cluster **1** und **2** wurden isoliert und vollständig charakterisiert, die Struktur der ungesättigten Spezies **1** wurde durch eine Einkristall-Röntgenstrukturanalyse aufgeklärt.

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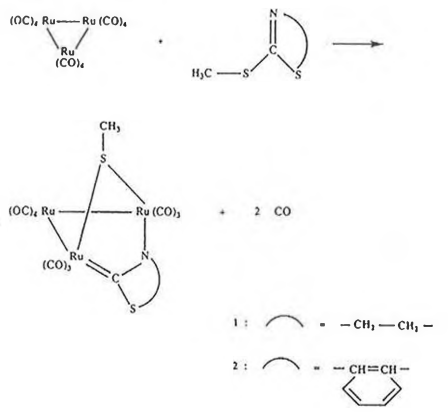
Chimie minérale et de coordination **55**

Dérivés cycliques de l'acide carbonimidodithioique en tant que source de carbène : fragmentation de ces ligands lors de leur coordination à un complexe trinucléaire de ruthénium

C. Renouard, H. Stœckli-Evans et G. Süss-Fink*
Institut de chimie, Université de Neuchâtel, CH-2000 Neuchâtel

Dans le cadre d'une étude de la réactivité du complexe trinucléaire $Ru_3(CO)_{12}$ vis-à-vis de systèmes trifonctionnels dérivés de l'acide carbonique, nous avons engagé des carbonimidodithionates cycliques.



Contrairement aux autres systèmes étudiés : carbamates, guanidines, urées, isourées et thiourées, ces composés subissent une fragmentation C-S et se coordonnent à l'ossature trinucléaire de ruthénium avec ouverture d'une liaison métal-métal.

Chimie minérale et de coordination **56**

Cu^{II} complexes of 2,5-bis(2-pyridyl)pyrazine. -The formation of coordination compounds with interesting magnetic properties

A. Neels and H. Stoeckli-Evans
Département de Cristallographie, Institut de Chimie, Université de Neuchâtel

A. Escuer and R. Vicente
Departement de Quimica Inorgànica, Universitat de Barcelona, Spain

Binuclear and multinuclear metal complexes comprising two or more metal centers bridged by multidentate ligands can exhibit metal-metal interactions, such as energy or electron transfer and magnetic coupling.

2,5-Bis(2-pyridyl)pyrazine (bppz) has been used as a bridging ligand in the construction of some interesting supramolecular species [1]. Binuclear complexes of bppz with some 3^d transition metals have also been studied [2,3].

Two bppz bridged Cu^{II} - complexes have been synthesized and characterized. We discuss the structures of a binuclear complex $[Cu_2(bppz)(NO_3)_2(H_2O)_4](NO_3)_2$ (1) and a coordination polymer $[Cu_4(bppz)(OAc)_8]_\infty$ (2).

The magnetic properties of the Cu(II)-coordination compounds have been studied by means of susceptibility measurements between 290 and 4K. The data indicate ferromagnetic coupling for (1) and antiferromagnetic coupling for (2).

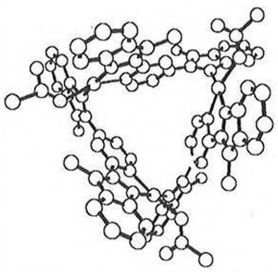
[1] G. Denti, S. Serroni, S. Campagna, V. Ricevuto, V. Balzani, *Coordination Chemistry Reviews* **1993** , *125* ,75.
[2] A. Escuer, T. Comas, R. Vicente, J. Ribas, *Transition Met. Chem.* **1993** , *18* , 42.
[3] A. Neels, H. Stoeckli-Evans, *Chimia* **1993** , *47* , 198.

Chimie minérale et de coordination **57**

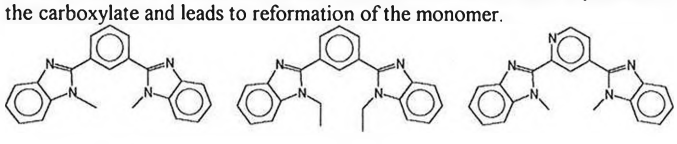
A Study of Self-Assembly About a Square Planar Pd(II) Centre

Riccardo F. Carina, Gérald Bernardinelli, Alan F. Williams
Département de Chimie Minérale, University of Geneva, 30 quai Ernest Ansermet, CH 1211 GENEVA 4 Switzerland

It was recently shown[1] that the reaction of ligand L^1 with $Pd(OAc)_2$ leads to formation of the cyclic trimer $[PdL^1(OAc)]_3$. While the acetate groups *trans* to the phenyl carbon are labile on a NMR timescale, the methylene protons of L^2 show an AB spectrum, confirming that the complex remains chiral, and thus that it is kinetically robust.



The ligand L^3 is structurally very similar to L^1 and L^2. Reaction with $Pd(O_2CEt)_2$ gives $PdL^3(O_2CEt)_2$ whose crystal structure is almost identical with a monomer $PdL^1(OAc)$ unit excised from the structure of $[PdL^1(OAc)]_3$. $PdL^3(O_2CEt)_2$ does not spontaneously form a trimer. However, addition of one equivalent of acid labilises one of the carboxylate ligands, and leads to formation of the trimer as shown by the diastereotopic methylene protons. The trimer may be destroyed by addition of one equivalent of base which deprotonates the carboxylate and leads to reformation of the monomer.



L^1 L^2 L^3

1) S. Rüttimann, G. Bernardinelli, A.F. Williams, Angewandte Chemie, Int. Ed. 32, 392 (1993).
2) S. Rüttimann, C. Piguet, G. Bernardinelli, B. Bocquet, A.F. Williams, J. Amer. Chem. Soc. 114, 4230 (1992).

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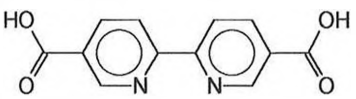
Chimie minérale et de coordination

Coordination Chemistry of a Functionalised Bipyridyl Ligand

Philipe Desmartin, Gérald Bernardinelli, Alan F. Williams

Département de Chimie Minérale, University of Geneva, 30 quai Ernest Ansermet, CH 1211 GENEVA 4 Switzerland.

The development of supramolecular coordination complexes[1] requires the preparation of multidentate ligands in which the different binding sites cannot all bind to the same metal. A possible candidate for such a ligand is 5,5'(2,2'-dipyridyl)dicarboxylic acid[2]:



This ligand combines a bidentate bipyridyl unit with two harder carboxylate sites which cannot complex a metal bound to the bipyridyl site. The different nature of the binding sites allows discrimination between different metal ions.

The crystal structure of the complex $[Co(LH)_3]$ shows octahedral coordination with an elaborate hydrogen bonding network between complexes of the same chirality.

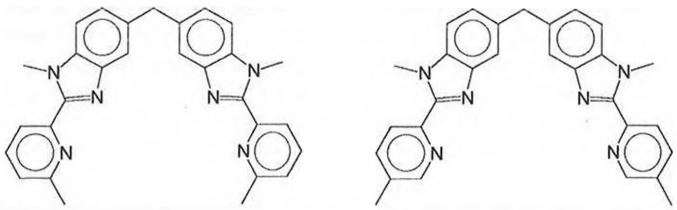
1) J.-M. Lehn, Angewandte Chemie, Int. Ed. 29, 1304 (1990).
2) G.M. Badger, W.H.F. Sasse, J. Chem. Soc. 616, (1956)

Chimie minérale et de coordination **59**

Synthesis, Structure and Resolution of a Dicobalt(III) Triple Helix.

Loïc Charbonnière, Claude Piguet, Gérald Bernardinelli, Alan F. Williams
Département de Chimie Minérale, University of Geneva

Helical coordination compounds are a subject of considerable current interest[1]. Although these complexes are chiral, the necessity of using labile metal ions for the assembly of the helix has hitherto precluded their resolution into enantiomers.



L^1 L^2

The triple helical complex[2] $[Co_2L^1_3]^{4+}$ could not be oxidised to a cobalt(III) complex. The crystal structure suggested that repulsion between methyl groups distorted the Co(II) coordination sphere, preventing the oxidation. This was confirmed by the crystal structure of $[Co_2L^2_3](ClO_4)_4$ which showed less distortion of the coordination sphere around Co(II). This complex is readily oxidised to a cobalt(III) complex whose crystal structure is reported. The Co(III) complex is kinetically stable and may be resolved into its enantiomers. The circular dichroism spectrum will be reported.

1) E.C. Constable, Tetrahedron, 48, 10013 (1992).

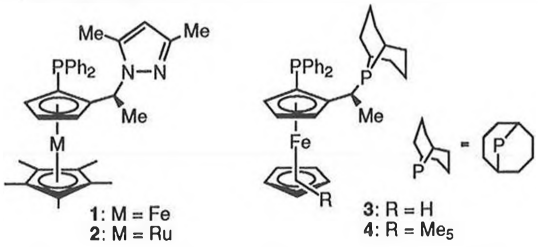
2) A.F. Williams, C. Piguet , G. Bernardinelli, Angewandte Chemie, Int. Ed. 30, 1490 (1991).

Anorganische Chemie / Koordinationschemie **60**

Versatile Synthesis of Optically Active Ferrocene Derivatives: Novel Chiral Modifiers for efficient Asymmetric Hydroboration and Hydrogenation

H.C.L. Abbenhuis, C. Köllner, I. Steiner and A. Togni
Laboratorium für anorganische Chemie, ETH-Z, Zürich

Ferrocenylphosphines are currently applied as the carriers of chiral information in enantioselective catalysis. Some of our recent contributions to this field are: 1) the application of fulvene synthons for the synthesis of simple, optically active cyclopentadienyl derivatives, and 2) the use of these derivatives for versatile synthesis of ferrocenyl- and ruthenocenyl phosphines [1]. In the last year, we have thus prepared metallocene derivatives, examples of these are shown below, that perform in asymmetric allylation, hydroboration and hydrogenation.



1: M = Fe
2: M = Ru

3: R = H
4: R = Me_5

The poster gives an account of catalytic reactions for which the complexes **1**-**4** have been used. Seemingly small modifications in the chiral modifiers turn out to have drastic effects on the performance of the catalytic systems employed. For instance, with the ferrocene derivative **1**, hydroboration of styrene can be achieved with 95 % e.e. while the ruthenocene, **2**, gives under identical conditions only 40 % e.e. Furthermore, we have used a, cheap, technical grade and virtually unknown, phosphine for the synthesis of complexes **3** and **4**. With these complexes, hydrogenation of dimethyl itaconate can be realized with more then 90 % e.e.

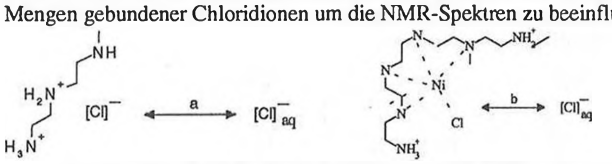
[1] H.C.L. Abbenhuis, A. Togni, A. Albinati, B. Müller, *Organometallics*, submitted for publication

Analytische Chemie **61**

Gegenionenkondensation von Chloridionen in Polyethyleniminlösungen pH-, $[Ni^{2+}]$ und Temperatur - Abhängigkeit - Untersucht mit ^{35}Cl- und ^{37}Cl-NMR

C.W. Schläpfer, U. Meier
Institut für Anorganische und Analytische Chemie, Universität Freiburg, CH-1700 Freiburg

Die beiden Chlorisotope ^{35}Cl und ^{37}Cl haben einen Kernspin von 3/2. Sie besitzen ein Quadrupolmoment. Die Relaxation dieser Kerne wird meistens durch die Quadrupolrelaxation dominiert, welche durch intramolekulare Wechselwirkungen verursacht wird. Die Relaxation enthält deshalb Informationen über molekulare Bewegungen und Assoziationen von Molekülen. Da die Quadrupolrelaxation sehr effizient ist, genügen kleine Mengen gebundener Chloridionen um die NMR-Spektren zu beeinflussen.



a) Relaxation in Polyethyleniminlösungen: Die Relaxationsrate nimmt mit dem Protonierungsgrad zu. Die Integrale bleiben im gesamten pH-Bereich konstant. Dies deutet auf einen schnellen Austausch hin. Die Temperaturabhängigkeit ist typisch für einen schnellen Austausch der Chloridionen zwischen der Polymerphase und der Lösung. Das Verhältnis der Relaxationsraten der beiden Isotope zeigt, dass die Quadrupolrelaxation dominant ist.

b) Relaxation in Polyethyleniminlösungen bei Zugabe von Ni^{2+}: Die Linienbreite in Abhängigkeit vom pH zeigt die Komplexbildung des Ni^{2+} durch den polymeren Liganden. Bei pH 4.5, im Gebiet des NiN_4-Komplexes ist die Linienbreite maximal. Die Temperaturabhängigkeit und das Verhältnis der Relaxationsraten der beiden Isotope bei pH=4.5 zeigen, dass die Linienbreite durch den Austausch der Chloridionen zwischen dem polymeren Komplex und der Lösung bestimmt wird.

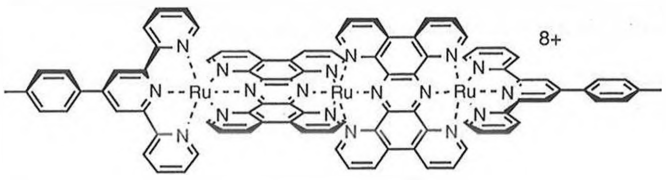
Coordination chemistry **62**

Bi- and Trinuclear Ruthenium Complexes containing Tetrapyridophenazine as a Bridging Ligand

Pierre Bonhôte[1] and Mark S. Wrighton
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Tetrapyridophenazine (tpp) was synthesized in four steps, as a potential ligand for the developpement of oligonuclear transition metal complexes with strong internuclear interactions. It allowed the preparation of ruthenium (II) bi- and trinuclear complexes capped with tolylterpyridine (ttp) which were characterized by NMR, UV-visible and mass spectroscopy as well as by electrochemistry and elemental analysis. The bi- and trinuclear complexes exhibit strong visible absorptions between 600 and 800 nm. The first oxidized state of the binuclear complex ($[ttpRutppRuttp]^{5+}$) appears to consist of two Ru(II) centers linked by the radical-cation $tpp^{+\cdot}$ and not to be the mixed-valent species, as shown by the absence of near-IR absorption. The rigid chelating site of tpp allows the existence of two isomers of the complex $ttpRutppRuttp^{4+}$, as shown by NMR and calculation.

Acknowledgement: This work was supported by the *Ciba-Geigy Jubiläums-Stiftung* and the *Swiss National Science Foundation.*



$ttpRutppRutppRuttp^{8+}$

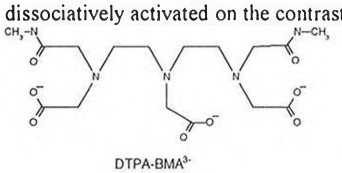
1) Postdoctoral fellow, present address: *Institut de chimie physique II, Ecole polytechnique fédérale de Lausanne, CH-1015 LAUSANNE, fax: +41-21-693-4111.*

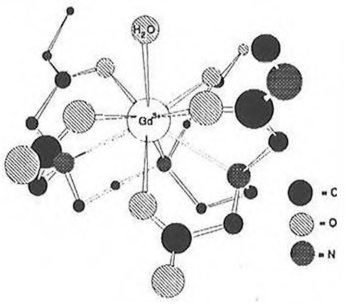
Chimie Minérale et de Coordination **63**

Water Exchange on Gadolinium Based Medical MRI Contrast Agents.

G. González, N. Graeppi, L. Helm, O. Ni Dhubhghaill, D. H. Powell, D. Pubanz, V. Tissières and A. E. Merbach
Institut de Chimie Minérale et Analytique, Université de Lausanne, Bâtiment de Chimie (BCH), 1015 Lausanne, Switzerland.
K. Micskei and E. Brücher
Institute of Inorganic and Analytical Chemistry, Kossuth University, Debrecen, Hungary.

Gd^{3+} chelates, due to their high proton relaxivity, are increasingly used as contrast agents in medical MRI. We have studied a series of Gd^{3+} complexes in solution, including the aqua ion and three commercial contrast agents (e.g. [Gd(DTPA-BMA)(H_2O)] shown below) using ^{17}O NMR and EPR techniques. The rates of water exchange are orders of magnitude slower on the contrast agents than on the aqua ion and can have a limiting effect on the proton relaxivity, and hence the efficacy of the contrast agents. Variable-pressure ^{17}O NMR measurements show that this is due to a change of water exchange mechanism, from associatively activated on the aqua ion to dissociatively activated on the contrast agents.



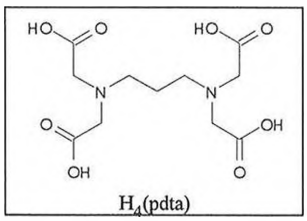


[1] G. González, D. H. Powell, V. Tissières, A. E. Merbach, *J. Phys. Chem.* **1994**, *98*, 53 and references therein.

Chimie Minérale et de Coordination **64**

Propylene diamine-N,N,N'N'-tetraacetate (pdta) Complexes with the Lanthanide(III) Ions: Water Exchange Kinetics Studied by ^{17}O NMR.

N.Graeppi, D.H.Powell and A.E.Merbach.
Institut de Chimie Minérale et Analytique, Université de Lausanne, Bâtiment de Chimie (BCH), 1015 Lausanne, Switzerland.



Rates of complex formation with oxyquinoline-sulfonate (oxs^{2-}) and tetramethylmuroxide (tmm^{-}) on the $[Ln(pdta)(H_2O)]^-$ ions are known to decrease along the lanthanide series. [1]

We have studied water exchange on a series of $[Ln(pdta)(H_2O)_2]^-$ complexes, using ^{17}O NMR technique at variable temperature and pressure. The exchange rate decreases monotonically from $[Gd(pdta)(H_2O)_2]^-$ ($k_{ex}^{298}=(1.02\pm0.1)\times10^8\ s^{-1}$) to $[Yb(pdta)(H_2O)_2]^-$ ($k_{ex}^{298}=(2.8\pm0.3)\times10^5\ s^{-1}$). Variable pressure ^{17}O NMR mesurements show that there is a change of water mechanism along the series. We observed an associatively activated mechanism for pdta-complexes of Gd(III) to (Er(III), ($\Delta V^{\neq}\approx-6\ cm^3mol^{-1}$) and a dissociatively activated mechanism for the pdta-complex of Yb(III) ($\Delta V^{\neq}\approx+7\ cm^3mol^{-1}$), with an interchange mechanism for $[Tm(pdta)(H_2O)_2]^-$ ($\Delta V^{\neq}\approx 0\ cm^3mol^{-1}$).

[1] M.Furrer, *Kinetik von schnellen Mischkomplexreaktionen der Seltenen Erden*, Ph.D.Thesis, ETHZ, 1974.

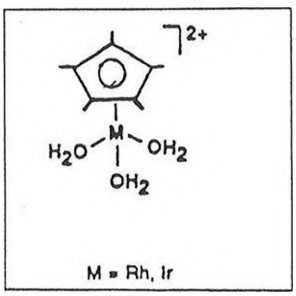
Chimie Minérale et de Coordination. **65**

High-pressure ^{17}O NMR study of water exchange kinetics on $[Cp^*M(H_2O)_3]^{2+}$(M = Rh, Ir).

L. Dadci,[1a] H. Elias,[1b] U. Frey,[1a] A. Hörnig,[1c] U. Kölle,[1c] A. E. Merbach,[1a] H. Paulus,[1b] and J. S. Schneider.[1b]

[1a] Institut de Chimie Minérale et Analytique, BCH, CH-1015 Lausanne, Switzerland. [1b] Eduard-Zintl-Institut für Anorganische Chemie, Technische Hochschule Darmstadt, D-64289 Darmstadt, Federal Republic of Germany. [1c] Institut für Anorganische Chemie, Technische Hochschule Aachen, D-52065 Aachen, Germany.

In a study of preparation, characterization and complex formation on half-sandwich complexes we determined the kinetic parameters of water exchange on $[Cp^*M(H_2O)_3]^{2+}$ (M = Rh, Ir) by variable temperature and pressure oxygen-17 NMR.The number of coordinated water molecules in solution is 3: 2.7± 0.3 and 2.8 ± 0.3 for Rh and Ir, respectively.



The values for $k_{ex}^{298}(s^{-1})$, $\Delta H^{\ddagger}$ ($kJmol^{-1}$), $\Delta S^{\ddagger}$ ($JK^{-1}mol^{-1}$) and $\Delta V^{\ddagger}$ (cm^3mol^{-1}) are: 1.6×10^5, 65.6, +75.3 and +0.6 for $[Cp^*Rh(H_2O)_3]^{2+}$ and 2.5×10^4, 54.9, +23.6 and +2.4 for $[Cp^*Ir(H_2O)_3]^{2+}$. The ratio $k_{ex}(Rh)/k_{ex}(Ir)$ for the species $[Cp^*M(H_2O)_3]^{2+}$ is very close to the ratio $k_i(average)(Rh)/k_i(average)(Ir)$ for the species $[Cp^*M(bpy)(H_2O)]^{2+}$. The kinetic finding support the operation of a dissociative interchange mechanisme (I_d) for the anation of the species $[Cp^*M(bpy)(H_2O)]^{2+}$ (M= Rh, Ir) as well as for the water exchange in $[Cp^*M(H_2O)_3]^{2+}$ (M = Rh, Ir).

Chimie minérale et de coordination **66**

Steric Effects on Water Exchange Mechanisms of Aquapentaaminemetal(III) Complexes (M=Cr, Co, Rh). A Variable Pressure Oxygen-17 NMR Study.

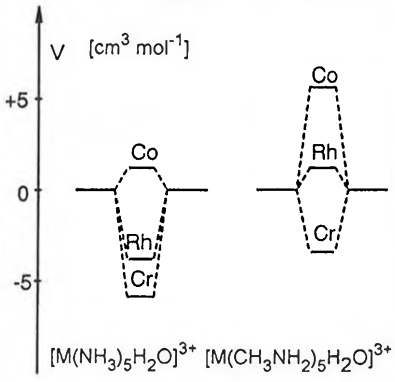
B. Moullet,[a] G. González,[b] M. Martinez,[b] and A. E. Merbach.[a]

a) Institut de Chimie Minérale et Analytique, Université de Lausanne, Bâtiment de Chimie (BCH), CH-1015 Lausanne, Switzerland. b) Universitat de Barcelona, Departament de Química Inorgànica, Diagonal, 647, E-08028 Barcelona, Spain.

The water exchange rate constants and activation parameters for the $[M(CH_3NH_2)_5H_2O]^{3+}$ (M = Cr(III), Co(III), and Rh(III)) complexes, have been determined by variable temperature and pressure ^{17}O NMR.

The following intermolecular exchange reactions were studied :

$$[M(RNH_2)_5H_2{}^*O]^{3+} + H_2O \rightleftharpoons [M(RNH_2)_5H_2O]^{3+} + H_2{}^*O$$



The volume profiles for the water exchange on $[M(NH_3)_5H_2O]^{3+}$ and $[M(CH_3NH_2)_5H_2O]^{3+}$ for three inert metal ions are illustrated. A shift to more positive (less negative) volumes is observed for complexes with the bulkier methylamine groups. Clearly, the crowding around the metal centre causes the mechanism to be shifted towards a more dissociatively activated position in the $I_a \leftrightarrow I_d$ mechanistic continuum.

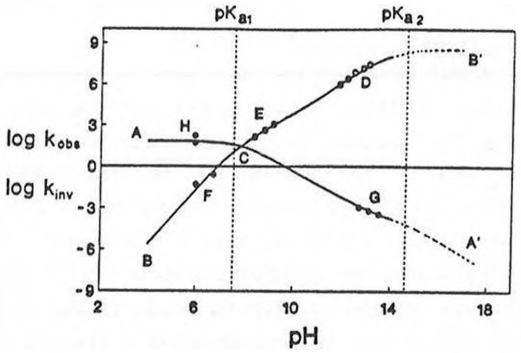
(1) González, G.; Moullet, B.; Martinez, M.; Merbach, A.E., submitted to Inorg. Chem.

Chimie minérale et de coordination **67**

Kinetics and Mechanism of Oxygen Exchange and Inversion Along the M=O Axis in the Diprotonated-, Monoprotonated- and Dioxotetracyanometalate Complexes of Re(V), Tc(V), W(IV) and Mo(IV).

Amira Abou-Hamdan[1], Andreas Roodt[2], Johann G. Leipoldt[2], Lothar Helm[1], and André E. Merbach[1]
[1]Institut de Chimie Minérale et Analytique, Université de Lausanne, Bâtiment de Chimie (BCH), CH-1015 Lausanne; [2]Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa

Oxygen-17 NMR was utilized to study the aqueous oxygen exchange (k_{obs}, line AA') of the mono- and diprotonated forms of the *trans*-dioxotetracyanometalate complexes of Re(V), Tc(V), W(IV) and Mo(IV) *i.e.* $[MO(OH)(CN)_4]^{(n+1)-}$ and $[MO(OH_2)(CN)_4]^{n-}$, and was correlated with the



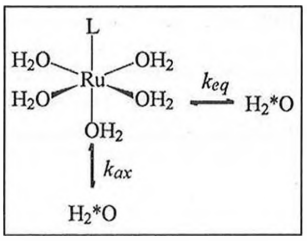
inversion rate (k_{inv}, line BB') of the metal complex along the M=O axis, as calculated from proton exchange data. This enabled the evaluation of these two kinetic processes as a function of pH over a 10 order of magnitude range as illustrated in the figure above for the W(IV) complex.

Chimie minérale et de coordination **68**

Comparative study of the electrochemical properties and of the water exchange rate on complexes of the type $[Ru(H_2O)_5L]^{2+}$.

N. Aebischer[†], G. Laurenczy[†], M. Ravera[¤], D. Osella[¤] and A.E. Merbach[†]
[†]Institut de chimie Minérale et Analytique, Université de Lausanne, Bâtiment de Chimie, (BCH), CH-1015 Lausanne; [¤]Dipartimento di Chimica Inorganica, Università di Torino, Via P. Giuria 7, I-10125 Torino

The redox potentials for the couples $[Ru(H_2O)_5L]^{2+}$/ $[Ru(H_2O)_5L]^{3+}$, where L = CH_3CN, $(CH_3)_2SO$, $H_2C{=}CH_2$, N_2, CO, $F_2C{=}CH_2$, have been determined by cyclic votammetry. The results show that the presence of a σ-donating and π-accepting ligand stabilizes the reduced form of the couple through electron π-back donation of the metal to the ligand. The π-back bonding is also responsible for an important deshielding on the two types of water molecules of the complex, as it can be seen from the ^{17}O-NMR chemical shifts.



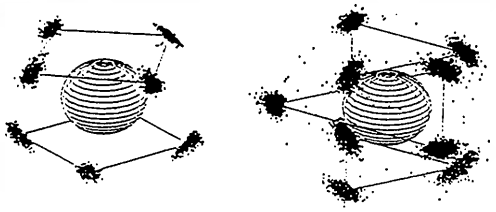
The exchange reactions for the water molecules in the axial and equatorial positions have also been investigated (see figure). The sequence for decreasing trans-effect (cis-effect) was established as follows: $F_2C{=}CH_2{\sim}$ $F_2C{=}CH_2{>}$ $(CH_3)_2SO{>}$ $CO{>}$ $H_2O{>}$ $CH_3CN{>>}$ N_2 ($H_2O{>>}$ $H_2C{=}CH_2{>}$ $CH_3CN{>}$ $N_2{\sim}$ $(CH_3)_2SO{>}$ $CO{\sim}$ $F_2C{=}CH_2$ respectively). Finally, the activation volume for the axial water exchange on the complexe $[Ru(H_2O)_5(CH_2{=}CH_2)]^{2+}$ was found equal to $+6.4 \pm 0.5$ cm^3mol^{-1}. This value indicates a dissociatively activated mechanism. Relations between the redox potentials, the chemical shifts and the rate constants will be presented.

Chimie minérale et de coordination **69**

Molecular Dynamics Simulation Study of Lanthanide Ions Ln(III) in Aqueous Solution Including Water Polarization - Structure and Internal Rearrangement of the First Hydration Shell

Th.Kowall, F.Foglia, L.Helm, A.E.Merbach
Institut de chimie minérale et analytique, Université de Lausanne, Bâtiment de Chimie (BCH), CH-1015 Lausanne

We have carried out MD-simulations for lanthanide ions Ln(III) in aqueous solution. The analysis of the structure and the internal rearrangement of the first hydration shell as well as of the water exchange mechanism is meant to promote a microscopic interpretation of experimental data [1].
By a usual pair potential approach the first hydration shell comes out to be by far too unstable both from a structural and a dynamical point of view. Therefore we propose a new 3-body potential function that takes into account the mean polarization of water molecules in the first hydration shell and that has been fitted to ab-initio results. The simulations reveal that the small relative change in the structural hydration number (CN) from 9 over 8.5 to 8 when going from Nd(III) to Yb(III) results in drastic changes concerning the water exchange rates.



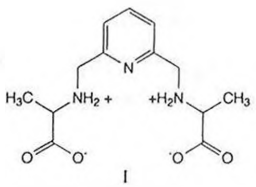
Combining a variety of analyzing approaches we were able to extract in detail the structure and dynamical behaviour of the first hydration shell. For the heavy lanthanide ions the eight water molecules of the hydration shell form a well-defined square antiprism with a lifetime of 10-20ps, whereas for a nine-coordinate light lanthanide ion the hydration shell adopts the geometry of a trigonal tricapped prism with a lifetime of only 1-2ps. For CN=8.5 we find an equilibrium between configurations of nine-fold and eight-fold coordination.
[1] L.Helm, F.Foglia, Th.Kowall and A.E.Merbach
J.Phys.: Condens.Matter 6,(1994) A137-A140

Chimie Minérale et de Coordination **70**

Kinetic Stereoselectivity in the Cu^{2+} Sequestration from Native or Mutant Plastocyanins by Optically Active Ligands

K. Bernauer[1], Ch. Nusbaumer[2], P. Schurmann[2], L. Verardo[1]
1 Institut de Chimie, Université, Av. de Bellevaux 51, 2000 Neuchâtel.
2 Laboratoire de Biologie Végétale, Université, Chantemerle 22, 2000 Neuchâtel.

The kinetics of Cu^{2+} sequestration by various ligands from the oxidized form of plastocyanin ($PcCu^{II}$) has been measured. Reversible, two-step kinetics are observed. When the two enantiomers of the optically active, pentadentate ligands N,N'-[(pyridine-2,6-diyl)bis(methylene)]bis[(R)- or (S)-alanine] I or N,N'-[(pyridine-2,6-diyl)bis(methylene)]bis[(R)- or (S)-proline] II are used, considerable stereoselectivity is found for both steps.



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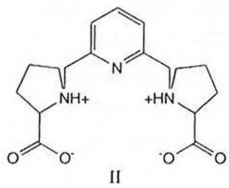

II

This is the first observation of a stereoselective ligand-exchange reaction involving a metalloprotein. As both steps are stereoselective, an associative mechanism is proposed. The first step consists of coordination of the ligand to the Cu^{2+} ion, displacing the histidine(87) and forming a mixed protein / ligand/Cu^{2+} complex. In the second, much slower step, dissociation of the protein from the Cu^{2+} ion takes place. The reactions are reversible, and, from the equilibrium states, a formation constant of $2.0 \pm 0.2 \cdot 10^{12}$ can be estimated for $PcCu^{II}$ at pH = 7.0.

The results are compared with the corresponding data obtained for different site-directed mutant plastocyanins.

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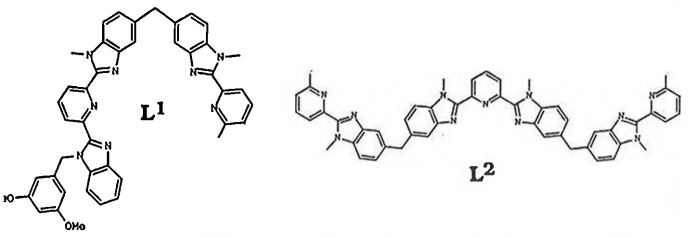
Chimie minérale et de coordination **71**

Self-Assembly of Heteronuclear Helical Complexes

C. Piguet,[a] G. Hopfgartner,[b] A.F. Williams [a] and B. Bocquet,[a]
[a] Department of Inorganic Chemistry CH-1211 Geneva 4
[b] F. Hoffmann-La Roche, Pharma Division CH-4002 Basel

The recent development of supramolecular devices working on the nanometric scale requires the preparation of heteropolynuclear complexes [1] and the use of highly selective self-assembly processes is very promising for this purpose. Detailed studies of the self-assembled homopolynuclear helical complexes have shown that a good matching of the intrinsic informations of the components (ligands and metal ions) controls formation of the final supramolecular organized architecture [2].



The new segmental ligands L^1 and L^2 are designed for helical coordination and contain different binding units along the strand which allow the self-assembly of double-helical heteronuclear complexes $[MM'(L^1)_2]$ and $[M_2M'(L^2)_2]$ with each cation occupying a site satisfying its coordinational preference (M: tetrahedral and M': octahedral). The combination of ES-MS, spectrophotometry and ^{1}H-NMR (NOE) measurements allows the detailed study of the self-assembly process.

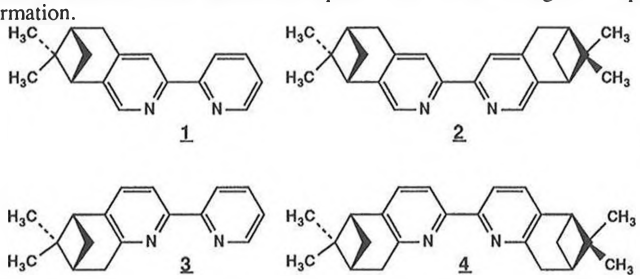
[1] C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, A.F. Williams, *J. Am. Chem. Soc.* **1993**, *115*, 8197
[2] C. Piguet, G. Bernardinelli, B. Bocquet, A. Quattropanni, A.F. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 7440

Anorganische Chemie/Koordinationschemie **72**

Enantioselective octahedral metal complex formation

P. Belser and Philippe Lainé
Institut für Anorganische Chemie, Universität Fribourg, CH-1700 Fribourg

Chiral co-ordination compounds are of interest due to use in the field of enatioselective catalysis, non linear optical properties or DNA intercalation reactions. A very important application is the construction of enantiomerical pure chiral polynuclear metal complexes with a well-defined stereo-chemistry. Such isomeric pure supramolecular structures show reproducible photophysical and photochemical properties. Here we report on the preparation of new bipyridine ligands L_1, L_2, L_3 and L_4 where the bulky pinene substituents control the stereo specific attachment during the complex formation.



The synthesis of optically active octahedral metal complexes (Δ- or Λ-isomers) from bidentate ligands follows a sequential procedure. The attachment of the first ligand is not stereo specific. The attachment of the second ligand determines the stereo chemistry of the product. The third ligand merely completes the co-ordination shell of the metal center. The important step in determining the stereo chemistry is the controlled attachment of the second ligand. One possible way of controlling the stereo specific complex formation is the construction of ligands with bulky substituents. These bulky groups have to be perpendicular to the molecular plane, to guarantee the promotion of the desired sterical interaction. The feasibility of the syntheses of the ligands L_1-L_4 is depicted in the reaction scheme also given in the present poster. We have prepared two different types of metal complexes $[Ru(L_{1-4})_3](PF_6)_2$ and $[Fe(L_{1-4})_3](PF_6)_2$ and measured their properties in the ground state, especially the corresponding CD-spectra.

Anorganische Chemie **73**

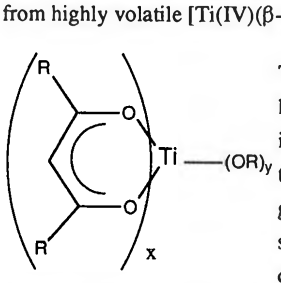
GROWTH KINETICS OF TiO_2-MOCVD WITH HIGHLY, VOLATILE [Ti(IV)(β-DIKETONATE)$_x$(OR)$_y$]

E. C. Plappert*, K.-H. Dahmen* and R. Hauert**

**Laboratorium für Anorganische Chemie, ETHZ, Zürich,Switzerland; **EMPA, Uberlandstr.129, 8600 Dübendorf, Switzerland*

Thin films of TiO_2 have been proposed for a variety of microelectronic and optical applications e.g. for dielectric layers, thin films capacitors and for optical wave guides or anti reflective films. In general such films can be prepared by CVD (chemical vapor deposition) from precursors such as $TiCl_4$, $Ti(OPr^i)_4$.

In our investigations thin metal oxide films were produced by MOCVD from highly volatile [Ti(IV)(β-DIKETONATE)$_x$(OR)$_y$], (x + y = 4).



The CVD experiments were carried out in a horizontal quartz reactor between 250-500°C in He or O_2. By variation of substrate temperature, source temperature and reaction gas flow, the growth kinetics of TiO_2 were studied and the optimum growth rate was determined.

It was possible to grow pure polycrystalline TiO_2 layers without the reaction gas O_2 as well as to form polycrystalline films of anatase at temperatures of 350°C.

The obtained films were characterized by profilometer, ellipsometer, XRD, AFM, UV, IR, Raman spectroscopy, AUGER and XPS measurements.

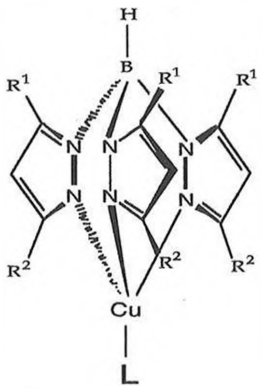
Anorganische Chemie **74**

INVESTIGATION AND CHARACTERIZATION OF THIN MOCVD COPPER FILMS FROM PYRAZOLYLBORATO-COPPER (I) COMPLEXES

E.-C. PLAPPERT*, K.-H. DAHMEN*, H. VAN DEN BERGH**, T. STUMM*** AND R. HAUERT****

Laboratorium für Anorganische Chemie, ETHZ, CH - 8092 Zürich ; **Laboratoire de Pollution Atmosphérique et Sols, EPFL, CH - 1015 Lausanne;*Laboratoire d'Optique Appliquée, EPFL, CH - 1015 Lausanne;**** EMPA , CH-8600 Dübendorf*

Thin copper layers were prepared via MOCVD from volatile pyrazolylborato - copper (I) complexes.



Experiments involved chemical vapour deposition in a low pressure reactor between 150 - 350°C in H_2/N_2/He mixtures. Substrate temperature, source temperature and gas composition were varied to obtain the optimum growth rate.

The copper layers were characterized by optical microscopy and scanning electron microscopy, XRD, and WDX. The metallic nature of the deposited films was proved by a four - point - probe measurement of the electrical resistivity.

A selective deposition on metal seeded surface sites was observed on Au, Al, Pt and W vs. SiO_2. Antiselective deposition was achieved on Pd seeded samples.

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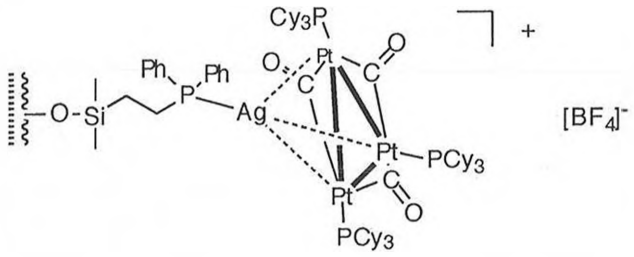
Anorganische Chemie

CHEMICAL FUNCTIONALIZATION OF SURFACES BY IMMOBILIZATION OF ORGANOMETALLIC COMPOUNDS

F. Lang, R. Frischknecht, K.-H. Dahmen
Laboratorium für Anorganische Chemie, 8092 ETH Zürich

The chemical modification of surfaces by reaction of specifically designed compounds with functional groups on the surface is a straight forward procedure for the preparation of heterogeneous catalysts and analytical devices such as modified electrodes and optical sensors.



In this paper we will discuss the preparation of linking-groups and the anchoring of those organometallic compounds on different surfaces (powder and plates), such as quartz, silicon and gold seeded silicon.

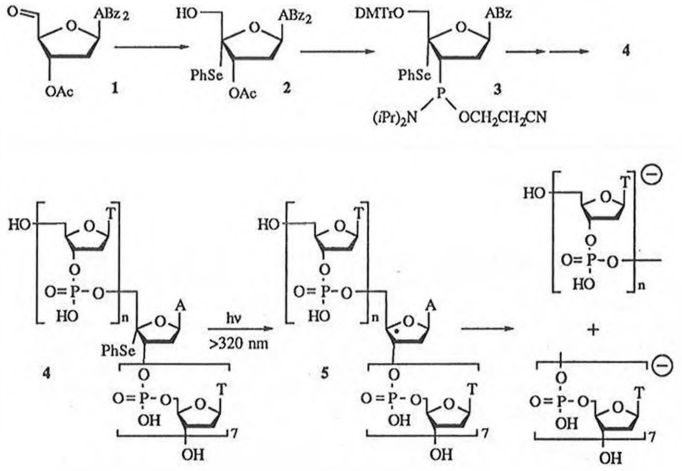
The surface reaction has been studied by reflection FT/IR studies and optical measurements.

Organische Chemie/Medizinische Chemie 76

Synthese und selektive Spaltung von modifizierten Oligonucleotiden

U. Schwitter, A. Dussy, C. Elie, P. Erdmann, B. Giese
Institut für Organische Chemie, Universität Basel, CH-4056 Basel

Die chemotherapeutische Wirkung der Antibiotika Bleomycin und Neocarzinostatin wird durch Abstraktion von H-Atomen aus der 4'- und/oder 5'-Position einer Desoxyribose von DNA eingeleitet. Uns ist es nun gelungen, die C-4'-Nucleotid-Radikale in Oligomeren gezielt zu erzeugen. Als Nucleosidmonomer, das als Radikal-Vorläufer dient, wurde das Selenid **3** aus dem Aldehyd **1** synthetisiert und nach der Phosphoramidit-Methode in die Oligonucleotide **4** eingebaut. UV-Bestrahlung von **4** liefert das Oligonucleotid-Radikal **5**, das selektiv die Kette an 3'- und/oder 5'-Position bricht.



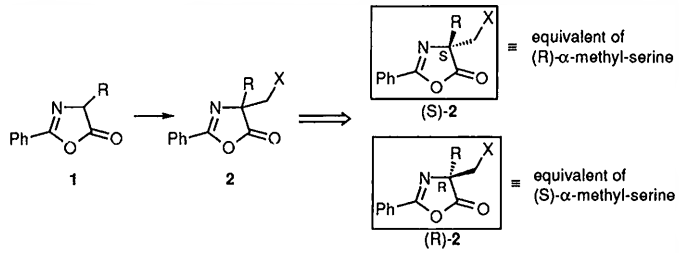
Diese gezielte Erzeugung von Radikalen eröffnet völlig neue Möglichkeiten für selektive Spaltungsreaktionen von Oligonucleotiden.

Organic Chemistry / Medicinal Chemistry 77

A Novel Strategy for the Synthesis of α-Methyl(alkyl)-serines and their Incorporation into Peptides

M. Altorfer, Ch. Abrecht, U. Bohdal, P. Schönholzer, D. Obrecht, K. Müller
F. Hoffmann-La Roche, Pharma Research New Technologies, 4002 Basel

Based on the finding that 4-methyl(alkyl)-2-phenyl-1,3-oxazol-5(4H)-ones of type **1** can be converted into the 4,4-disubstituted-2-phenyl-1,3-oxazol-5(4H)-ones of type **2** (X = I, Br) by simple alkylation [1], a novel strategy for the synthesis of α-methyl(alkyl)-serines was developed. The optically pure azlactones (R)- and (S)-**2** were obtained efficiently using L-phenylalanine-cyclohexylamide [2,3] as chiral auxiliary.



These optically pure building blocks can be regarded as synthetic equivalents of fully protected and activated (R)- or (S)-α–methyl(alkyl)-serines which are ready for incorporation into small peptides.
In addition, it will be shown that (S)-α-methyl-serine is an efficient building block for the C-terminal stabilisation of right handed α-helical peptides.

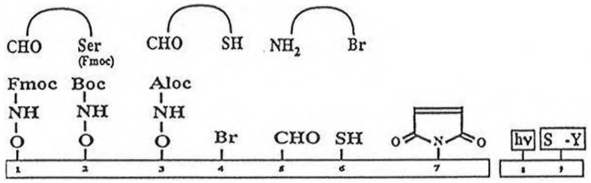
[1] D. Obrecht, U. Bohdal, R. Ruffieux, K. Müller, *Helv. Chim. Acta*, to be published in **1994**
[2] D. Obrecht, C. Spiegler, P. Schönholzer, K. Müller, *Helv. Chim. Acta*, **1992**, 75, 1666
[3] D. Obrecht, U. Bohdal, Ch. Lehmann, R. Ruffieux, P. Schönholzer, C. Spiegler, K. Müller, *Helv. Chim. Acta*, to be published in **1994**

Organische Chemie 78

Template Assembled Synthetic Proteins (TASP) by Chemoselective Ligation Methods

P. Dumy, I. Ernest, J. Kapron, M. Mutter, O. Nyanguile, and G. Tuchscherer
Institute of Organic Chemistry, University Lausanne, CH-1005 Lausanne

The TASP approach has become a widely accepted strategy in protein de novo design [1, 2]. By assembling secondary structure forming amphipatic peptides on topological templates, macromolecules featuring protein-like structural and functional properties are accessible. So far, the construction of these branched macromolecules was somewhat hampered by the well known limitations in conventional peptide synthesis. We report on recent progress for overcoming these problems by introducing a variety of chemoselective ligation methods for the attachment of solubilized peptide blocks to orthogonally protected template molecules (Figure).



The novel methodology is exemplified for the design and total synthesis of anti-parallel helical bundle proteins with unusual conformational and functional properties.

[1] M. Mutter, S. Vuilleumier, *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 535.
[2] G. Tuchscherer, M. Mutter, *J. Biotechnology* 1994, in press.

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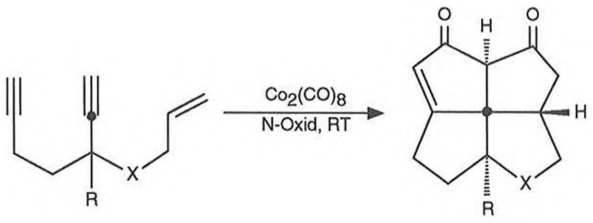
Organische Chemie

79

Kaskadenreaktionen mit Übergangsmetallverbindungen

M. Thommen, A. Veretenov, R. Keese*
Institut für Organische Chemie, Universität Bern, CH-3012 Bern

Für die Herstellung quaternärer C-Atome in Polycyclen eignen sich Kaskadenreaktionen von offenkettigen Edukten mit Übergangsmetallverbindungen [1] [2] [3]. So ergibt die Pauson-Khand Reaktion von **1** in einem Schritt das all-cis-[5,5,5,5] Fenestran **2** (R= $OSiMe_2tBu$, X= C) in 23% Ausbeute.



1 **2**

Unsere Untersuchungen haben ergeben, dass für Selektivität und Ausbeute der Pauson-Khand-Kaskadenreaktion die Struktur des offenkettigen Eduktes (R= $OSiMe_3$, $OSiMe_2tBu$, H; X= C, O) sowie die Wahl der Reaktionsbedingungen (thermisch-, oberflächen- oder N-Oxid induzierte Cyclisierung; Wassergehalt des eingesetzten N-Oxids) von entscheidender Bedeutung sind.
Alternative Synthesekonzepte zur Herstellung von quaternären C-Atomen mittels Kaskadenreaktionen werden diskutiert.

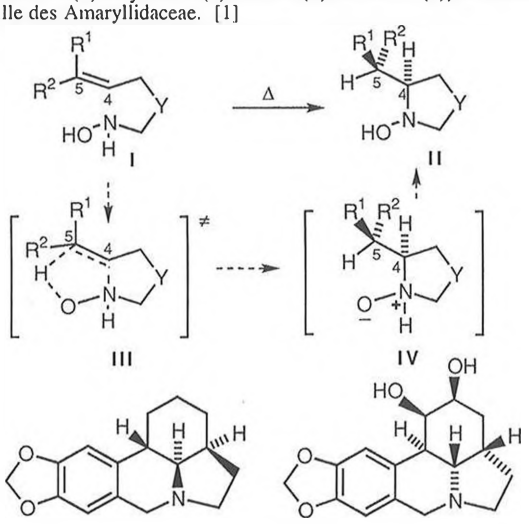
[1] A. van der Waals, R. Keese, *J. Chem. Soc., Chemm.Commun.* **1991**, 570.
[2] M. Thommen, P. Gerber, R. Keese, *Chimia* **1991**, 45, 21.
[3] R. Guidetti, Inaugural-Dissertation in Vorbereitung, Universität Bern.

80

Suprafacialité des Cyclisations Thermiques de N-4-Alcényl-hydroxylamines: Synthèses du (±)-α-Lycorane et de la (+)-Trianthine.

Wolfgang Oppolzer, Alan C. Spivey et Christian G. Bochet
Département de Chimie Organique, Université de Genève, CH-1211 Genève 4, Suisse

La cyclisation thermique I → II des (E) et (Z) 4-alcénylhydroxylamines-5,5 disubstituées s'effectue exclusivement de manière suprafaciale, en accord avec un mécanisme d'élimination rétro-Cope (I → III → IV → II). Cette réaction stéréospécifique constitue l'étape clé des synthèses efficaces du (±) α-lycorane (1) et de la (+)-trianthine (2), alcaloide de la famille des Amaryllidaceae. [1]



(±)-α-Lycorane **1** (+)-Trianthine **2**

[1] W.Oppolzer, A.C.Spivey, C.G.Bochet *J.Am.Chem.Soc.* **1994**, *116*, 3139

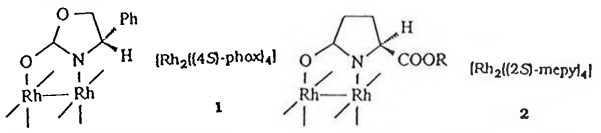
Chimie Organique

81

Induction Asymétrique dans l'Insertion Intramoléculaire lors de la Décomposition des Diazoesters avec des Catalyseurs Chiraux du Rh^{II}

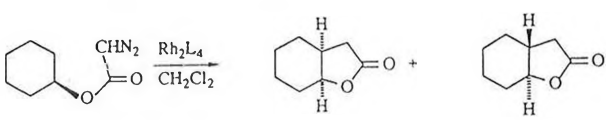
P. Müller, P. Polleux
Département de Chimie Organique, Université de Genève
CH-1211 Genève 4

Nous avons étudié la décomposition de certaines diazocétones et diazoesters en présence des catalyseurs chiraux $[Rh_2\{(4S)\text{-phox}\}_4]$ (**1**) et $[Rh_2((2S)\text{-mepy})_4]$ (**2**) [1].



1 **2**

L'insertion intramoléculaire dans la liaison CH des métallocarbènes dérivés de diazocétones se fait pratiquement sans aucune énantiosélectivité. Par contre, un diazoester tels que le diazoacétate de cyclohexyle conduit, en présence de **2**, à un mélange 3:1 des *cis* et *trans* lactones avec un excès énantiomérique de 95 et 90 %. Le catalyseur **1**, plus encombré, est moins efficace quant au rendement chimique et à l'énantiosélectivité [2].



Avec les diazoacétates de cyclohexyle, conformationnellement bloqués, l'insertion dans la liaison CH équatoriale est nettement préférée par rapport à l'insertion dans la liaison axiale. L'application de l'insertion intramoléculaire à d'autres diazoacétates sera présentée.

[1] M. P. Doyle, W. R. Winchester, M. N. Protopopova, P. Müller, G. Bernardinelli, D. Ene, S. Motallebi, *Helv. Chim. Acta* **1993**, *76*, 2227.
[2] P. Müller, P. Polleux, *Helv. Chim. Acta* **1994**, *77*, 645.

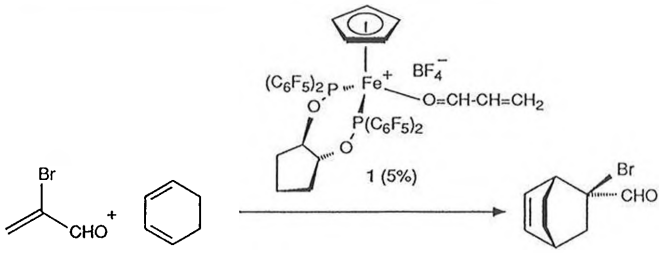
82

Organic Chemistry

Asymmetric Diels-Alder Reactions Catalyzed by a Chiral Iron Lewis Acid:

Bernadette Bourdin and E. Peter Kündig
Département de Chimie Organique, Université de Genève 30 quai Ernest Ansermet, CH-1211 Genève 4

We recently reported the synthesis of both enantiomers of several new C_2-chiral phosphorous ligands.[1] They were designed to emulate the bonding characteristics of CO and thus give access to chiral analogues of this ligand. We here show that this concept is valid. Complex **1**, readily obtained from a dicarbonyl precursor by photolytic ligand exchange, catalyzes the Diels Alder reaction between reactive enals and dienes to afford products with enantioselectivities in the range of 84 - 99%.



[1] E. P. Kündig, C. Dupré, B. Bourdin, A. Cunningham, Jr., D. Pons, *Helv. Chim. Acta.* **1994**, *77*, 421.
[2] E. P. Kündig, B. Bourdin, *Angew. Chem.* **1994**, in press.

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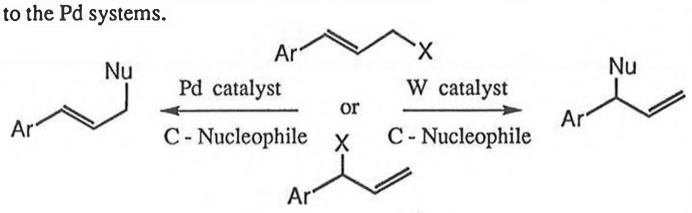
Organic Chemistry **83**

Tungsten-Catalysed Allylic Alkylation: Stereospecificity, Stereoselectivity, Mechanism.

G. C. Lloyd-Jones§ and A. Pfaltz.
Institut für Organische Chemie, Universität Basel, CH-4056 Basel

Metal-catalysed carbon-carbon bond forming processes and their enantioselective variants have now become routine in organic chemistry. Asymmetric Pd-catalysed allylic alkylation has enjoyed considerable attention and, in some cases, near-perfect enantioselectivities have been achieved utilising P-P[1], N-N[2] and P-N[3] chiral ligand systems. When non-symmetrical allylic substrates are employed there is selective nucleophillic attack at the least hindered allylic terminus - a significant problem if the alternative regioisomer is desired. We report an enantioselective tungsten catalyst that offers the opposite regioselectivity in good yield. The W-catalysed system displays mechanistic aspects that are significantly different to the Pd systems.



§ Royal Society Post-doctoral Fellow 1992-1994.

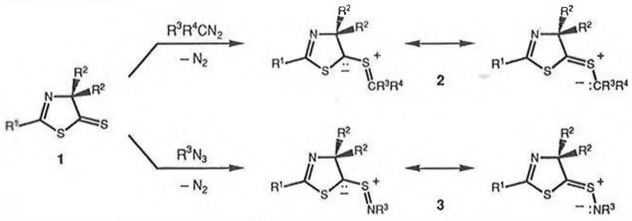
[1] Hayashi, T.; Yamamoto, A.; Ito, Y. *Chem. Lett.* **1987**, 177-180. Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 857-871.[2] Togni, A. *Tetrahedron: Asymmetry* **1991**, *2*, 683-690. Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339-345. [3] von Matt, P.; Pfaltz, A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 566-568. Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769-1772. Dawson, G. J.; Frost, C. G.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Lett.* **1993**, *34*, 3149-3150.

Organische Chemie **84**

Neue Reaktionen von Thiocarbonyl-yliden und -imiden

M. Kägi, G. Mloston[a], M. Petit und H. Heimgartner
Organisch-chemisches Institut, Universität Zürich, 8057 Zürich

Während 1,3-Dipole mit einem zentralen N-Atom gut untersucht sind, ist über Dipole mit zentralem S-Atom (Thiocarbonyl-ylide, -imide, -oxide, -sulfide) wenig bekannt. Die Thiocarbonyl-ylide **2** und -imide **3** entstehen bei der Umsetzung von 1,3-Thiazol-5(4*H*)-thionen **1** mit Diazoalkanen bzw. organischen Aziden über eine 1,3-dipolare Cycloaddition und N_2-Abspaltung.



Während die Imide **3** einheitlich *via* Cyclisierung und Desulfurierung zu 1,3-Thiazol-5(4*H*)-iminen reagieren [1], gehen die Ylide vom Typ **2** in Abhängigkeit von der Art der Substituenten R^3 und R^4 eine Reihe von Folgereaktionen ein [2]: Bildung von spirocyclischen Thiiranen und Entschwefelung zu 5-Methyliden-4,5-dihydro-1,3-thiazolen, 1,3-dipolare Cycloaddition zum *Schönberg*-Produkt, Dimerisierungen, Umlagerungen und Additionsreaktionen. Mit Dipolarophilen können einige Thiocarbonylylide und -imide abgefangen werden.

a) Institut für Chemie, Universität Lodz, PL-90-136 Lodz, Polen

[1] S. Pekcan, H. Heimgartner, *Helv. Chim. Acta* **1988**, *71*, 1673.
[2] G. Mloston, M. Petit, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1994**, *77*, 435.

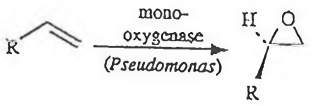
Organische Chemie / Medizinische Chemie **85**

Enantioselective Oxidation of unfunctionalized olefins by engineered bacteria

M.G. Wubbolts, J.B. van Beilen and B. Witholt
Institut für Biotechnologie, ETH Hönggerberg, HPT, CH-8093 Zürich

Enantioselective synthesis methods are required to satisfy the increasing demand for drugs that contain only the active stereoisomer (eutomer) of chiral pharmaceuticals.

Chiral metal complexes have successfully been applied to perform enantioselective oxidations, but in general it is not easy to attain high stereospecificity. One reaction that is difficult to perform by organic chemistry, but is efficiently catalyzed by enzymes is the stereospecific oxidation of unfunctionalized olefins to optically active epoxides.



Two non-heme iron mono-oxygenase enzymes of bacterial origin will be presented that can perform such reactions on either aliphatic or aromatic substrates and typically yield optically active products with enantiomeric excesses of over 90%.

The alkane hydroxylase system from *Pseudomonas oleovorans*, a bacterium that consumes linear alkanes, produces optically active epoxides from 1-alkenes and terminal alkadienes at high enantiomeric excess.

Similarly, xylene oxygenase, which originates from the toluene degrading bacterium *Pseudomonas putida* mt-2, catalyses the stereospecific oxidation of (substituted) styrenes to the corresponding styrene epoxides.

These enzymes were introduced into *Escherichia coli*, a micro-organism that in contrast to Pseudomonas, is not able to degrade the desired products. The engineered micro-organism allowed the production of optically active epoxides in an *n*-octane based two-liquid phase fermentation system under conditions of reduced substrate and product toxicity. The two phase approach also allowed selective accumulation of the products in the organic phase thus facilitating product recovery.

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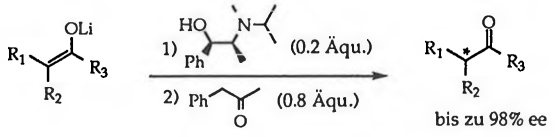
Organische Chemie

Katalytische enantioselektive Protonierung von Enolaten

C. Fehr und J. Galindo

Firmenich SA, Research Laboratories, CH-1211 Geneva 8

Es ist uns erstmals gelungen, Enolate mit katalytischen Mengen eines enantiomerenreinen, chiralen Protonendonors und einer achiralen Protonenquelle enantioselektiv zu protonieren.



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Medicinal Chemistry **87**

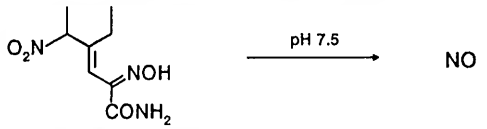
FK 409 : An Unusual Way to Store and Release Nitric Oxide

J.C. Muller, P.H. Williams, D. Loyaux, M. Fontecave*, J.L. Decout*, B. Roy*
Preclinical Research Department
SYNTHELABO Recherche 31, avenue Paul Vaillant-Couturier - BP 110 92225 BAGNEUX (France)
*Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité - BP 53X 38041 GRENOBLE Cedex (France)

Amongst the various categories of NO donors, FK 409 (1), an oximinoalkane derivative isolated from *Streptomyces griseosporeus*, behaves in a rather peculiar way. Like organic nitrates, nitrothiols and sydnonimines, FK 409 relaxes the isolated rabbit aorta through an increase in intracellular cyclic GMP, due to nitric oxide-induced activation of guanylate cyclase. Unlike most NO donors, FK 409 spontaneously and rapidly decomposes, without activation, in aqueous solution at physiological pH to release nitric oxide. Decomposition products were identified through NMR, Mass Spectrometry (LC/MS), Electronic Paramagnetic Resonance Spectrometry (E.P.R.) and chemical analyses. The presence of NO was fully established through :

- its trapping by a diethyldithiocarbamate-iron complex,
- its reversible reaction with the tyrosyl radical of ribonucleotide reductase,
- the identification of nitrite as a oxidation product.

A plausible mechanistic pattern for this NO liberation will be disclosed.



1

Medizinische Chemie **88**

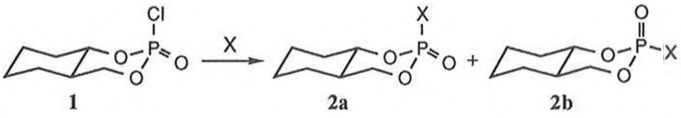
Konfigurativ und konformativ fixierte Organophosphate als Inhibitoren der Acetylcholinesterase

Franco A. Merckling und Peter Rüedi

Organisch-chemisches Institut der Universität, 8057 Zürich

Trotz der Fülle von Forschungsarbeiten, die zum Verständnis der Struktur und Wirkungsweise des Enzyms (AChE) beigetragen haben, konnte bisher noch kein konsistentes Bild von den chemischen Reaktionsmechanismen der Katalyse erhalten werden. Wesentliche strukturelle Merkmale der AChE wurden erst kürzlich durch Röntgenstrukturanalyse bewiesen. Offene Fragen betreffen insbesondere Aspekte der Reaktionsdynamik und der Stereochemie des Reaktionsverlaufes.

Mit dem Ziel, Einblicke in die Chemo-, Regio- und Stereoselektivität der Inhibierungsreaktion der AChE zu erhalten, haben wir 2-substituierte 2-Oxo-1,3,2-dioxaphosphorinane (**1**, **2**) hergestellt und ihre Hemmwirkung untersucht. Ausgehend vom Chloridat **1** konnten je nach Reaktionsbedingungen in unterschiedlicher, wesentlich durch Stereoelektronik bestimmter Diastereoselektivität die formalen Substitutionsprodukte **2a** und **2b** isoliert werden. Diese Ergebnisse geben zusätzlichen Einblick in den sterischen Verlauf von nucleophilen Reaktionen am Phosphor. Alle Verbindungen sind starke Hemmer der AChE mit **1** als potentestem Vertreter (k_i=8,6·10^6 M^{-1}min^{-1}).



X = Hal, O-, N-, S-Nucleophile, Enzym

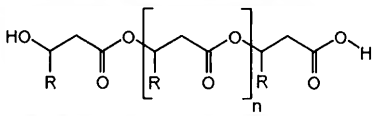
Neben der Synthese und Analytik von **1**, **2a** und **2b** werden erste NMR-spektroskopische Experimente zur direkten Beobachtung des Phosphors im Enzym/Inhibitor-Komplex (Übergangszustands-Analoge) vorgestellt.

Organische Chemie/Medizinische Chemie **89**

Synthese neuer biokompatibler und biodegradierbarer Blockcopolymere für die medizinische Anwendung

A. Lendlein, P. Neuenschwander und U.W. Suter
Institut für Polymere, ETH Zürich, CH-8092 Zürich

Die Anforderungen, die an biodegradierbare und biokompatible Materialien gestellt werden, sind stark von ihrer Anwendung abhängig und umspannen ein breites Mass von Eigenschaften, die mit den wenigen, kommerziell erhältlichen Produkten nicht in gewünschtem Mass erfüllt werden können. Eine wichtige Gruppe von biokompatiblen und biodegradierbaren Materialien sind die Poly(hydroxycarbonsäuren) [1].



Aufgrund ihrer mechanischen Eigenschaften sind sie jedoch nur für wenige, spezielle Anwendungen geeignet. Aus diesem Grund wäre es wünschenswert, heute gebräuchliche, kommerziell erhältliche Polymere durch neue Materialien zu ergänzen.

Es war nun möglich eine Reihe neuer, thermoplastischer, biokompatibler und biodegradierbarer Polyester und Polyurethane für die temporäre Anwendung herzustellen.

Die neuen Polymere wurden mit ^{1}H-NMR hinsichtlich ihrer chemischen Struktur charakterisiert. Die thermischen Eigenschaften wurden mittels DSC bestimmt. Die Verarbeitbarkeit der Materialien zu Fäden, Folien und Schläuchen wurde getestet. Die mechanischen Eigenschaften der Polyester bzw. Polyurethane wurden mit Zug-Dehnungsexperimenten und mit dynamisch mechanischer Thermoanalyse ermittelt.

Schließlich wurden die Hydrolysegeschwindigkeiten der einzelnen Polyester und Polyurethane in 'In Vitro'- Experimenten bestimmt.

[1] M.Vert, *Makromol. Chem., Makromol. Symp.* **6**, 109-122 (1986)

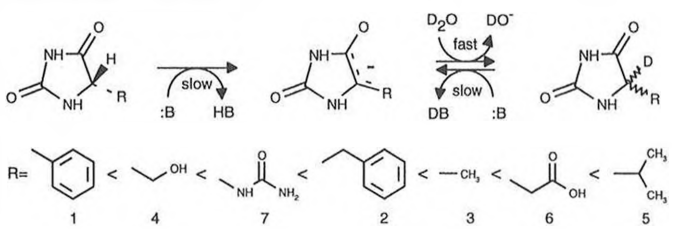
Chimie thérapeutique **90**

Hydantoins as models for non-enzymatic racemization of chiral drugs

M. Reist*, P.-A. Carrupt*, B. Testa,* S. Lehmann#, J.-J. Hansen#
* Institut de chimie thérapeutique, Ecole de Pharmacie, Université de Lausanne, CH-1015 Lausanne
# Department of Medicinal Chemistry, Royal Danish School of Pharmacy, DK-2100 Copenhagen

A chiral center in a drug molecule may increase the complexity of synthetic, metabolic, pharmacological and clinical studies [1], a major problem being a possible lack of configurational stability. Thus, special attention to this problem is required and general rules would be an asset to medicinal chemists and pharmacologists.

To predict how functional groups affect the configurational stability of chirally substituted carbons of the type R''R'RC-H, we are applying experimental [2] and theoretical methods. As a model case, the non-enzymatic isomerization of seven chiral hydantoins **1** - **7** was studied by ^{1}H-NMR and RP-HPLC. Molecular orbital calculations were performed at the AM1 level in order to support the proposed isomerization mechanism. The configurational stability increases as described below, the experimentally determined activation energy being related to the calculated acidities of the C-H bond.



[1] B. Testa, P.-A. Carrupt, J. Gal, *Chirality* **1993**, 5, 105-111
[2] B. Testa, P.-A. Carrupt, L. Christiansen, P. Christoffersen, M. Reist, *In: Trends in Drug Research* (Ed. V. Claassen). Elsevier, Amsterdam **1993**, pp 1-8

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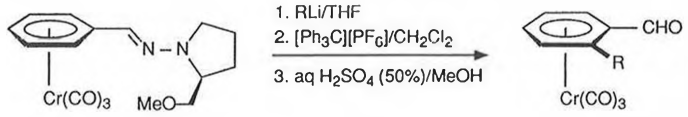
Organische Chemie

Planar Chirale Aren Chromtricarbonylkomplexe via Alkylierung/Arylierung und Hydrid Abstraktion.

Angelika Fretzen und E. Peter Kündig
Département de Chimie Organique, Université de Genève, 30 quai Ernest Ansermet, CH-1211 Genève 4

Als attraktive Ausgangssubstanzen für asymmetrische Synthesen können *ortho*-substituierte (η^6-benzaldehyd)$Cr(CO)_3$ Komplexe durch die Titelreaktionsfolge aus [(η^6-benzyliden(cyclohexyl)amin)$Cr(CO)_3$] (**1**) erhalten werden. Wird an Stelle des Imin Komplexes **1** der SAMP-Hydrazon Komplex **2** eingesetzt, ergibt sich eine hoch diastereoselektive Synthese von **3**. [1]



Wir berichten hier über weitere Beispiele dieser Reaktionssequenz mit **1** und **2** und insbesondere über die nukleophile Addition β-substituierter α-Lithium Naphthalensysteme. Anschliessende endo-Hydridabstraktion führt zu planar chiralen Komplexen mit axialer Chiralität. Die Atropisomere des Biarylchromtricarbonylsystems wurden isoliert und charakterisiert. Der Einfluss eines chiralen Auxiliars wie SAMP auf planare sowie axiale Chiralität wird dargestellt und diskutiert.

[1] E. P. Kündig, R. Liu, A. Ripa, *Helv. Chim. Acta* **1992**, *75*, 2657.

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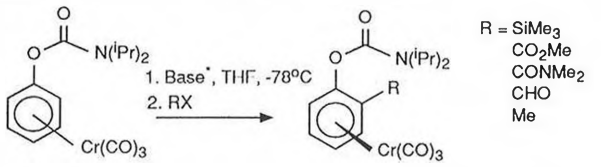
Organic Chemistry

Planar Chiral Arene Tricarbonylchromium Complexes via Enantioselective Deprotonation/Electrophile Addition Reactions :

Anna Quattropani and E. Peter Kündig
Département de Chimie Organique, Université de Genève, 30 quai Ernest Ansermet, CH-1211 Genève 4

Sequential reaction of substituted (η^6-arene)$Cr(CO)_3$ complexes with chiral amide bases and electrophiles yielded planar chiral complexes. Benzaldehyde acetal and phenyl carbamate complexes gave *o*-substituted products with 64 to 81% enantiomeric excess. With the benzaldehyde acetal complex, competitive benzylic deprotonation occurred. Enantiomeric purity of the substituted carbamate complexes could be increased to >90% ee by fractional crystallization. The racemate crystallized selectively, leaving the enantiomerically enriched complex in solution [1].



The results of structural studies will be presented. They were carried out in order to understand the origin of asymmetric induction and the preferential crystallization of the racemic product.

[1] E. P. Kündig, A. Quattropani, *Tetrahedron Lett.* **1994**, *35*, in press.

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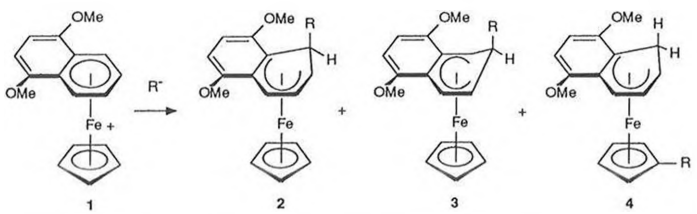
Organic Chemistry

New Aspects of C-Nucleophile Additions to Cationic [(Arene)(Cyclopentadienyl)Fe(II)]$^+$ Complexes

Patrick Jeger and E. Peter Kündig
Département de Chimie Organique, Université de Genève, 30 quai Ernest Ansermet, CH-1211 Genève 4

C-Nucleophiles react with the title compounds by addition to give (cyclohexadienyl)FeCp complexes [1]. We report here new results in this area. We found that:
As in $Cr(CO)_3$ chemistry [2], nucleophilic addition to the $FeCp^+$ complexes can be reversible.
Complex **1**, prepared by thermal arene exchange, reacts with carbanions to give benzocyclohexadienyl complexes **2** and **3**. Under the same conditions, carbanions do not add to but reduce the parent complex (naphthalene) $FeCp^+$. Competitive addition to the cp ring occurs with bulky C-nucleophiles to give, after H-migration, complex **4**.
Complexes **2** and **4**, but not **3**, undergo $\eta^5 \rightarrow \eta^3$ ring slippage when treated with CO [3].



[1] Review: D. Astruc, *Tetrahedron* **1983**, *39*, 4027.
[2] E. P. Kündig, V. Desobry, D. P. Simmons, E. Wenger, *J. Am. Chem. Soc.* **1989**, *111*, 1804.
[3] For a precedent see: K. Jonas, *Pure Appl. Chem.* **1990**, *62*, 1169.

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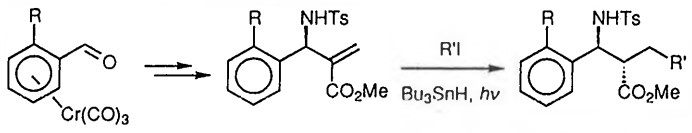
Organic Chemistry

Diastereoselective Synthesis of β-Aminoacid Derivatives by Alkyl Radical Addition to α-Aminoacrylates

Long-He Xu and E. Peter Kündig
Département de Chimie Organique, Université de Genève, 30 quai Ernest Ansermet, CH-1211 Genève 4

We have reported an efficient asymmetric synthesis of α-amino-acrylate derivatives **2** from planar chiral *o*-substituted η^6-benzaldehyde $Cr(CO)_3$ complexes **1**.[1] We here show that alkyl radicals add to acrylates **2** to give β-amino acid derivatives **3** in high yield.



Diastereoselectivity in the radical addition depends primarily on the alkyl iodide with *anti*-**3** being the major product. Extension of this new methodology to the synthesis of piperidine derivatives will be presented.

[1] a) E. P. Kündig, L.-H., Xu, P. Romanens, G. Bernardinelli, *Tetrahedron* Lett. **1993**, *34*, 7049. b) E. P. Kündig, L.-H., Xu, B. Schnell, *Synlett*, **1994**, in press.

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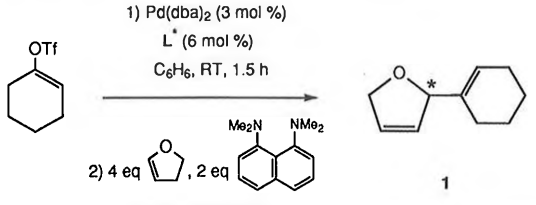
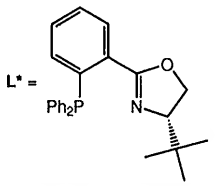
Organic Chemistry **95**

Palladium-Catalyzed Enantioselective Alkenylation of Olefins

O. Loiseleur, P. Meier, A. Pfaltz
Institut für Organische Chemie, Universität Basel, CH-4056 Basel

Palladium-catalyzed alkenylation of olefins is an attractive method for C-C bond formation and the development of efficient enantioselective catalysts for this reaction is an important goal of current research in this area [1], [2], [3]. We have found that cyclohexenylation of 2,3-dihydrofuran catalyzed by a 2-(2-phosphinoaryl)-oxazoline-palladium(0) complex gives 2-(cyclohexenyl)-2,5-dihydrofuran **1** with 98.5% *ee* and in 88% yield.





[1] F. Ozawa, Y. Kobatake, T. Hayashi, *Tetrahedron Letters*, **1993**, 34, 2505.
[2] Y. Sato, S. Nukui, M, Sodeoka, M. Shibasaki, *Tetrahedron*, **1994**, *50*, 371.
[3] S.Sakuraba, K. Awano, K. Achiwa, *Synlett*, **1994**, *4*, 291.

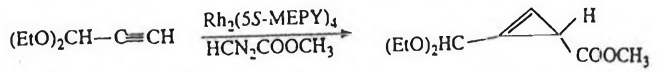
Chimie Organique **96**

Cyclopropanations et Cyclopropénations Intermoléculaires Asymétriques

P. Müller, D. Ene
Département de Chimie Organique, Université de Genève
CH-1211 Genève 4

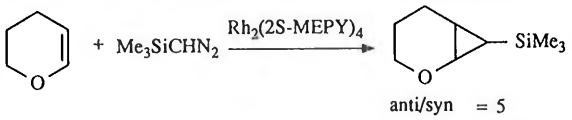
Le diazoacétate d'éthyle est décomposé en présence de catalyseurs de rhodium(II) pour former un métallocarbène. L'addititon de ce dernier aux double et triple liaisons conduit à des cyclopropanes [1] ou cyclopropènes [2].

Les cyclopropènes obtenus à partir d'alcynes terminaux avec le catalyseur $[Rh_2\{(2S)\text{-mepy}\}_4]$ ont des excès énantiomériques de *ca.* 70 %. Si l'alcyne porte une fonction oxygène en position α, l'énantiosélectivité peut augmenter jusqu'à 98%. Les cyclopropènes synthétisés avec le catalyseur de configuration *S* ont tous la configuration *S* au C(1).



La diastéréosélectivité de la cyclopropanation intermoléculaire dépend des substituants du catalyseur. Ainsi, avec $[Rh_2(OAc)_4]$ et $[Rh_2\{(2S)\text{-mepy}\}_4]$ le *trans*-cyclopropane est formé de préférence. Par contre, avec $[Rh_2\{(4S)\text{-phox}\}_4]$, l'isomère *cis* devient majoritaire.

Le triméthylsilyldiazométhane forme également des cyclopropanes avec des alcènes en présence de catalyseurs de Rh^{II}. Le cyclopropane *anti* est formé de préférence, mais l'énantiosélectivité est modeste.



anti/syn = 5
e.e. anti = 54%

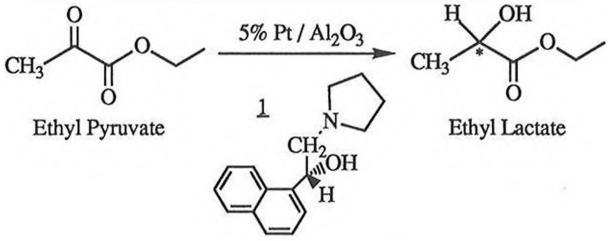
[1] M. P. Doyle, W. R. Winchester, M. N. Protopopova, P. Müller, G. Bernardinelli, D. Ene, S. Motallebi, *Helv. Chim. Acta* 1993, *76*, 2227.
[2] M. N. Protopopova, M. P. Doyle, P. Müller, D. Ene, *J. Am. Chem. Soc.* **1992**, *114*, 2755.

Organische Chemie **97**

ENANTIOSELECTIVE HYDROGENATION OF ETHYL PYRUVATE OVER PT/ALUMINA WITH NOVEL CHIRAL MODIFIER

B. Minder[1], T. Mallat[1], A. Baiker[1], T. Heinz[2], G. Wang[2] and A. Pfaltz[2]
[1] Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092 Zürich, Switzerland, fax: (++41-1) 262 17 62.
[2] Institute of Organic Chemistry, University of Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland, fax: (++41-61) 322 60 17.

The platinum-catalysed enantioselective hydrogenation of ethyl pyruvate to ethyl lactate (scheme) has been studied in the presence of a new chiral modifier 1, possessing a flat aromatic moiety promoting the adsorption on Pt and a polar functional group, providing the specific interaction with the substrate.



The influence of reaction conditions on the kinetics and enantioselectivity of the reaction in the presence of the new modifier can be summarized as follows. Both initial reaction rate and optical yield increase with ascending modifier concentration in the low concentration range, reaching a plateau at around 10^{-4} M. Similarly, with increasing catalyst/reactant weight ratio, the optical yield increases in acetic acid up to 75 %.

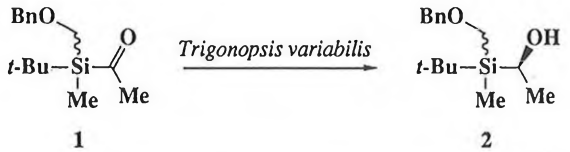
Solvent polarity has a strong influence on the reaction rate (400 - 2300 mmol h^{-1} g^{-1}) and optical yield (45 - 75 %). The best solvent is acetic acid, in which the optical yield is considerably higher (by about 25 %) than what would be expected from the optical yield - solvent polarity correlation. The optimum reaction temperature, measured in toluene, is around 0 °C (71 % ee); above 30 °C the enantiomeric excess decreases rapidly.

Organische Chemie **98**

Synthese optisch aktiver alkoxymethyl-substituierter Silane durch Biotransformation mit der Hefe *Trigonopsis variabilis*

S. Bienz*, S. Bratovanov, A. Chapeaurouge, P. Huber, C. Syldatk[1)]
OCI, Universität Zürich, Winterthurerstrasse 190, 8057 Zürich
1) Institut für Bioverfahrenstechnik, Allmandring 31, D-70569 Stuttgart

Wir zeigten anhand des Acylsilans **1**, dass die chirale Si-Gruppe bei Additionsreaktionen am Carbonyl-C Stereoselektivität induziert [1, 2]. In der Folge wurde unter anderem nach einer Methode zur enantiospezifischen Reduktion von Acylsilanen des Typs **1** gesucht, um nach Trennung der erwarteten Diastereoisomerengemische **2** und deren Oxidation enantiomerenreine Acylsilane **1** zu erhalten. Unter Verwendung der von *Tacke* und *Syldatk* entwickelten Methode zur biotechnologischen Reduktion von Acylsilanen mit der Hefekultur *Trigonopsis variabilis DSM 70714* [3, 4] konnten wir die enantioselektive Umsetzung des Acylsilans **1** zum Alkohol **2** mit guter chemischer und optischer Ausbeute durchführen.



Auf dem Poster wird die Optimierung dieser Biotransformation beschrieben sowie auf die Vor- und Nachteile beim Arbeiten mit ruhenden oder immobilisierten Zellen eingegangen. Schliesslich wird gezeigt, wie die absolute Konfiguration des neu generierten chiralen Zentrums am Alkohol 2 aufgeklärt wurde.

[1] S. Bienz, A. Chapeaurouge, *Helv. Chim. Acta* **1991**, *74*, 1477.
[2] A. Chapeaurouge, S. Bienz, *Helv. Chim. Acta* **1993**, *76*, 1876.
[3] C. Syldatk, A. Stoffregen, F. Wuttke, R. Tacke, *Biotechnol. Letters* **1988**, *10*, 731.
[4] C. Syldatk, H. Andree, A. Stoffregen, F. Wagner, B. Stumpf, L. Ernst, H. Zilch, R. Tacke, *Appl. Microbiol. Biotechnol.* **1987**, *27*, 152.

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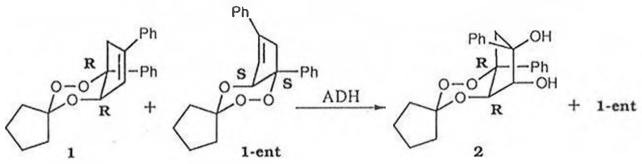
Chimie Organique

Asymmetric Dihydroxylation of *cis*-Fused Cyclopenteno-1,2,4-trioxanes

C.W. Jefford, D. Misra, A.P. Dishington, J.C. Rossier, G. Bernardinelli and G. Timári
Department of Organic Chemistry, University of Geneva
CH-1211 Geneva 4

The racemic *cis*-fused cyclopenteno-1,2,4-trioxanes (**1** and **1-ent**) were submitted to osmium-catalyzed asymmetric dihydroxylation [1]. By a careful choice of the experimental conditions, in particular the solvent and co-oxidant, complete kinetic resolution was obtained. The absolute configurations of the reactants and products were assigned by preparing the *bis*-camphanates of the diols (*e.g.* **2**) and determining their structures by X-ray analysis. Typically, dihydroxylation of **1** and **1-ent** in the presence of the chiral ligand $(DHQD)_2$-PHAL gave exclusively **2** together with **1-ent**. Conversely, the use of $(DHQ)_2$-PHAL led, somewhat less efficiently, to **2-ent** and **1** [2]. However, success was only possible with *N*-methylmorpholine *N*-oxide as co-oxidant. When potassium ferricyanide was used instead, reaction was uneven and slow, resulting in no resolution. These matters and the role of the cinchona ligands will be discussed as well as the utility of the products, namely **2**, as chiral ligands in their own right.



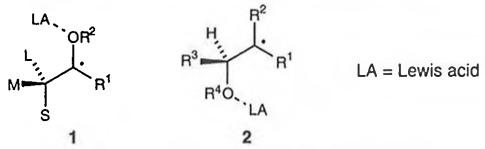
[1] B.B. Lohray, *Tetrahedron: Asymmetry* **1992**, *3*, 1317.
[2] K.B. Sharpless, W. Amberg, Y.L. Bennani, G.A. Crispino, J. Hartung, K. Jeong, H. Kwong, K. Morikawa, Z. Wang, D. Xu, X. Zhang, *J. Org. Chem.* **1992**, *57*, 2768.

Organic Chemistry **100**

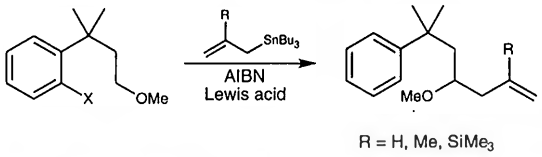
Reactivity and Stereochemical Study of 1-(Alkoxy) and 2-(Alkoxy)alkyl Radicals Complexed with Lewis Acids.

M. Gerster, N. Moufid and P. Renaud
Institut de Chimie Organique, Université de Fribourg, CH-1700 Fribourg

In the last decade, a general approach to the control of acyclic stereochemistry in free radical reactions has emerged.(1) Interestingly, the models which have been developed for enolate and enamine alkylation as well as nucleophilic addition to ketones, aldehydes and unsaturated carbonyl compounds can be used without significant change in radical chemistry. However, the use of Lewis acids which represents a unique way of controlling the stereoselectivity of ionic and concerted reactions has not found many applications in radical chemistry. We report here a study of alkoxy-substituted radicals of type **1** and **2** in the presence of Lewis acids.



The generation of type **2** radicals is straightforward from the corresponding iodides and alteration of the stereoselectivity induced by Lewis acids will be discussed. Type **1** radicals have been prepared in the presence of Lewis acids by 1,5-hydrogen transfer from an aryl iodide. The change of the nucleophilicity of radical **1** due to complexation has been examined by competition reaction between different allylstannanes.



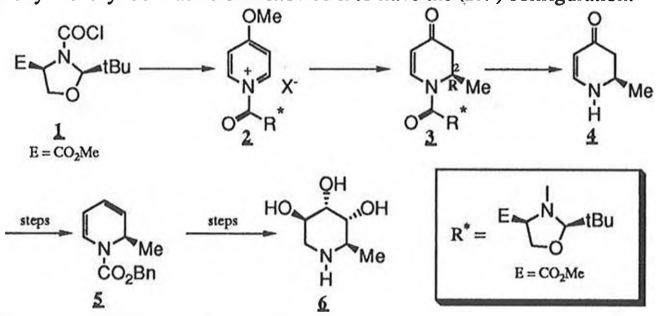
(1) N. A. Porter, B. Giese, D. P. Curran, *Acc. Chem. Res.* **1991**, *24*, 296-303; W. Smadja, *Synlett* **1994**, 1-26.

Organic Chemistry **101**

A Simple Asymmetric Synthesis of 2-Methyl-1,2-dihydropyridine and of the ensuing (D)-1,5,6-Trideoxy-5-aminoaltrose

Arnaud Boiron, Théophile Tschamber, and Jacques Streith
Ecole Nationale Supérieure de Chimie, Université de Haute-Alsace
3, rue Alfred Werner F-68093 MULHOUSE CEDEX, FRANCE.

Homochiral oxazolidine **1** was prepared in two steps from L-serine by a Seebach procedure [1]. Treatment of 4-methoxypyridine with **1**, in the presence of NaI, led to **2** which when reacted with MeMgI, and finally with HCl, led to crude dihydropyridone **3** (*de* 95 %, HPLC). A single recrystallisation gave **3** as a homogenous chiral compound (74 %), m.p. 157,5-159°C. Acid hydrolysis of **3** with HCl led to removal of pivalaldehyde. At pH = 11 the resulting primary alcohol induced intramolecular cleavage of the urea functionality leading to enantiopure **4**, $[\alpha]^{20}_D = +495$. This compound was also obtained by the classical Comins method. X- ray analysis of a phenylmenthyl derivative of **4** showed it to have the (*2R*) configuration.



Conversion of **4** to enantiopure **5** was performed according to Comins' method [2]. Eventually, catalytic double osmylation of **5** [3], followed by hydrogenation/hydrogenolysis (Pd/C), gave enantiopure aminoaltrose-derivative **6**.

[1] Seebach, D.; Stucki, G.; Renaud, P. *Chimia* **1988**, *42*, 176.
[2] Comins, D.L.; Hong, H.; Salvador, J.M. *J. Org. Chem.* **1991**, *56*, 7197.
[3] Tschamber, Th.; Backenstrass, F.; Neuburger, M.; Zehnder, M.; Streith, J. *Tetrahedron* **1994**, *50*, 1135.

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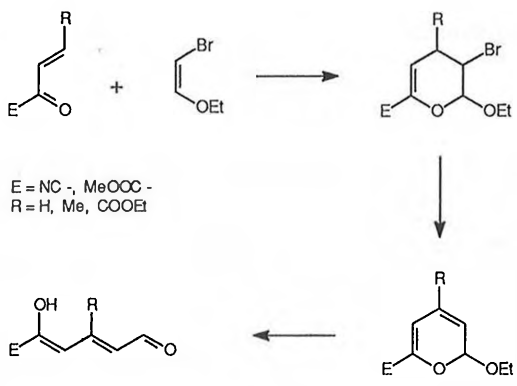
A Synthesis of 2-Ethoxy-2*H*-pyranes via Hetero-*Diels-Alder* Cycloaddition, and their Reactivity

by Jincong Zhuo and Hugo Wyler
Institut de Chimie Organique, Université de Lausanne, Rue de la Barre 2, CH-1005 Lausanne

Oxabutadienes bearing electron withdrawing groups at the carbonyl carbon (α,β-unsaturated acyl cyanides, methyl 2-oxobut-3-enoates) are exceptionally reactive in hetero-*Diels-Alder* cycloadditions with various dienophiles. The cycloaddition of bromo-ethoxy-ethene leads to 3-bromo-2-ethoxy-3,4-dihydro-2*H*-pyrans from which 2-ethoxy-2*H*-pyrans can be produced. The reactivity of these has been investigated. Of particular interest are ring opening reactions which afford 2-hydroxy-6-oxohexa-2,4-dienoates.



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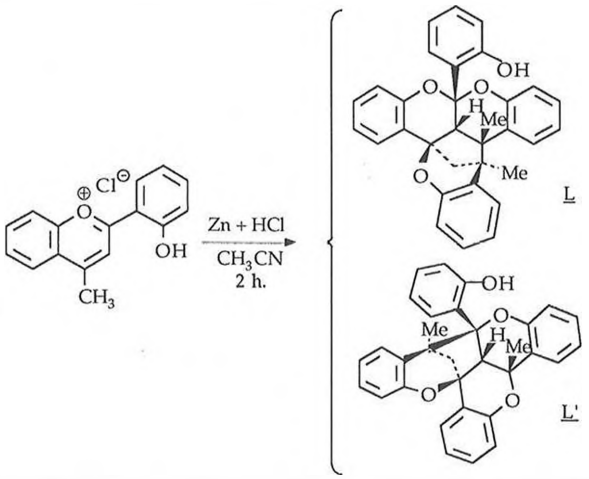
Chimie Organique **103**

Nouvelle classe de composés heptacycliques préparés en une seule étape à partir de sels de flavylium.

B. Diab, H. Jolibois, B. Laude, L. Ouahab et A. Chambaudet
Laboratoire de Microanalyses Nucléaires, Université de Franche-Comté , 25030 Besançon Cedex - France

Les études consacrées à la réduction des sels de flavylium montrent que des produits très divers peuvent être obtenus. Ainsi le perchlorate de flavylium conduit par réduction à des composés polycycliques [1].

La présence d'un groupe OH phénolique dans nos sels de flavylium[2] permet d'accéder à une nouvelle classe de composés heptacycliques (L, L', L'') en une seule étape, en faisant appel à une réduction par Zn et HCl en milieu CH_3CN. Les structures radiocristallographiques de L et L' ont été établies.



[1] Ben R. Brown and A. William R. Tyrrell. *J. Chem. Soc. Perkin Trans.* 1, **1984**, 1963-1970.
[2] H. Jolibois, F. Théobald, J. Vebrel. *Helv. Chim. Acta*, **1988**, 71, 812-818.

Organische Chemie **104**

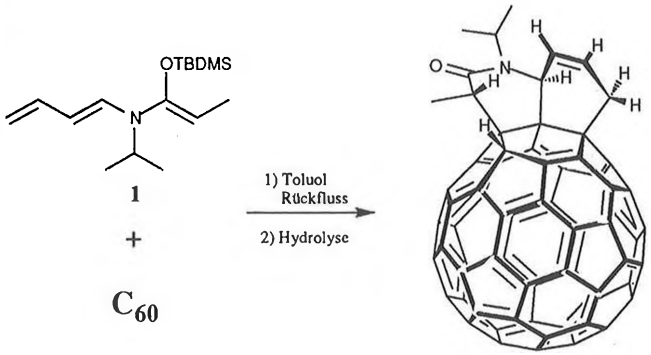
Tandemreaktion von *N*-Butadienyl-*N*-Alkylketen-*N,O*-Silylacetalen

Andreas Franz, Yves Rubin und Reinhard Neier
Institut de Chimie de l'Université de Neuchâtel, CH-2000 Neuchâtel

Tandemreaktionen stellen wichtige Reaktionsprozesse in der Organischen Synthese und in der Biosynthese dar [1].

Um Hinweise über den Reaktionsmechanismus der von uns untersuchten Tandemreaktion (*Diels-Alder*/Acylation) [2] zu bekommen, wurde das TBDMS-*N,O*-Ketenacetal **1** synthetisiert. Die Reaktion von **1** mit ungesättigten Säurechloriden führte diastereoselektiv zu bizyklischen Produkten.

In einer Zusammenarbeit mit der Gruppe *Rubin* an der U.C.L.A wurde die Tandemreaktion von **1** mit Buckminsterfulleren durchgeführt, wobei ein hochfunktionalisiertes Triadditionsprodukt von C_{60} dargestellt werden konnte.



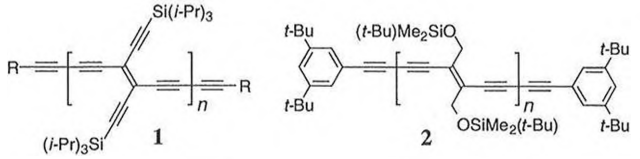
[1] L.F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137.
[2] M. Baak, Y. Rubin, A. Franz, H. Stoeckli-Evans, L. Bigler, J. Nachbaur, R. Neier, *Chimia* **1993**, *47*, 233.

Organische Chemie / Medizinische Chemie **105**

Nanoscale Carbon - Rich Rods

M. Schreiber, J. Anthony, F. Diederich, C. Boudon, J.-P. Gisselbrecht, and M. Gross.
Laboratorium für Organische Chemie, Universitätstrasse 16, ETH-Zentrum, CH-8092 Zürich.

Oxidative polymerization (CuCl, TMEDA, O_2) of *trans*-bis(triisopropylsilyl)-protected tetraethynylethene and end-capping with phenylacetylene afforded the remarkably stable, soluble oligomers **1** (R = Ph, n = 1-5) [1]. The persilylethynylated polytriacetylene backbones of these oligomers are 1.94, 2.68, 3.43, 4.18, and 4.92 nm in length, respectively, and electronic absorption data predict a band gap of E_g = 2.3 eV for the infinite polymer. In a modified procedure, the oxidative polymerization of *trans*-bis(triisopropylsilyl)-protected tetraethynylethene was carried out in the presence of 2 mol-% 3,5-bis(*tert*-butyl)phenylacetylene as end-capping reagent, and the conditions were modified such that the average molecular weight of the polymer could be increased to values of approximately 11300 Daltons for **1** (R = 3,5-bis(*tert*-butyl)phenyl, $n \approx 25$) and 9500 Daltons for **2** ($n \approx 30$), as determined by quantitative ^{1}H-NMR and VPO. For **1**, the predicted band gap has been proven correct by UV/VIS spectroscopy. The stability and facile preparation of these linear, highly conjugated, nanometer-sized carbon-rich rods make them ideal as molecular wires and for other applications in molecular electronics.



[1] J. Anthony, C. Boudon, F. Diederich, J.-P. Gisselbrecht, V. Gramlich, M. Gross, M. Hobi, P. Seiler, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 763.

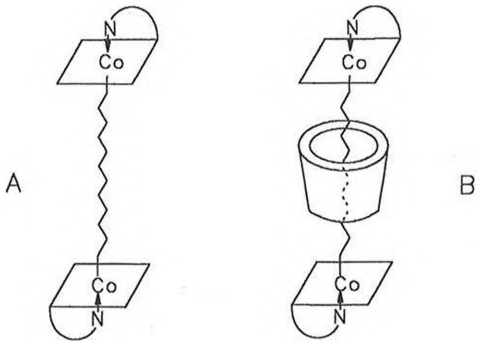
Organische Chemie **106**

An Organometallic Rotaxane

R.Hannak, T.Derer, W.Mühlecker, R.Konrat, B.Kräutler *
Institut für Organische Chemie, Universität Innsbruck, A-6020 Innsbruck

The reaction of 1,12-dibromododecane with Co(I)-cobalamin led to the formation of the symmetric, organometallic B_{12}-dimer **A** with a dodecamethylene bridge. The analogous reaction in the presence of an excess of α-cyclodextrin in water produced rotaxane **B**.

The structures of the two organometallic B_{12}-dimers were established by modern spectroscopic means. The NMR-spectra of the chiral dimer **A** are simplified due to its C_2-symmetry. In the asymmetric [2]-rotaxane **B** the C_2-symmetry of the organometallic guest-component is broken by the rotationally symmetric cyclodextrin ring and its NMR-spectra are correspondingly more complex.



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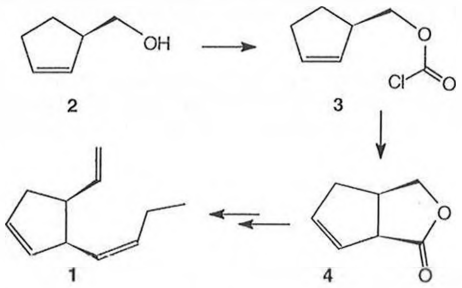
Organische Chemie **107**

Synthesis of (+)-Multifidene

S. Hemamalini and R. Scheffold
Institut für Organische Chemie, Universität Bern, CH-3012 Bern

Multifidene (**1**) is a major constituent of the pheromone released by the brown algae *Cutleria multifida* . Although several syntheses of racemic multifidene have been reported [1], only one synthesis of enantiomerically pure compound has been accomplished so far [2].



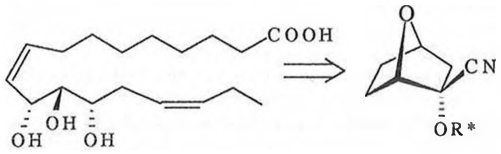
Cyclopent-2-enylmethanol (**2**) was chosen as the requisite starting material. Treatment of **2** with trichloromethylchloroformate afforded the chloroformate **3**. The key step in the synthesis involves a cobalt mediated radical cyclization [3] of **3** to furnish the bicyclic lactone **4**. The lactone **4** was converted to the naturally occuring (+)-multifidene (**1**) in two steps: (i) introduction of the cis-butenyl side chain *via* reductive alkenylation, (ii) oxidation of the resulting alcohol with PCC followed by *Wittig* olefination.

[1] P. Kramp, G. Helmchen, A.B. Holmes, *J. Chem. Soc., Chem. Commun.* **1993**, 551
[2] W. Boland, L. Jaenicke, D.G. Müller, *Liebigs Ann. Chem.* **1981**, 2266
[3] V.F. Patel, G. Pattenden, D.M. Thompson, *J. Chem. Soc., Perkin Trans. 1* **1990**, 2729.

Chimie Organique **108**

Total Asymmetric Synthesis of (11*R*,12*S*,13*S*)-Trihydroxy-9(Z),15(Z)-octadecadienoic Acid, a Self-defensive Agent Against Rice Blast Disease.

Alain Baudat and Pierre Vogel
Section de Chimie de l'Université de Lausanne, 2, rue de la Barre, CH 1005 Lausanne, Switzerland



1 (-)-2 R*=(1*R*)-camphanoyl

The Diels-Alder adduct of furan and 1-cyanovinyl (1'*R*)-camphanate was converted into (11*R*,12*S*,13*S*)-trihydroxy-9(Z),15(Z)-octadecadienoic acid **1** which is believed to be an endogenous fungicide in the rice variety resistant to the fungus *Pyricularia oryzae*. In a effort to establish the structure of **1**, Kato et al.[1] derived **1** form α-linoleic acid. More recently, Yadav and Chander[1a] have proposed a stereoselective synthesis of **1** starting form D-ribose. We report here a new synthesis of **1** based on the "naked sugar" technology.[2]

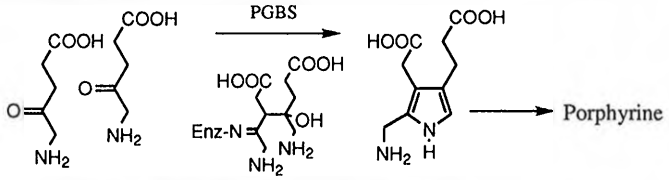
(1) Kato, T.; Yamaguchi, Y.; Ohnuma, S.-i.; Uyehara, T.; Namai, T.; Kodama, M.; Shiobara, Y. *Chem. Lett.* **1986**, 577; (1a) Yadav, J. S.; Chander, M. *Tetrahedron Lett.* **1990**, *31*, 4349.
(2) Warm, A.; Vogel, P. *J. Org. Chem.* **1986**, *51*, 5348; Vogel, P.; Auberson, Y.; Bimwala, R. M.; de Guchteneere, E.; Vieira, E.; Wagner, J. in "Trends in Synthetic Carbohydrate Chemistry", ACS Symposium Series 386; Horton, D.; Hawkins, L. D.; McGarvey, G. J., Eds.; American Chemical Society, Washington, D. C., USA **1989**, 197; Vogel, P.; Fattori, D.; Gasparini, F.; Le Drian, C. *Synlett* **1990**, 173; Vogel, P. *Bull. Soc. Chim. Belg.* **1990**, *99*, 395; Vogel, P. *Chimica Oggi* **1992**, 9.

Organische Chemie **109**

Eine neue, 6-stufige Synthese von Porphobilinogen - Realisierung eines biomimetischen Konzeptes

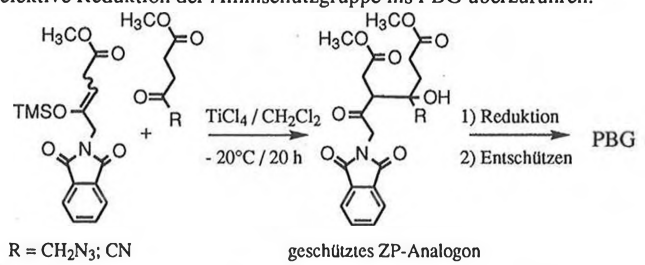
Hugo Bertschy, André Chaperon und Reinhard Neier
Institut de Chimie de l'Université de Neuchâtel, CH-2000 Neuchâtel

In der Biosynthese der Tetrapyrrole stellt Porphobilinogen (PBG) das zentrale Zwischenprodukt dar. Mit Hilfe von Porphobilinogen Synthase (PBGS) wird aus zwei Molekülen δ-Aminolävulinsäure (δ-ALA) das PBG synthetisiert [1].



δ-ALA postuliertes Zwischenprodukt PBG

Basierend auf dem von *D. Shemin* postulierten Enzymmechanismus [2] entwickelten wir ein allgemein anwendbare Pyrrolsynthese [3]. Gemäss dieses biomimetischen Konzeptes gelang es, geschützte ZP-Analoge durch selektive Reduktion der Aminschutzgruppe ins PBG überzuführen.



$R = CH_2N_3$; CN geschütztes ZP-Analogon

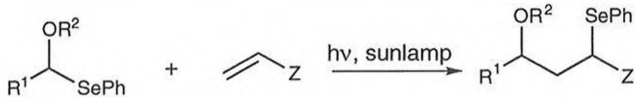
[1] F.J. Leeper, *Natural Product Reports*, **1989**, 171.
[2] D.L. Nandi, D. Shemin, *J. Biol. Chem.*, **1968**, 234(6), 1236.
[3] H.Bertschy, A. Meunier, R. Neier, *Angew. Chem.* **1990**, *102(7)*, 828.

Organic Chemistry **110**

Use of O,Se-Acetals for Radical Mediated Phenylselenenyl Group Transfer Reactions

S. Abazi, J.P. Vionnet and P. Renaud
Institut de Chimie Organique, Université de Fribourg, CH-1700 Fribourg.

Organoselenium compounds are highly versatile and have found many applications in organic synthesis. Moreover, the homolytic cleavage of a carbon-selenium bond is an efficient method for radical generation. Byers has recently demonstrated that it is possible to run radical reactions without loosing the selenium by using dimethyl 2-(phenylselenenyl)propanedioate.(1) We report here, that O,Se-acetal of type **1** (R^1 =COOR) are suitable precursors for intermolecular C,C-bond formation via a phenylselenenyl group transfer (**1**→**3**). Several examples of intramolecular reactions will also be presented.



(1) Byers, J.H; Lane, G.C *J.Org. Chem.* **1993**, *58*, 3355.

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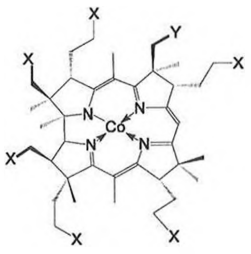
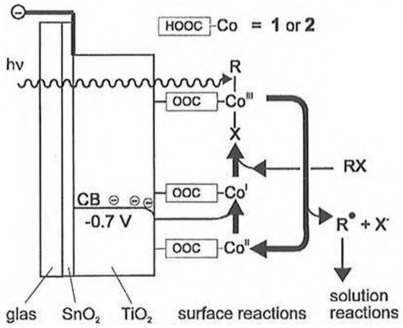
Organische Chemie **111**

Photo-Electrosynthesis on Nanocrystalline TiO_2-Electrodes Modified with Vitamin B_{12}.

Marcel Mayor [1], Anders Hagfeldt [2], Michael Grätzel [2], Lorenz Walder [1,2]
[1] Institut für Organische Chemie, Uni. Bern, CH-3012 Bern.
[2] Institut de Chimie Physique II, EPFL, CH-1015 Lausanne.

Free acid derivatives of vitamin B_{12}, *e.g.* **1** and **2**, were synthesized and irreversibly attached *via* -COO(H) ···· (HO)Ti^{IV} linkages to the surface of thin film nanocrystalline TiO_2 on conductive glas. With 3 µm thick, transparent, red-colored semi-conductor electrodes, the Co(II) reduction is fast and occures at potentials close to the TiO_2 conduction band (CB). B_{12}-surface concentrations up to $5 \cdot 10^{-8}$ mol/cm^2 are observed. Alkyl halides are





reduced to R• and X^-, if such an electrode is illuminated with visible light and biased at E < -0.7 V.
The B_{12}-TiO_2 electrode is currently checked for its scope:
- in organic photo-electrosynthesis, related to the mild generation of R•
- as an optical/electrochemical sensing device for RX.

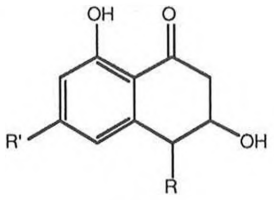
Organic Chemistry **112**

Isolation of Phytotoxic Metabolites from Culture Medium of *Ceratocystis fimbriata* f.sp. *platani*

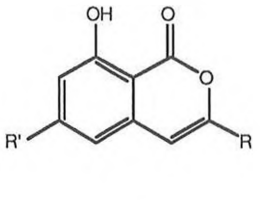
N. Burki and R. Tabacchi
Institut de Chimie de l'Université de Neuchâtel, CH-2000 Neuchâtel

Ceratocystis fimbriata f.sp. *platani* is the plane tree's canker stain disease agent, a widely expanded infection in Italy and in the south of France [1].

In the course of our scientific research carried out on that pathogenic agent, fungal metabolites were isolated and were submitted to biological tests. Resulting toxines, naphtalenones **1** or isocoumarines **2**, are reported metabolites from various strains of *Ceratocystis* (*C. minor* [2], *C. ulmi* [3] or *C. fimbriata coffea* [4]) :



1



2

Compounds **1** and **2** were shown to induce extended necrosis of the vascular system. On the other hand, we could further identify other metabolites with minor biological activity. One of them was a novel monoterpene whose absolute configuration could be determined.

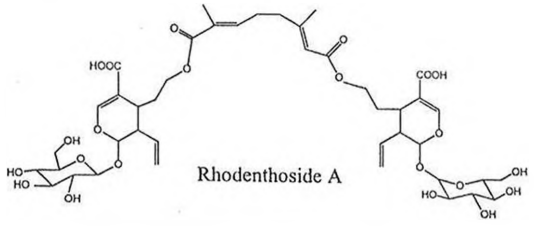
[1] Walter J.M., *U.S. Dept. Agric. Cir.* 742 (1946)
[2] W.A. Ayer et al., *Can. J. Chem.* **65**, 765-769 (1987)
[3] N. Claydon et al., *Phytochemistry* **13**, 2567-2571 (1974)
[4] G. Gremaud and R. Tabacchi, *Natural Product Letters* (in press)

Organic chemistry **113**

A new type of acylated secoiridoid glycoside from *Gentiana rhodentha*

Wei-Guang Ma, Nicola Fuzzati, Jean-Luc Wolfender, Kurt Hostettmann
Institut de Pharmacognosie et Phytochimie, Ecole de Pharmacie, Université de Lausanne, BEP, CH-1015 Lausanne
and Chong-Ren Yang
Kunming Institute of Botany, Chinese Academy of Science, Kunming -650204, Yunnan, China

In the course of our systematic studies on secondary metabolites typical of the Gentianaceae family [1], a phytochemical investigation of *Gentiana rhodentha* Fr. has been undertaken. Preliminary LC-UV and LC-MS investigations of the methanolic extract of the whole plant of *G. rhodentha* suggested the presence of common secoiridoids, iridoids and xanthones. There was also evidence for less polar high MW secoiridoids. Isolation and structure determination of the latter compounds was performed.
Rhodenthosides A and B are member of a new class of acylated secoiridoids composed of swerosidic acid units connected with a "nerol-type" or "foliamenthic-type" monoterpene acid by esterification.



Rhodenthoside A

Rhodenthoside B is an analogoue of A with two swerosidic acid units each connected to a carboxylic acid group by esterification.
The structures were established by 1D- and 2D-NMR, EI-MS, D/CI-MS, FAB-MS, CF-FAB LC-MS, TSP LC-MS and LD-MS data in combination with chemical reactions.

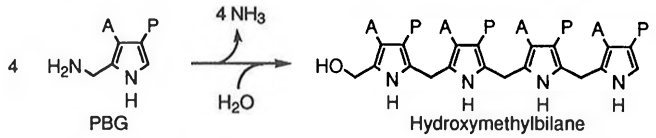
[1] J-L. Wolfender, K. Hostettmann, *J.Chromatogr.* 1993, 647, 191.

Organic Chemistry **114**

A Kinetic Analysis of the Reaction Catalysed by Porphobilinogen Deaminase (PBGD) from *Escherichia coli*

A. Hädener and A. Niemann-LeibundGut
Institut für Organische Chemie, Universität Basel, CH-4056 Basel

Porphobilinogen deaminase (PBGD) catalyses the conversion of monopyrrolic porphobilinogen (PBG) to hydroxymethylbilane, a precursor for hemes, chlorophylls, vitamin B_{12} and other tetrapyrrolic pigments. The reaction belongs to the class of polymerisations and displays overall Michaelis-Menten kinetics [1]. During the reaction four intermediate covalent enzyme-substrate complexes are formed consecutively before the product is released [2].



A = CH_2COOH / P = CH_2CH_2COOH

Our analysis focused on the pre-steady state kinetics of the formation of these complexes. We succeeded in generating the enzyme-substrate complexes by treating wild-type, selenomethionine (SeMet)-labelled, or Lys-59Gln-PBGD, immobilised on an anion exchange support, with a solution of PBG at low [PBG] and high flow rate. After the treatment, the chromatographic separation and quantification of the different species was possible due to their remarkable chemical stability. To derive values of specificity constants for individual polymerisation steps, the pre-steady state period was simulated by a computer programme and the simulation was fitted to the experimental data by chi-square minimisation. Whereas the kinetic parameters of [SeMet]PBGD match those of the wild-type enzyme fairly well, Lys-59Gln-PBGD shows significant changes in the reaction kinetics, thus demonstrating the large influence of a small structural change on the catalytic reaction cycle.

REFERENCES
[1] D. C. Williams *et al.* (1981) *Biochem. J. 193*, 301-310.
[2] A. R. Battersby & F. J. Leeper (1990) *Chem. Rev. 90*, 1261-1274.

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Organische Chemie **115**

Pseudo-Prolines in Peptide Synthesis

A. Nefzi, T. Wöhr, T. Haack, D. Ryan and M. Mutter
Institute of Organic Chemistry, University Lausanne, CH-1005 Lausanne

Pseudo-prolines have been introduced recently as structure disrupting, solubilizing protection technique in peptide synthesis [1]. As a particular feature, serine- and cysteine- derived oxazolidines and thiazolidines [Ser(Ox); Cys(Th)] have shown to prefer a cis-bond formation when incorporated in the peptide backbone, resulting in dramatic effects upon the physicochemical properties, e.g. coupling kinetics or solvation. Here, we elaborate the use of these novel building blocks in common strategies of peptide synthesis. In particular, we describe the syntheses of the sterically hindered dipeptides of type Fmoc-Xaa-Ser(Ox) and Fmoc-Xaa-Cys(Th) which serve as building blocks in SPPS. Special emphasis is given to the influence of the C^2-substituents on the chemical stability of the ring systems. For the example of the SPPS and the structural investigation of several model peptides it is demonstrated, that: (i) pseudo-prolines are compatible with standard Fmoc/t-Bu based strategies in SPPS; (ii) difficult peptide sequences (e.g. β-sheet forming, hydrophobic peptides) become synthetically accessible by the incorporation of a single pseudo-proline; (iii) by variation of the C^2-position (benzyl-, methyl-, no substituent) of the oxazolidines a broad spectrum of cleavage conditions of the cyclic system becomes available.

In conclusion, pseudo-prolines are shown to be readily accessible and versatile building blocks for overcoming some fundamental problems in peptide synthesis.

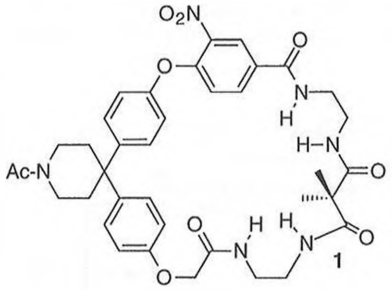
[1] T. Haack and M. Mutter, *Tetrahedron Lett.* 1992, *33*, 1589.

Organische Chemie / Medizinische Chemie **116**

De Novo Design of Macrocyclic Amino Acid Receptors as Synthetic Vancomycin-Analogs

B. Hinzen and F. Diederich*
Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

The antibiotic effect of naturally occuring vancomycin is thought to arise from selective binding of the dipeptide N-Acetyl-*d*-Ala-*d*-Ala **2**. In an effort to gain further insight into the mode of action of vancomycin and to provide a family of peptide receptors that can be easily adapted to various substrates we designed macrocyclic receptors such as **1**.



Molecular modeling studies of **1** and **2** show that, in a manner similar to vancomycin, the carboxylate of the guest would be bound by a network of hydrogen bonds and its C-terminal methyl group by the host's electron rich aromatic systems. This hydrophobic interaction is the major driving force for complexation in polar solvents, especially in the biological relevant and highly competitive aqueous medium.

While hydrophobic interactions are readily modulated by changing the phenyl substitution pattern, modification of the amid-chain of **1** allows to evaluate the importance of individual hydrogen bonds to the guest. These are important for the stability of the complex in organic solvents but are also necessary for binding in water to compensate for the desolvation of the guest's polar subbinding sites during complexation.

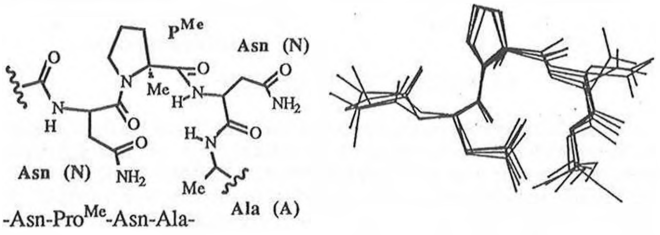
The synthesis of **1** and preliminary binding studies with **2** will be presented.

Organische Chemie/Medizinische Chemie **117**

Stabilization of ß-Turn Conformations in the NPNA-Repeat Motif of a Synthetic Malaria Vaccine

Christian Bisang, Christoph Weber and John A. Robinson
Institut für Organische Chemie, Universität Zürich, 8057 Zürich

Surface loops on proteins have been frequently identified as important in immune recognition and thus have become the target of peptide based vaccine design. Although anti-peptide antibodies often fail to recognize or only weakly bind the corresponding native protein, this can be explained by bad mimicry of a constrained protein epitope by a small, flexible peptide. Substitution of proline by α-methylproline (P^{Me}) in predicted ß-turns has been shown to stabilize turn conformations and improve peptide antigenicity [1]. This approach has been applied to the $(NPNA)_n$-motif of the circumsporozoite surface protein of the malaria parasite *P. falciparum*. The solution structures of $(NP^{Me}NA)_n$ peptides were studied by CD & 2D-NMR spectroscopy.



Distance geometry calculations based on the analysis of NOEs and coupling constants as well as amide-shift temperature coefficients, indicate that within each $NP^{Me}NA$-unit, a type-I ß-turn conformation, with the Asn-side chain hydrogen-bonded to backbone peptide linkages, is significantly stabilized in comparison to the corresponding native peptide. A rabbit antiserum raised against $(NP^{Me}NA)_3$ was also shown by immunofluoresence assays to react strongly with *P. falciparum* sporozoites, while a monoclonal antibody directed against the circumsporozoite protein also binds the methylated peptide, indicating that we may have stabilized a native-like structure.

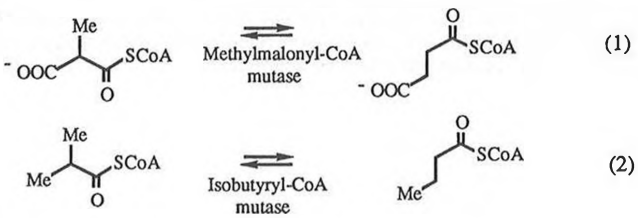
[1] Hinds, M. G. et al., *J. Med. Chem.* **1991**, *34*, 1777.

Organische Chemie/Medizinische Chemie **118**

Coenzyme B_{12}-Dependent Methylmalonyl-CoA Mutase from *Streptomyces cinnamonensis*. Isolation of the Enzyme and Cloning and Sequencing of its Structural Gene

Katja Burkhardt, Natalie Philippon, Ashley Birch, Andreas Leiser and John A. Robinson
Institut für Organische Chemie, Universität Zürich, 8057 Zürich

The conversion of succinyl-CoA into methylmalonyl-CoA is catalyzed by the B_{12}-dependent methylmalonyl-CoA mutase (MCM). In the monensin-producing organism, *Streptomyces cinnamonensis*, the occurrence of this and a second closely related rearrangment of isobutyryl-CoA into n-butyryl-CoA mutase has been demonstrated [1]. To determine whether these two reactions are catalyzed by the same or different proteins, we set out to isolate and characterize the MCM from *S. cinnamonensis*.



The purified MCM is a heterodimer, with subunits of 69 and 73 kDa, and cannot catalyze rearrangement (2). The structural gene for the MCM, isolated from a genomic DNA library, was shown to encode two proteins of 616 and 733 residues, whose sequences show high similarity to each other and to MCM from other sources [2]. When this gene was expressed in *S. lividans*, only MCM and not isobutyryl-CoA mutase activity was detected. Thus, the rearrangement of isobutyryl-CoA to n-butyryl-CoA is catalyzed by a distinct isobutyryl-CoA mutase. This isobutyryl-CoA mutase appears by gel filtration to be of similar size to the MCM, but can be easily separated from it by ion-exchange chromatography.

[1] Brendelberger, G. et al., *Angew. Chem. Int. Ed.* **1988**, *27*, 1089.
[2] Birch, A. et al., *J. Bacteriol.* **1993**, *175*, 3511.

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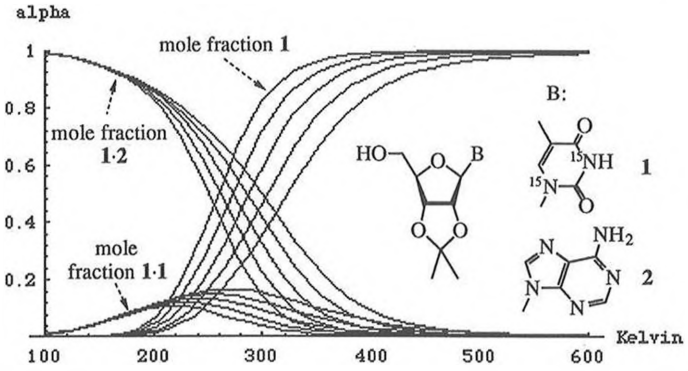
Organische Chemie/Medizinische Chemie **119**

Calculating the Thermodynamics of Weakly Interacting H-Bonded Complexes from ^{15}N NMR Spectroscopical Data

P. Strazewski, A. Amantea, M. Walser
Institut für Organische Chemie, Universität Basel, CH-4056 Basel

The selfpairing of ^{15}N-labelled 5-methyluridine derivative **1** and its pairing with unlabelled adenosine derivative **2** in deuterochloroform was investigated by ^{15}N NMR spectroscopy. The melting curves, as measured by the temperature dependence of the chemical shift of N(3), showed that a mixture of monomeric and complexed specimens prevailed at all concentrations and temperatures (c = 46.13–1.44 mM, T = 0–55°C). A function $\alpha(c,T)$ was fitted onto the datapoints and produced temperature-dependent Gibbs free energies of base pairing as optimised parameters. The respective enthalpy $\Delta H°$ and entropy $\Delta S°$ of base pair formation was calculated from a linear regression of $\Delta G°(T)$ *versus* T. ^{15}N NMR spectroscopy proved to be an ideal means for this purpose, but ^1H NMR, UV spectroscopy or other monitoring methods are also suitable. The fitting procedure could be automated and used for the analysis of UV-monitored melting curves of short or mismatched DNA or RNA fragments that do not fully pair or denature within the temperature range of liquid water. It could also be used for the determination of pairing stabilities in organic solvents involving supramolecular complexes of any molecularity above 1.



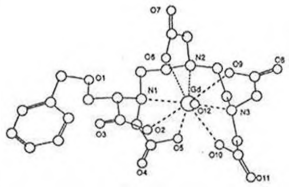
Organische Chemie/Medizinische Chemie **120**

Synthesis, Atropisomerism, Crystal Structure and Albumin Binding of the Gadolinium Chelate Gd-BOPTA/Dimeg, a Liver-Specific Contrast Agent for Magnetic Resonance Imaging

C. de Haën, E. Felder, F. Uggeri and A. Gallotti
Research and Development Division, Bracco SpA, Via Folli 50, I-20134 Milano

Gd-(III)-chelates based on the diethylenetriaminepentaacetate skeleton are contrast agents for magnetic resonance imaging. Such compounds carrying plain or modified benzyloxymethyl substituents on a terminal acetic group are liver directed agents. The synthesis of chelators with substituted aromatic rings is made possible by a novel one-pot alkoxymercuration-bromodemercuration reaction.

Gd-BOPTA^{2-}



The product now in clinical development, Gd-BOPTA/Dimeg, is the meglumine salt of the gadolinium complex of the racemic chelator BOPTA. Crystal structure analysis of its sodium salt analogue shows an enantiomeric pair of molecules in the unit cell. Each molecule has two chiral positions, one of which is carbon centered and the other is gadolinium centered. The stereochemistry of the two molecules are described by the prefixes *TPS*-9-145337286-*C-S* and *TPS*-9-145337286-*A-R*. In principle 16 stereoisomers of the Gd-BOPTA^{2-} anion are possible.

During the synthesis of the chelator, BOPTA, a side-product with two benzyloxymethyl substituents on opposite ends of the molecule is obtained. The Gd complex of this molecule permits the slow interconversion of conformers, which differ in their stereochemistry at the Gd-center, to be observed.

Gd-BOPTA relative to Gd-DTPA shows an enhanced proton magnetic relaxivity in the presence of albumin. This is explained by the weak binding of Gd-BOPTA to albumin mediated by the benzyloxymethyl moiety. This binding, with a dissociation constant in the millimolar range, translates into a substantial benefit for imaging efficacy without detrimental effects on the pharmacokinetics of the compound.

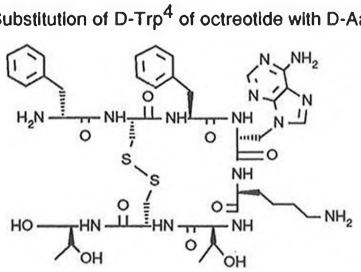
Organic Chemistry and Medicinal Chemistry **121**

Molecular Modelling of Somatostatin Analogues Incorporating Nucleo Amino Acids.

Robin Breckenridge, Ian Lewis and Christian Bruns
Sandoz Pharma Ltd., CH-4002, Basel, Switzerland.

Ala-Gly-Cys-Lys-Asn-Phe-Phe-Trp-Lys-Thr-Phe-Thr-Ser -Cys-OH, somatostatin, has been shown to inhibit the release of a large number of hormones such as growth hormone (GH), insulin, glucagon, gastrin and secretin. It is of potential therapeutical importance in clinical treatment of acromegaly and gastroenteropancreatic tumours. A process of rational design led to the potent, selective, minimal sequence, long acting octapeptide somatostatin analogue, known as octreotide, (D)-Phe-Cys-Phe-(D)Trp-Lys-Thr-Cys-Throl (SMS 201-995). The incorporation of special hydrogen bonding amino acids, termed nucleo amino acids[1,2] into the peptide backbone of octreotide presented an opportunity to extend this rational design process.

Substitution of D-Trp^4 of octreotide with D-Aala^4



We will report molecular modelling studies analysing the influence of incorporating these nucleo amino acids on the octapeptide conformation, and on the resultant synthesis and biological activity of these analogues. Illustrated above is an example of this study where D-Trp^4 in octreotide is replaced by D-Aala^4, the adenine nucleo amino acid.

1. I. Lewis, *Tetrahedron Letters* **1993**, *34*, *5697*.
2. I. Lewis and C. Bruns, *Tetrahedron* **1994**, *50*, *7485*.

Medizinische Chemie **122**

Prediction of Hemoglobin Binding , Carcinogenicity and Mutagenicity of Arylamines and Nitroarenes

Gabriele Sabbioni
Institut für Toxikologie, Universität Würzburg, D-97078 Würzburg

Arylamines and nitroarenes are important environmental and occupational pollutants. These compounds form covalent adducts with hemoglobin and DNA. Several hemoglobin adducts have been found in different populations (e.g. Bryant et al. Cancer Res. 47: 602-608, 1987). We investigated the structural prerequisite to form hemoglobin adducts for several arylamines and nitroarenes in Wistar rats and compared them to the structure activity relationships (SAR) for mutagenicity, carcinogenicity and cytotoxicity of arylamines and nitroarenes.

Most arylamines and nitroarenes form hydrolyzable (e.g. sulphinamide) adducts with hemoglobin in rats. The degree of hemoglobin binding {(HBI = hemoglobin binding index) = [(mmol compound / mol Hb)/dose (mmol/kg)]} decreases with the oxidizability of the arylamines, except for compounds where halogen is substituted in the ortho and/or meta position. Mutagenicity or carcinogenicity of arylamines is inversely related to their oxidizability. For arylamines this first set of data suggests that differing electronic properties determine the degree of hemoglobin binding, mutagenicity and carcinogenicity. Hemoglobin binding of nitroarenes increases with the reducibility of the nitro group. The SAR of hemoglobin binding of nitroarenes and arylamines are comparable. For nitroarenes the mutagenic and cytotoxic potency and hemoglobin binding increase with the reducibility of the nitro group. Insufficient data regarding the carcinogenicity of nitroarenes are available to make a comparison with hemoglobin binding. According to the currently available data, large HBIs of nitroarenes may indicate high mutagenic and cytotoxic potency. Therefore, for some compounds hemoglobin adducts are not only an exposure monitor, but an indicator for the cytotoxic and genotoxic burden.

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Medicinal Chemistry **123**

MOLECULAR MODELLING OF D_2-LIKE DOPAMINE RECEPTORS

Frédéric Billois*, Pierre-Alain Carrupt*, Philip G.Strange#, and Bernard Testa*.

* Institut de Chimie Thérapeutique; Ecole de Pharmacie; Université de Lausanne; CH-1015 Lausanne.
# The Biological Laboratory; The University; Canterbury; Kent; CT2 7NJ; UK.

Three-dimensional computer models of the rat D_2-like dopamine receptor subtype have been constructed based on the diffraction coordinates for bacteriorhodopsin, another membrane bound protein containing seven transmembrane domains arranged in a similar spatial orientation. These models were assembled by aligning the putative transmembrane domains of the dopamine receptors with those of bacteriorhodopsin using sequence similarities, and then superimposing these modelled α-helices to the bacteriorhodopsin-derived coordinates [1].

Our models explore the potential hydrogen bonding, electrostatic and stacking interactions within the receptor which may be important for maintaining the protein conformation, thereby provide target sites for agonist binding. The module DOCK in the SYBYL software was used to providing the docking of dopamine and a number of agonists.

Three-dimensional Molecular Electrostatic Potential (3D-MEP) [2] and three-dimensional Molecular Lipophilic Potential (3D-MLP) [3] were computed for the binding site, dopamine and the agonists. Comparison of 3D-MEP and 3D-MLP distributions were used to study the affinity and specificity of these ligands.

Such models and computational tools will be useful for establishing structure-function relationships between ligands and dopamine receptors, and may ultimately provide a template for the design of receptor-specific drugs.

1. Livingstone CD, Strange PG, and Naylor LH, Molecular modelling of D_2-like dopamine receptors. *Biochem J* **287:** 277-282, 1992.
2. El Tayar N, Carrupt P-A, van de Waterbeemd H, and Testa B, Modeling of .beta-adrenoceptors based on molecular electrostatic potential studies of agonists and antagonists. *J Med Chem* **31:** 2072-2081, 1988.
3. Gaillard P, Carrupt P-A, Testa B, and Boudon A, Molecular Lipophilicity Potential, a tool in 3D-QSAR. Method and applications.. *J Comput -Aided Mol Des* 1994.

Medicinal Chemistry **124**

Molecular modelling and QSAR study of the binding of HEL(52-61) and related peptides by I-A^k class II Mhc molecule.

Peter Weber[1], Pierre-Alain Carrupt[1], Joelle Paris[2], Denis Gerlier[3], Chantal Rabourdin-Combe[4], Laurent Ettouati[2] and Bernard Testa[1].

1 Institut de Chimie Thérapeutique, Université de Lausanne, CH-1015 Lausanne.
2 Laboratoire de Chimie Thérapeutique, Faculté de Pharmacie, Université Lyon I, 8 avenue Rockefeller, F-69373 Lyon Cedex 08.
3 Immunité et infections virales, IVMC, UMR30, CNRS-UCBL, F-69373 Lyon Cedex 08.
4 Immunologie Moléculaire, UMR 49, CNRS-ENS Lyon, F-69364 Lyon Cedex 07.

The I-A^k class II major histocompatibility complex (Mhc) is a protein of the mouse immune system. It is a cell surface molecule located on antigen-presenting cells (APC). After endosomal degradation of a foreign protein, I-A^k binds the peptidic fragments and brings them to the cell surface to present them to the T cells. This interaction will stimulate the proliferation of the T cells and thus activate the immune response.

This study uses biological *in vitro* data on the binding of 35 peptides derived from the hen egg lysosyme (HEL) fragment 52-61 [1]. A QSAR analysis was performed using the molecular lipophilicity potential (MLP) [2] to see if the three-dimensional lipophilicity of the peptides can explain their binding affinity.

The molecular modelling of the I-A^k is based on a crystallographic structure of the human HLA-DR1 molecule complexed with an influenza virus peptide (306-318) [3]. The coordinates were kindly provided by J.H.Brown. The sequence homology is 60%, so the I-A^k molecule was build by "mutating" the non-homologous amino-acids. One incision and one excision were made. The MLP applied to the binding groove of the I-A^k served as a guide to postulate the conformation of the bound peptide. Different conformers of the peptide were then placed in the groove and evaluated in terms of energy reached after minimisation of the complex.

[1] Hernandez J.-F., Cretin F., Lombard-Platet S., Gerlier D., Salvi J.P., Walchshofer N., Paris J., Rabourdin-Combe Ch., *Peptides*,1994, in press.
[2] Gaillard P., Carrupt P.-A., Testa B. , Boudon A., *J. Comput.-Aided Mol. Des.* in press.
[3] Stern J.L., Brown J. H., Jardetzky T. S., Gorga J. C., Urban R. G., Strominger J.L., Wiley D. C., *Nature* **368**, 215-222 (1994).

Physikalische Chemie **125**

Photodissociation of CF_3Br studied in the first UV-band

Marie-Anne Thelen and Peter Felder
Physikalisch-Chemisches Institut der Universität Zürich

The photochemistry of CF_3Br has been studied under collisionless conditions by polarized photofragment translational spectroscopy at 193 nm. The parent molecules in a collimated beam are photolysed by means of a pulsed laser and the nascent fragments are detected after having passed a well defined flight distance.

Bromine compounds are of atmospherical interest as Br can promote the depletion of the stratospheric ozone layer and hence it is important to know the atmospheric fate of these compounds. CF_3Br (halon 1301) is widely used as a fire retardant and the percentage contribution to ozone loss has been calculated to be 2.5 % [1].

Besides, the investigation of CF_3Br completes a series of studies carried out over the last few years on CH_3I, CF_3I and CH_3Br. These compounds are of theoretical interest because of their C_{3v} symmetry, which allows for an approximate treatment as linear pseudo-triatomics and because of their strong spin-orbit coupling, which gives rise to the two reaction channels

$$CX_3Y + h\nu \longrightarrow CX_3 + Y^*(^2P_{1/2})$$
$$CX_3Y + h\nu \longrightarrow CX_3 + Y(^2P_{3/2})$$

with (X = H,F; Y = Br,I). This gives us the opportunity to study the non-adiabatic coupling between two excited potential energy surfaces. Our results permit us to determine approximately the relative quantum yields of the two channels and to make a statement on the effectiveness of the non-adiabatic coupling.

[1] R.P. Wayne, Chemistry of Atmospheres, Oxford Science Publications, Claredon Press, 1991, Oxford.

Physikalische Chemie **126**

From Monomers to Clusters: Photodissociation of RONO and $[RONO]_n$

E. Kades, M. Rösslein and J. Robert Huber
Physikalisch-Chemisches Institut, Universität Zürich, CH-8057 Zürich

The photodissociation of the monomer RONO and of the clusters $[RONO]_n$ with an average size $\langle n \rangle \approx 20$ were investigated in a supersonic jet using laser excitation to the $S_1(n\pi^*)$ state and 2+1 LIF fragment state probing of the NO product including photofragment yield spectroscopy (PHOFRY) [1]. We measured the scalar – vibrational, rotational and translational energy distributions – and vectorial properties of the NO emerging from the monomer and the clusters. The measurements of the partial cross sections of the monomer and clusters provides additional information, such as the absorption spectrum at very low temperatures [2]. The knowledge of the partial cross sections which were found to be significantly different between the monomer and the clusters allowed us to excite selectively the monomer or the cluster and hence to study their photodissociation dynamics. Furthermore we were able to distinguish between the dissociation dynamics of a molecule on the surface of a cluster and one in the inner part of the cluster. The implication of our results with respect to the different dissociation dynamics of a monomer and a cluster and to the structure of the clusters are discussed.

[1] E. Kades, M. Rösslein and J.R.Huber, *J.Phys.Chem.* **97**, 989 (1993).

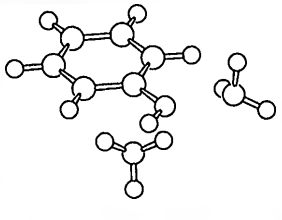
[2] E. Kades, M. Rösslein and J.R.Huber, *Chem.Phys.Letters* **209**, 275 (1993).

Physikalische Chemie **127**

Large Amplitude Motions of the Phenol•$(NH_3)_n$ n=1,2 Clusters

W.Mohr and S.Leutwyler,
Institut für anorganische, analytische und physikalische Chemie, Universität Bern, Freiestr.3, CH-3000 Bern 9

The calculation of hydrogen-bonded complexes containing NH_3 such as $(NH_3)_2$ and $NH_3 \cdot H_2O$ have been shown to be a critical task even for high-level *ab initio* calculations [1]. On the other hand, it has also been found difficult to relate the theoretical r_e predictions to the experimental r_0 values, even at the highest levels of theory studied [2].



We have measured the intermolecular vibrations of phenol·NH_3 and phenol·$(NH_3)_2$ in the S_0 and S_1 electronic states by mass- and isomer-resolved laser spectroscopic techniques, and performed a series of SCF/6-311(d,p) calculations. Several rotamers and conformers were fully optimized and normal mode analyses were performed. Despite the above mentioned difficulties we will show that the calculations predict the experimentally observed frequencies rather well. For the phenol·NH_3 the NH_3 torsion, low-frequency bend and hydrogen-bond stretching and bending modes were of special interest. For the phenol·$(NH_3)_2$ cluster the most important low-frequency mode is the "windshield-wiper" motion of the second ammonia. One-dimensional anharmonic effective potentials were calculated for several of these motions. The results are compared with the R2PI and fluorescence emission data, including Franck-Condon factors.

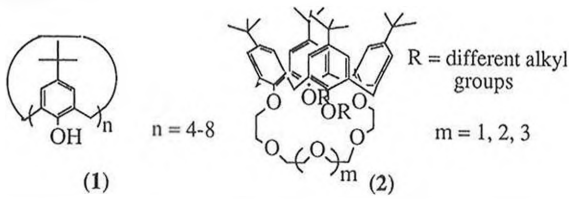
[1] D.M.Hasset, C.J.Marsden and B. J. Smith, Chem. Phys. Lett. **183**, 449 (1991); A.van der Avoird, E.H.T.Olthof, and P.E.S.Wormer, Faraday Discuss. **96**, 1 (1994).
[2] D.D.Nelson, G.T.Fraser and W.Klemperer, J.Chem.Phys.**83**,6201(1985).

Chimie physique **128**

A Study of the Cs^+/Na^+ Selectivity in Calixcrowns

F. Arnaud, S. Fanni, M.J. Schwing.
EHICS, Laboratoire de Chimie-Physique, 1 Rue Blaise Pascal, 67008 Strasbourg, France

Calixarenes (**1**) are macrocyclic phenol-formaldehyde condensates which after opportune chemical modifications show binding abilities towards metal ions. The capping of two distal phenolic units of the calix[4]arene with polyethylene glycol chains of different length has led to *calixcrowns* (**2**), which are a combination on the same molecule of a calixaryl structure and a crown ether[1,2].



(1) (2)

Thermodynamic studies were carried out with eight calix[4]crown derivatives in order to examine the binding abilities of these ligands.
It is noteworthy that some of the ligands studied showed a very high Cs^+/Na^+ selectivity. The origin of this selectivity has been deeply investigated and discussed in terms of solvation and conformation of the ligand, possible formation of π-bonding, and size of the crown part.

1) P. J. Dijkstra, J. A. Brunik, K. E. Bugge, D. N. Reinhoudt, S. Harkema, R. Ungaro, F. Uguzzoli and E. Ghidini: *J. Am. Chem. Soc.* , **1989**, *111*, 7567.
2) A. Arduini, A. Casnati, O. Ori, A. Pochini, F. Uguzzoli, in "Computational Approches in Supramolecular Chemistry" G. Wipff Ed., Kluwer, **1994**, 000.

Acknowledgements : This work has been done in collaboration with the University of Parma (Pr. R. Ungaro) and financially supported by the CEC in the framework of the "Nuclear Waste Programme".

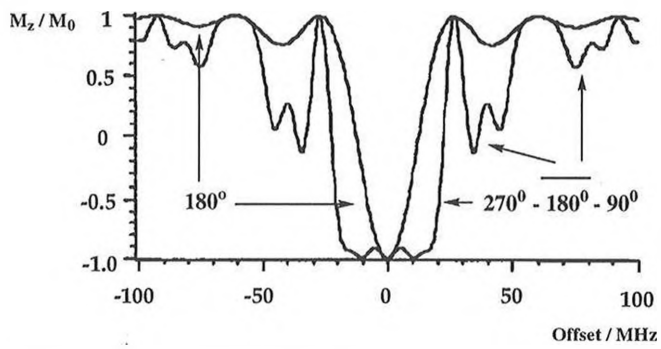
Physikalische Chemie **129**

FT-ESR-Studien in mikroheterogenen Systemen

S. H. Bossmann[a)], I. Koptyug[b)], N. J. Turro[b)] und A. M. Braun[a)].
[a)]Lehrstuhl für Umweltmeßtechnik, Universität Karlsruhe, 76128 Karlsruhe
[d)]Columbia University in the City of New York, Havemeyer Hall, New York, NY 10027 / USA

Ein neues FT-ESR - Verfahren zur Messung der T_1 - Relaxationszeiten nach der "inversion recovery"-Technik wird vorgestellt. Die Methode nutzt die für stabile Radikale vom TEMPO - Typ (2,2',6,6'-Tetra-methyl-piperidin-1-oxid) charakteristischen T_1-Relaxationszeiten in verschiedenen Mikro - Umgebungen zur Messung der inneren Diffusion dieser Systeme. Mizellen, DNA und Huminsäuren wurden als mikroheterogene Systeme von besonderem Interesse mit Hilfe dieser Methode untersucht und werden vergleichend nebeneinandergestellt.

Magnetisierung nach einem 180-Puls im Vergleich zu einer Mehrpuls - Sequenz



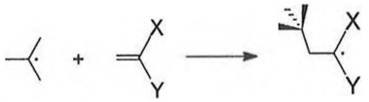
Die Methode beruht auf der gezielten und rechnerunterstützten Anwendung eines Mehrpulsverfahrens , bei dem die sonst eher als störend empfundenen Seitenbanden der FT-ESR-Pulse durch konstruktive Überlagerung zur Anregung eines breiteren Spektralbereiches genutzt werden können, als dies mit einzelnen Pulsen möglich ist.

Physikalische Chemie **130**

ESR Messung der Reaktionskinetik spinpolarisierter Radikale in Konkurrenz zur Relaxation

C. Blättler und H. Paul
Physikalisch-Chemisches Institut der Universität Zürich, CH-8057 Zürich

Schnelle Additionsreaktionen ($k_A > 10^6$ $M^{-1}s^{-1}$) von Radikalen an Olefine sind mit konventioneller kinetischer ESR-Spektroskopie schwierig zu bestimmen. Bei hohem Substratumsatz wird k_A häufig unterschätzt, weil die Additionsreaktion



X = CN, COOMe, Py, Ph, CHO Y = H, Me, Ph

nicht mehr streng einer Kinetik pseudo-erster Ordnung folgt. Aus Anpassungen numerisch integrierter modifizierter Bloch-Gleichungen an CIDEP-Zeitprofile nach pulsphotolytischer Radikalerzeugung lassen sich Geschwindigkeitskonstanten schneller Additionen in Konkurrenz zur Spinrelaxationsrate bestimmen, die meist in der Grössenordnung von 10^6 s^{-1} liegt. Die dabei erforderlichen hohen Olefinkonzentrationen vermeiden eine merkliche Substratverarmung. Obwohl vier Parameter simultan angepasst werden (k_A, erzeugte Radikalkonzentration, 2 Spinpolarisationen), lässt sich zeigen, dass k_A relativ unabhängig von den übrigen Parametern ist und deshalb genau bestimmt werden kann.
Durch Pulsphotolyse von Azo-t.Butan wurden t.Butylradikale erzeugt und deren Additionskinetik an einige Olefine vermessen. Die resultierenden Geschwindigkeitskonstanten, im Bereich zwischen $1x10^5$ $M^{-1}s^{-1}$ (Styrol) und $5x10^6$ $M^{-1}s^{-1}$ (Acrylnitril), verbessern die Korrelation zwischen k_A und den Elektronenaffinitäten der Olefine, die auf polare Effekte im Übergangszustand hinweist [1].

[1] K. Münger, H. Fischer, *Int. J. Chem. Kinet.* , **1985**, *17*, 809.

Physikalische Chemie **131**

Chemische Reaktion und Spinaustausch zwischen dem Ethylradikal und Sauerstoff in der Gasphase

H. Dilger*, E. Roduner*, M. Schwager*, I.D. Reid†, D. G. Fleming‡
*Physikalisch-Chemisches Institut der Universität Zürich, CH-8057 Zürich
†Paul Scherrer Institut, CH-5232 Villigen PSI
‡TRIUMF and Department of Chemistry, University of British Columbia, Vancouver, B.C. Canada, V6T 2A3

Präzise kinetische Parameter sind nötig für Modellrechnungen in der Atmosphärenchemie und bei Verbrennungsprozessen. Es besteht jedoch oft eine mangelnde Übereinstimmung zwischen gemessenen und theoretisch vorhergesagten Daten.

Als Modellsystem wurde die Addition von Ethylradikalen an molekularen Sauerstoff in der Gasphase untersucht. Um die Geschwindigkeitskonstante zu bestimmen, wurde die zeitdifferentielle μSR-Technik eingesetzt. Hierbei werden die Radikale durch Anlagerung von Myonium (einem leichten Wasserstoffisotop mit einem positiven Myon als Kern) an Doppelbindungen erzeugt. Das Myon selbst dient als Spinlabel.

$$CH_2MuC\dot{H}_2 + O_2(+M) \xrightarrow{k_1} CH_2MuCH_2O\dot{O}(+M) \qquad (1)$$

Die Messungen wurden bei einem Gesamtdruck von 1.5 bar und Temperaturen zwischen 295 K und 425 K durchgeführt.

Unsere Resultate können theoretische Berechnungen von Wagner et al.[1], die auf RRKM-Extrapolationen basieren, nicht bestätigen. Bei Experimenten mit Drücken von bis zu 60 bar wurde keine signifikante Druckabhängigkeit der Geschwindigkeitskonstanten festgestellt.

Die Geschwindigkeitskonstante für den Spinaustausch zwischen dem Radikal und dem paramagnetischen Sauerstoff konnte bei kleinen Magnetfeldern bestimmt werden.

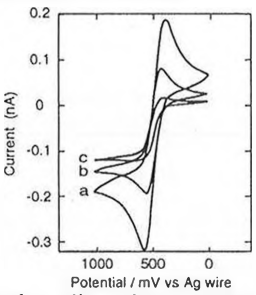
[1] A.F. Wagner et al., J. Phys. Chem. **94** (1990) 1853.

Physikalische Chemie **132**

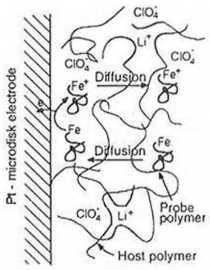
Electrochemical Measurements of Diffusion Coefficients of Redox-Labelled Poly(ether) Dissolved in Poly(ether) Electrolyte Melts

O. Haas*, Ch. Velasquez**, Z. Porat**, R.W. Murray**
* Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
** Kenan Laboratories of Chemistry, Univ. of N. Carolina, Chapel Hill NC 27514-3290, USA

We used ferrocene-labelled monomethyl poly(ethylene glycol) as an electrochemical diffusion probe in poly(ethylene glycol) melts in order to investigate diffusion properties of polyelectrolytes such as polyethers [1]. The diffusion coefficients of these probes were measured with microdisk electrodes using cyclic voltammetry and chronoamperometry. In addition, viscosity and conductivity measurements of the solvent polymer were made in order to investigate the ion transport properties of this technically interesting polyelectrolyte.



Typical cyclic voltammograms obtained from ferrocene-labelled poly (ethylene glycole) in poly(ethylene glycole)/$LiClO_4$ melt at a microdisk electrode (r=5µm).
a) 100 mV/sec, b) 20 mV/sec, c) 2 mV/sec



Electron transfer and diffusion process of a probe polymer in the polymeric electrolyte system (host polymer) at a microdisk electrode.

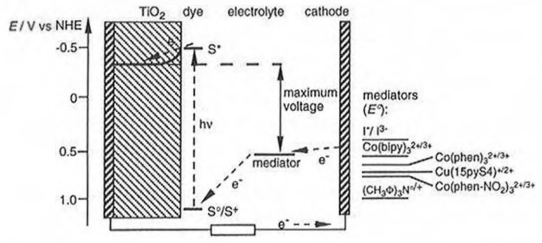
[1] M.L. Longmire, M. Watanabe, H. Zhang, T.T. Wooster, Royce W. Murray, Analytical Chemistry (1990), 62, 747.

Physical chemistry **133**

Redox mediators for electrochemical photovoltaic cells based on dye-sensitized TiO_2 electrodes

Pierre Bonhôte, Michael Grätzel, Marie Jirousek, Paul Liska, Nicholas Pappas, Nicolas Vlachopoulos, and Lorenz Walder.
Inst. de chimie physique II, EPFL, 1015 LAUSANNE, fax: 021/693.4111

A crucial step for the successful operation of dye-sensitized porous TiO_2 photovoltaïc cells is the electron transfer from the cathode to the photoanode through an electrolyte, by a suitable redox mediator. After electron injection from the excited dye S* into the TiO_2 conduction band, rapid reduction of the resulting S^+ by Red must take place to prevent recombination between S^+ and e^-_{CB}. E_{eq}(Ox/Red) should be as close as possible to $E_{eq}(S^+/S°)$, in order to generate the highest possible voltage. The couple must be reversible at the cathode, well soluble and diffusing to allow sufficient electronic transport at current densities of 20mA/cm^2. Ox and Red must be stable towards the solvent and the photoanode and exhibit low extinction coefficients in the absorption domain of the sensitizer.



The performances of several mediators will be compared toward the most efficient dye used: $RuL_2(SCN)_2$ (L=2,2'-bipyridine–4,4'-COOH). They include I^-/I_3^-, Co and Cu complexes as well as triphenylamines, with $E°$ ranging form 0.3 to 1.0 V. *Acknowledgement:* This work was supported by the CERS in cooperation with ASULAB S.A. (SMH).

Chimie phyisque **134**

The Surface Science Aspect of Laser Desorption Mass Spectrometry

Pierre Voumard, Renato Zenobi and Qiao Zhan
LPAS (bâtiment de chimie), Ecole Polytechnique Fédérale, 1015 Lausanne

Laser desorption methods, in particular in conjunction with postionization, are among the most sensitive mass spectrometric techniques available today. Lasers also allow access to gas-phase ions even for nonvolatile, high molecular weight, and themally labile samples [1]. However, the mechanism underlying the intact desorption of complex molecules is not fully understood.

We present measurements on a model system, aniline (C_6H_5-NH_2) adsorbed on quartz (SiO_2), that give insight into the mechanism of laser-induced thermal desorption from surfaces. These measurements are carried out under well-controlled conditions, i.e., submonolayer surface coverages, and in an ultra-high vacuum environment. We first determine the equilibrium desorption parameters at classical heating rates using temperature-programmed desorption. The experimental data can be simulated and are then extended to the regime of rapid laser heating. For aniline/quartz, we find a desorption peak at $T_{des} \approx 240$ K at low heating rates, which moves up to $T_{des} \approx 460$ K at heating rates typically encountered in laser desorption experiments (ca. 10^9 K/s). These results are then compared with the excitation of various degrees of freedom (kinetic energy, vibrational energy) of laser-desorbed molecules from the same system, measured by pump-probe and laser spectroscopic methods. Velocity distributions can be fitted with a Maxwell-Boltzmann distribution and are characterized by a temperature of $T_{kin} \approx 350$ K. Information on the internal energy of the desorbing molecules can be obtained from relative intensities of vibrational hot bands seen in the REMPI spectrum. A preliminary analysis of our data gives a vibrational temperature of about 300K for aniline laser-desorbed from a submonolayer coverage on quartz. The results thus seem to indicate that a non-equilibrium mechanism is operative. This is surprising, since the desorption process is still fairly slow (nanosecond timescale) compared to normal intramolecular vibrational redistribution processes (picosecond timescale).

1 R. Zenobi and R. N. Zare, in *Adv. Multiphoton. Spectr. Proc.* 7, S. H. Lin (Ed.), 1991, p. 1.

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Physikalische Chemie **135**

AFM and XRD Investigation of Crystalline Vapor-Deposited C_{60} Films

F. Atamny and A. Baiker
Laboratorium für Technische Chemie, ETH-Zentrum, 8092-Zürich

H.-J. Muhr and R. Nesper
Laboratorium für Anorganische Chemie, ETH-Zentrum, 8092-Zürich

The nucleation, growth and structure of C_{60} films deposited on several substrates such as metals [1], NaCl and mica [2] have been investigated by means of various methods. The thickness of the films varied between a few monolayers and 100 nm. In other studies [3], C_{60} single crystals in the millimeter size range were investigated using X-ray diffraction and microscopic techniques.

Here we focused on the structural characterization of C_{60} films deposited on quartz substrates by sublimation under high vacuum conditions at 400-500^{0}C using a Knudsen cell. The thickness of the films varied between 0.1 µm and 100 µm. AFM showed that C_{60} single crystals in the micrometer size range grew under these conditions. The crystals adopted different shapes. Some crystals exhibited morphologies comparable to those calculated by Marks [4]. AFM revealed that also other shapes including e.g. some with hexagonal symmetry were coexisting. The studies indicate that the degree of purity of the C_{60} materials has a significant influence on the crystal structure. XRD is used as an intergral method for the crystallographic characterization. The AFM results are discussed in the frame of the XRD-analysis.

[1] E.I. Allman, R.J. Colton; in "Atomic and Nanometer-Scale Modification of Materials: Fundamentals and Applications", Ed. P. Avouris, Kluwer Acad. Publ. 1993.
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[3] M. Haluska, H. Kunzmany, M. Vybornov, P. Rogl, P. Fejdi, Appl. Phys. 1993, A56, 161.
[4] L.D. Marks, J. Crystal Growth 1983, 61, 556.

Physikalische Chemie **136**

Surface Morphology and Electrical Properties of Copper Thin Films prepared by MOCVD

M. Becht and K.-H. Dahmen
Laboratorium für Anorganische Chemie, ETH-Zentrum, 8092 Zürich

F. Atamny and A. Baiker
Laboratorium für Technische Chemie, ETH-Zentrum, 8092 Zürich

Thin copper films were grown in a vertical MOCVD (Metal-Organic Chemical Vapor Deposition) reactor for using bis(2,2,6,6-tetramethyl-3,5-heptandionato)copper(II), $Cu(thd)_2$, as precursor. Deposition was carried out in a pure hydrogen atmosphere (pressure: 20mbar) at a substrate temperature of 450^{0}C.

An unusual dependence of the film thickness with deposition time was observed. Rapid growth occurred in the first minutes and resulted in badly conducting films (thickness below 100nm). Good electrical resistivities were obtained above 200nm. The surface morphology of films with different thicknesses was investigated by AFM, STM and SEM. The three-dimensional character of the islands has been investigated. Small grains grew in the beginning and the electrical proporties were governed by the highly Ohmic bridges between the individual grains. The grain size and surface roughness increased with increasing film thickness.

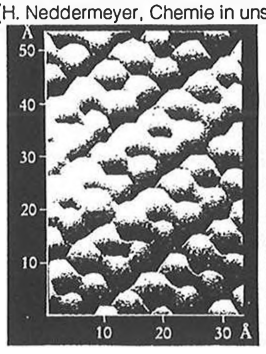
Physikalische Chemie **137**

The Interpretation of STM Images Using Tight Binding Calculations - Electronic Structure of the Si(100) Surface

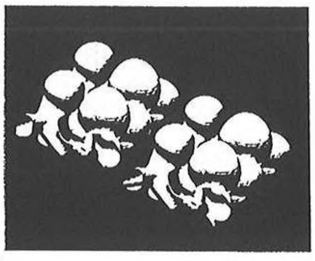
T. Fässler and R. Nesper
Laboratorium für Anorganische Chemie, ETH Zürich, 8092 Zürich

Results of STM experiments are coupled to the electronic structure of surfaces and may help therefore to develop chemical concepts for an understanding of the reactivity and stability of surfaces. Albeit the large potential of STM investigations the resulting pictures and surface models are often not uniquely interpretable and in many cases it stays an open question how electrons are distributed and localized on a surface.
Density of states (DOS), local density of states (LDOS) analysis have been applied in a model study of the reconstruction of the Si(100) surface. Three different surface models - the unreconstructed surface, symmetric and asymmetric pairing of surface atoms (*Si(100)- (2x1)*) - are investigated. The advantage of ***computer graphics for the visualization of tight binding calculation*** results is emphasized. Two- and three-dimensional images of the electron density, as well as partial electron densities are shown. Partial electron densities are used to analyze constant current mode STM images, which were obtained applying bias voltages of different sign. They show full agreement with the STM experiments (H. Neddermeyer, Chemie in unserer Zeit 26(1) 1992 18).

Experiment



Calculation

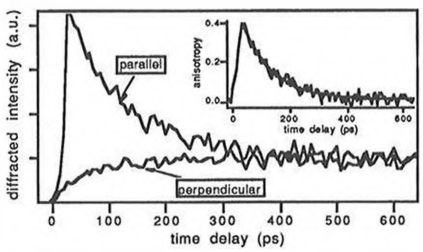


Physikalische Chemie **138**

Rotational relaxation time of ruthenium(II) - bis (2,2'-bipyridine) (2,2'-biquinoleine) measured by transient grating holography

Arthur Henseler, Eric Vauthey
Institut für physikalische Chemie, Universität Freiburg, CH - 1700 Freiburg

Time-resolved transient grating holography is a powerful method to investigate both photophysical and photochemical dynamic processes . By using appropriate polarizations of the pump respectively probe pulses the rotational relaxation time of molecules in condensed phases can be determined [1].



We report the ground state rotational dynamics of the title compound in different polar, protic and non-protic solvents [2]. Upon excitation at 532 nm the ^{1}MLCT-state undergoes intersystem crossing within less than 15 ps to the triplet, wich decays with a life time of 280 ns. Thus, the rotational dynamics in the ground state can be determined by measuring the dichroism of the ground state recovery, without any interference produced by excited states. As expected from Stokes-Einstein-Debye hydrodynamic theory, the rotational relaxation time τ is linearly proportional to the solvent viscosity. However, the intrinsic molecular volume is overestimated by a factor of 1.5. This is explained by the presence of solvent molecules intercalated between the Ru-ligands and stabilised by electrostatic interaction with the charge of the metal atom. These solvent molecules follow the rotation of the bulk complex, thus slowing down the rotational time

To our knowledge, this is the first time the ground state rotational relaxation time of a metal complex has been measured, the molecules considered so far being restricted essentially to oblate and prolate dye species.

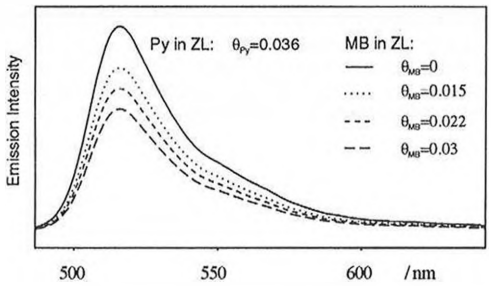
[1] Eric Vauthey, *Chem. Phys. Letters*, **1993**, *216*, 530
[2] to be published

Physikalische Chemie **139**

Dye Molecules in Zeolites as Artificial Antenna System

F.Binder, G.Calzaferri, and N.Gfeller
Institut für Anorganische und Physikalische Chemie, Universität Bern, Freiestrasse 3, 3000 Bern 9

When cationic dye molecules are exchanged into zeolite L [1], they are arranged in the parallel channels and are so close together that energy transfer can occur. The restricted geometry of the zeolite channels excludes aggregation and self-quenching, even at very high dye concentrations. Depending on the choice of chromophores, light of different spectral regions is absorbed by this antenna system. We have exchanged the dyes pyronine, oxonine and thionine as monomers into the zeolite.
To show that excitation energy is transferred to the outer surface of the zeolite, an experiment has been performed with pyronine in zeolite L and methylene blue aggregates on its surface. Since methylene blue aggregates are not able to emit light, they only quench the emission of pyronine. This is shown in the figure below for different amounts of added methylene blue.



The formation of aggregates on the outer surface of the zeolite can be avoided when it is modified with trimethylchlorosilane. Appropriate dyes can still be exchanged into the so modified zeolites.

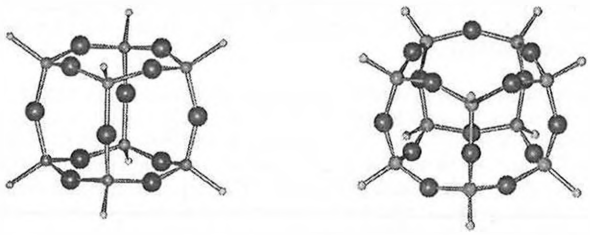
1) G.Calzaferri and N.Gfeller, J.Phys.Chem. 96 (1992) 3428

Physikalische Chemie **140**

Correlation of the Vibrational Structure of $H_8Si_8O_{12}$ and $H_{10}Si_{10}O_{15}$

M. Bärtsch, P. Bornhauser, G. Calzaferri, and R. Imhof
Institut für anorganische, analytische und physikalische Chemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9

The vibrational structure of the highly symmetrical octahydridosilasesquioxane $H_8Si_8O_{12}$ has been investigated in detail, and we succeed in obtaining a modified general valence force field in terms of internal force constants, based on extensive IR and FT-Raman data as well as on a normal coordinate analysis of $H_8Si_8O_{12}$ and $D_8Si_8O_{12}$ [1].



We have now measured the IR and FT-Raman spectra of $H_{10}Si_{10}O_{15}$, the crystal structure of which has lately been determined by X-ray crystallographic analysis [2]. A normal coordinate analysis of $H_{10}Si_{10}O_{15}$ has been performed with the harmonic force field of $H_8Si_8O_{12}$. The calculated frequencies, relative infrared intensities, and the use of group theoretical considerations resulted in quantitative correlation of all IR and Raman active fundamentals of the two molecules.

The results lead to the main conclusion that the harmonic force field of $H_8Si_8O_{12}$ can be used for quantitatively investigating the vibrational structure of the higher members of the oligomeric $(HSiO_{3/2})_{2n}$ molecules.

[1] M. Bärtsch, P. Bornhauser, G. Calzaferri, and R. Imhof, *J. Phys. Chem.* **1994**, *98*, 2817.
[2] H.-B. Bürgi, H. Bürgy, G. Calzaferri, K.W. Törnroos, *Inorg. Chem.* **1993**, *32*, 4914.

Physikalische Chemie **141**

Electrochemical formation of a conductive polymer in absence of supporting electrolyte. A copolymer of o-aminosulfonic acid and aniline.

C. Barbero, O. Haas and R. Kötz
Paul Scherrer Institute, Electrochemistry Section, CH-5232 Villigen PSI

An electroactive polymer (p(oASA-co-Ani)) can be obtained by anodic copolymerization of o-aminosulfonic acid and aniline in absence of supporting electrolyte. Good polymerization rates are observed for feed ratios (aniline/o-aminosulfonic) as low as 1:125. The presence of sulfonated units in the polymer was corroborated by the detection of sulfur by chemical analysis (Lassaignes's test) and XPS. The reflectance FTIR spectrum of films deposited onto Pt present similar bands to that of polyaniline. Additional bands are observed at 1000, 1080 and 620 cm^{-1} . The former can be assigned to the asymmetric and symmetric stretching modes of the SO_3^- group and the later to the C-S stretching. In addition a new band at 820 cm^{-1} corresponding to a 1,2,4 trisubstituted aromatic ring is also observed further confirming the presence of sulfonated rings units in the polymer.

Due to the presence of sulfonate groups in the matrix, the polymer is soluble in basic solution. The solubility is strongly affected by the polymerization conditions. The UV-visible spectra of a p(oASA-co-Ani) solution in 0.1 M NH_4OH/H_2O presents bands at 320 and 560 nm. The spectra is similar to that of chemically sulfonated polyaniline (SPAN), but both maxima are shifted towards lower wavelength.

The ion exchange of the modified electrode was studied using Probe Beam Deflection (PBD). The dominant process of charge compensation in aqueous solution is proton exchange. The leucoemeraldine form of p(oASA-co-Ani) contains negatively charged groups ($-SO_3^-$), compensated by protons. Positive charges are formed in the polymer backbone during oxidation, that compensate the $-SO_3^-$ groups, inducing the expulsion of the protons form the polymer. During the second oxidation process, the fully oxidized state deprotonates liberating protons that are expelled.

Physikalische Chemie **142**

Alkaline Secondary Zn/O_2 Battery using Pasted Zn-Electrodes

S. Müller and F. Holzer
Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

Because of their high theoretical specific energy (1200 Wh/kg), the low cost, low toxicity and compatibility with aqueous electrolytes electrically rechargeable Zn/O_2 batteries are very attractive candidates for electric vehicles and portable electric-powered equipment.

A fundamental problem of the Zn/air battery is its insufficient durability during cycling (degradation of the bifunctional catalyst at the oxygen electrode, dendrites and shape change at the zinc electrode).

In our previous work we demonstrated promising cycle life behaviour of $La_{0.6}Ca_{0.4}CoO_3$ (perovskite) catalyzed bifunctional electrodes in 45 % KOH [1]. In the next step we constructed 2.5 Ah Zn/O_2 batteries with pasted Zn/ZnO anodes (25 cm^2) [2] sandwiched between two perovskite catalyzed bifunctional cathodes.

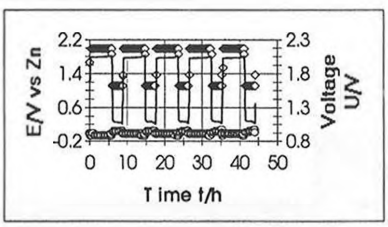


Fig. 1 Measured potentials (E vs. Zn) of the Zn (O) and O_2 electrode (◊) and voltage (V) of the battery (—) for the first five cycles. Cycle life performance was measured at C/6 (charge) and C/3 (discharge).

The cycle life performance of the battery, its power at different currents and the change in the physical and electrochemical properties of each electrode during cycling will be presented.

1. S. Müller, K.A. Striebel and O. Haas, Electrochim. Acta, accepted for publication.
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Physikalische Chemie **143**

Surface Energies and Surface Reconstruction of Ion-Containing Polymers - A Dynamic Contact Angle Study

D. Weber, H. P. Brack*
Organic Interfacial Science Laboratory, EMPA, CH-8600 Duebendorf
*Present Address: Laboratory for Energy and Process Technology, Paul Scherrer Institute, CH-5232 Villigen PSI

The introduction of a small amount of ionic functional groups into a relatively nonpolar polymer has a profound effect on its structure and properties[1]. Systematic variations in properties with ionic content and counterion identity have been found in many cases. In the present work the total surface energy, as well as its polar and dispersive components, were determined from contact angle measurements for two ion-containing copolymers, copolymers of ethylene/methacrylic acid and ethylene/acrylic acid. The surface energy and its components were found to vary in a systematic manner with ion content and cation identity for these ion-containing copolymers.

Non-polar polymers, such as polyolefins, that have been surface oxidized to introduce polar surface groups, as well as bulk ion-containing polymers, are known to undergo surface reconstruction processes in which polar surface groups migrate to a subsurface region. Surface reconstruction can result from thermal treatment and can lead to a degradation of wetting and adhesive properties. The effect of ion-exchange on the surface reconstruction process in ion-containing polymers was examined in the present work. It was found that the ion-exchanged samples underwent surface reconstruction more slowly and to a lesser extent than the unexchanged hydrogen-form polymers. This apparent inhibition of surface reconstruction upon ion-exchange may be related to the well-known regions of restricted mobility resulting from strong Coulombic, polar, and dipolar forces in these materials.

[1] *Ionic Polymers,* Holliday, L., Ed.: Applied Science: London, 1975.

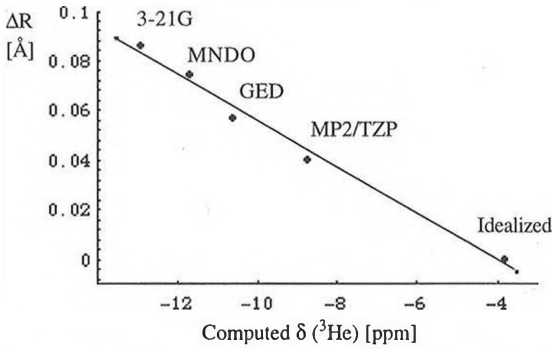
Computerunterstützte Chemie **144**

Helium And Lithium NMR Chemical Shifts of Endohedral Fullerene Compounds - An Ab Initio Study.

M. Bühl and W. Thiel
Organisch-Chemisches Institut, Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich

The ab initio (GIAO-SCF) computed ^{3}He NMR chemical shifts of He@C_{60} and He@C_{70}, -8.7 [tzp(He),dz(C)//MP2/TZP level] and -24.0 ppm [//3-21G], respectively, are in reasonable accord with the recent experimental values, -6.3 and -28.8 ppm, respectively [1]. For the isostructural Li^+@C_{60} and Li^+@C_{70}, $\delta(^7Li)$ of -14.5 and -29.7, respectively, is predicted. For $\delta(^3He)$ of the highly aromatic He@C_{60}^{6-}, a substantial upfield shift is computed, -58.3 ppm. These data support the ring current models which have been proposed for the neutral fullerenes and for C_{60}^{6-} [2].

The computed He chemical shift of He@C_{60} is sensitive to the degree of CC bond alternation, ΔR. The trend toward bond equalization in the 3-21G, the MNDO, the GED (gas-phase electron diffraction), and the MP2/TZP geometries is paralleled by a decrease of the calculated He shielding:



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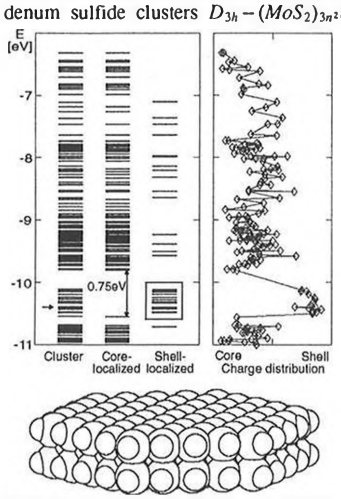
[2] A. Pasquerello, M. Schlüter, R. C. Haddon, *Phys. Rev. A* **1993**, *47*, 1783

Computerunterstützte Chemie **145**

Size Quantization and Surface States of Molybdenum Sulfide Clusters

Martin Brändle, Gion Calzaferri and Martin Lanz
Institute for Inorganic and Physical Chemistry, University of Berne, Freiestrasse 3, 3000 Berne 9, Switzerland

The discussion of *surface states* has continued since the memorable 1932 paper of Tamm in which he created this expression [1]. This term now slowly becomes material from the chemists point of view, which means that it can be assigned to specific atoms, molecules, coordination numbers, oxidation states and connectivities.
The so-called *Quantum-Size Effect* describes the size dependence of semiconductor particles' behaviour. It has come into awareness due to a theoretical work of L.E. Brus in 1983 and it has since contributed to the development of nanotechnology [2].
We have carried out quantum chemical calculations of the EHMO type on molybdenum sulfide clusters $D_{3h}-(MoS_2)_{3n^2}S_2(H_2S)_{6n}, n = 1, 2, \ldots$ To our initial surprise, these particles do not show any size quantization. Different attempts to analyse this result have shown that the one-electron states can be divided into those that have to be assigned to the inside of the cluster, the core, and those that lie on the surface atoms, the shell. The core shows the expected size quantization. The calculated band gap of the core decreases from 1.42eV for n=2 to 0.9eV for n=3 and to 0.75eV for n=4. The shell states fill up the band gap, which creates the misleading impression of a "metallic" density-of-states. The surface states correspond exactly to the extremity layer of Mo atoms and can be fully described by their d_{z^2}, d_{xy} and $d_{x^2-y^2}$ orbitals. In the picture we illustrate the calculation results on D_{3h}-$Mo_{48}S_{122}H_{48}$.



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[2] L.E. Brus, J. Chem. Phys., **79** (1983), 5566.

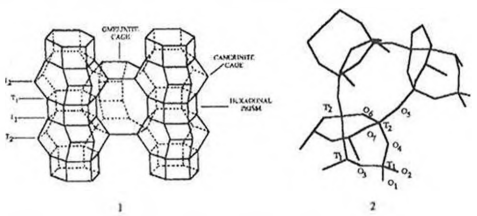
Computational Chemistry **146**

First Principles Molecular Dynamics Calculation of the Structure and Acidity of a Bulk Zeolite

L. Campana[a,b], A. Selloni[a], J. Weber[a], A. Pasquarello[b], I. Papai[c], and A. Goursot[c].

[a]Department of Physical Chemistry, University of Geneva,
30 quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland.
[b]Institute IRRMA, Swiss Federal Institute of Technology,
PHB-Ecublens, CH-1015 Lausanne, Switzerland.
[c]National School of Chemistry
URA 418, 8 rue de l'Ecole Normale, F-34053 Montpellier, France.

Local density functional theory within the framework of the Car-Parrinello method [1] has been used to study the structural parameters and the energetics of the zeolite offretite, when a Si^{4+} ion is substituted by (Al^{3+},H^+). The calculations have been performed for a bulk system (1) made of periodically repeated unit cell with 54 atoms (2) and a proton.



In agreement with previous cluster calculations, we conclude that the sites with the lowest (Al,H)/Si substitution energies are also those with the largest proton affinity. In addition, a correlation previously reported [2] between acidity and Al-O-Si bond angles is confirmed.

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[2] A. Redondo and P.J Hay, J. Phys. Chem. 97 (1993) 11754.

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Chimie informatique

Excited State Properties of d^0 Tetroxo Ions - a Density Functional Study

A. C. Stückl [a], C. A. Daul [a], and H. U. Güdel [b]
[a] Institut de Chimie Inorganique et Analytique, Université de Fribourg, CH-1700 Fribourg
[b] Institut für Anorganische und Physikalische Chemie, Universität Bern, CH-3000 Bern

Although extensive spectroscopic investigations were performed to assign the broad and partially structured bands of the optical spectra of d^0 tetroxo ions to their transitions at low energies [1], the assignment of overlapping bands or weak features remained incomplete.

Therefore several calculations by different methods have been carried out to study the low lying electronic states of these compounds, MnO_4^- being hereby of special interest [2]. Most of these calculations are based on a tetrahedral symmetry of the complex molecules. But, as recent results [3] have shown, the Jahn-Teller instability has to be taken into account when the excited state properties of these ions are discussed.

A chemical variation series of d^0 tetroxo ions is studied by density functional calculations in order to investigate the excited state properties [4]. The comparison between experimental and calculated data, concerning transition energies, vibrational energies and geometric distortions in the excited state, is discussed.

[1] S.L. Holt, C.J. Ballhausen, *Theor. Chim. Acta* **1967**, *7*, 313
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[3] J.H. van der Waals, J. van Tol, *Pure & Appl. Chem.* **1993**, *65*, 1611
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Computational chemistry

Modeling of the Coordination Sphere of Hydrated Lanthanide Ions with DFT Methods.

Olivier Schafer, Claude Daul
Institut de Chimie Inorganique et Analytique, Université de Fribourg,
CH-1700 Fribourg, Switzerland

Hydrated Lanthanides(III) ions $Ln^{3+}(H_2O)_x$ (x=8,9) with $Ln^{3+} = Gd^{3+}$, Sm^{3+} and Dy^{3+} have been studied using density functional theory (DFT) and the results are compared with similar *ab-initio* results [1]. The calculations are related to experimental results in order to elucidate the hydratation behaviour of lanthanide(III) ions. It has been established that the coordination number of the Lanthanides changes in the middle of the serie (Nd^{3+}, Sm^{3+}, Eu^{3+}) [2].
The energies between different conformations (*i.e.*, cube, square antiprism and dodecahedron) of the first solvation sphere are compared. The binding energy as a function of ion-water distance is presented. The charge polarization of the coordinated water molecules at different geometries is described and repercussion for molecular dynamics (MD) simulations of such systems is discussed.

[1] S. Hengrasmee, M.M. Probst, *Z. Naturforsch.* **1991**, *46a*, 117.
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Chimie informatique

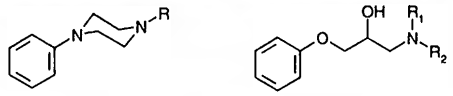
Benefits of the MLP, an empirical molecular field, in 3D-QSAR

P. Gaillard, P.-A. Carrupt and B. Testa
Institut de Chimie Thérapeutique, Ecole de Pharmacie, CH-1015 Lausanne-Dorigny

The Molecular Lipophilicity Potential (MLP) is shown to be sensitive to intramolecular and intermolecular effects [1,2]. The MLP, based on atomic contributions to logP and a distance function, is calculated as follows:

$$MLP_k = \sum_{i=1}^{N_{at}} f_i \cdot e^{-d_{ik}/2}$$

The lipophilic molecular field used as a third field in CoMFA is shown to improve 3D-QSAR models on the binding of two classes of ligands to the 5-HT_{1A} receptor, i.e. 101 arylpiperazines and 30 aryloxypropanolamines.



CoMFA models were obtained with the three molecular fields (steric, electrostastic and lipophilic). The analyses were conducted in each structure class and with the two classes mixed which improved the models. A new polar region (due to the lipophilic field) enhances the affinity and appears when combining the two classes. The affinity of 16 molecules was successfully predicted by the CoMFA model generated with the lipophilic field alone.
While the lipophilic field is a useful and quantitative tool in 3D-QSAR, its interpretation in terms of intermolecular interactions remains difficult.

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[2] P. Gaillard, P.-A. Carrupt and B. Testa, *Bioorg. & Med. Chem. Let.* **1994**, 4, 737-742

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Computerunterstützte Chemie

Calculation of Electronic CT Transition Oscillator Strength

G. Calzaferri and R. Rytz
Inst. for Inorg. and Phys. Chem., Univ. of Berne, Freiestr. 3, CH-3012 Berne

We have developed a FORTRAN 77 program called EDiT (Electronic Dipole iduced Transitions) which allows to calculate oscillator strengths of molecules and complexes consisting of up to 999 atoms. *All* transition-matrix elements are considered what makes our treatment exact within the EHMO theory, an essential demand to describe CT transitions! Calculations on molecules such as formaldehyde, bipyridyl, p-N,N'-Dimethylaminobenzonitril (DMABN) as the classical TICT molecule [1], MnO_4^- and others show that the first electronic transitions can be well described by this procedure and that the information obtained is useful despite of the well known restrictions of one electron procedures. We give some details for the $Ru(bipy)_3^{2+}$ complex.

Band	Range in nm	Osc. Strength $f_{x,y}$	f_z	Type ref. [2] / this work
1	448 – 433	0.18	0.0	MLCT / MLCT
2	323 – 314	0.56	1.06	LC / LC
3	275 – 256	0.63	0.0	MLCT / LC
4	> 232	s	s	

Its absorption spectrum shows four maxima at 450, 285, 240 and 185 nm. The calculated transition energies, polarisations and oscillator strengths are shown in the table, where we also compare our assignments with those reported in literature [2]. It was possible — based on a comparison of the relative *f*-values of the experimental and the computed absorption bands — to assign them to the different transition types (MLCT, LMCT, MC and LC). *Band 4* lies too high in energy to be fully treated in terms of a frontier orbital theory. However, a large LMCT contribution is predicted. We found that the band at 240 nm — described as MLCT in the literature [2] — has to be attributed to a LC ($\pi^* \leftarrow \pi$) transition.

[1] S. Bergamasco, G. Calzaferri and K. Hädener; J. Photochem. Photobiol. A: Chem. 66, 327 (1992)
[2] V. Balzani, F. Bolletta, M. T. Gandolfi and M. Maestri; Top. Curr. Chem. 75, 1 (1978)

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Computerunterstützte Chemie **151**

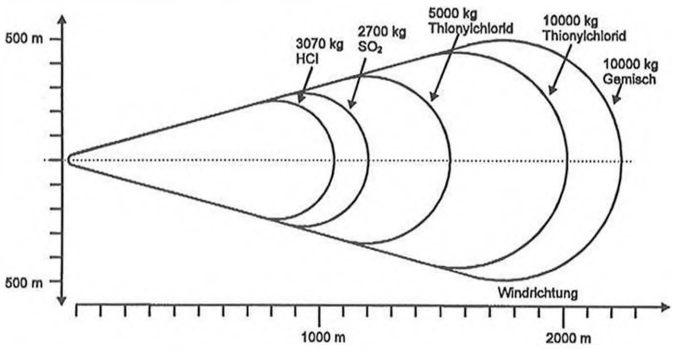
Die grossräumige Wirkung von toxischen Gasgemischen

P. Bützer, I. Silvestri
Bützer+Silvestri, Trogenerstr.13, CH-9450 Altstätten

Die Wirkung einer einzelnen, reinen, gasförmigen Substanz auf den Menschen lässt sich mit einer Simulation mit dem Modell für Effekte mit toxischen Gasen (MET)[1] abschätzen. Bei vielen Störfällen treten Gasgemische aus, die mit einer Erweiterung des mathematischen Modells erfasst werden können.
In einer Studie wurde das Ausbreitungsverhalten von 10'000 kg Thionylchlorid, welches sich zu 50 % mit Wasser zersetzt hatte, untersucht:

$$SOCl_2 + H_2O \rightarrow SO_2 + 2\,HCl$$

Die Auswirkungen, die zu 10 % Reizungen bei ungeschützten Personen im Freien führen, zeigen sich wie folgt:



Die Resultate lassen den Schluss zu, dass einzelne Komponenten in Reingasmodellen für Gemische die Gefährung unterschätzen.

[1] P. Bützer, H. Naef, Modell für Effekte mit toxischen Gasen (MET), *Swiss Chem.* 14 (1992) 7-20

Computerunterstützte Chemie **152**

Cyclic Voltammetry Equipment Tuning - CV Data Handling under WINDOWS

Beat Flückiger, Lorenz Walder
Institut für Organische Chemie, Universität Bern, CH-3012 Bern

We have build a digital data acquisition system for cyclic voltammetry in the range of 0.02 to 500 V/s and have developed instrument control and CV data handling programs. The hardware is based on a PC and a 12-bit 166 kcs A/D-converter (DAP 1200/4) in combination with any analogue, but high quality potentiostat/programmer such as PAR 173/175 or AMEL 553/568. Both channels, current and potential, are simultaneously A/D converted and x-y represented on the screen.
The programs, written in TURBO PASCAL and in VISUAL BASIC, include such options as:

- single and multiple scan acquisition and representation
- continuous scan acquisition and representation (polymer electrodes)
- assisted analysis of peak currents, peak potential and charge
- filtering, zoom
- CV data and experimental conditions storing
- overlaid and '3-dim.'-representations of stored cyclic voltammogramms
- direct export of such representations into other WINDOWS programs (e.g. Word, Corel Draw).

Computerunterstützte Chemie **153**

Die Elektronenlokalisierung in intermetallischen Aluminiden

Ulrich Häußermann, Steffen Wengert, Reinhard Nesper
Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

Die Elektronen-Lokalisierungs-Funktion (ELF) hat sich als nützliches Werkzeug für die Interpretation der chemischen Bindung entwickelt [1]. Die ursprünglich von Becke und Edgecombe [2] abgeleitete Funktion ist ein Maß für die Wahrscheinlichkeit ein Elektron gleichen Spins in der Umgebung eines anderen Elektrons zu finden. ELF ist so normiert, daß ihre dimensionslosen Werte zwischen Null und Eins liegen. Große Werte entsprechen hoher Lokalisierung und bedeuten, daß sich in der Umgebung eines Elektrons am Ort (x,y,z) mit beliebigen Spin kein anderes Elektron mit gleichem Spin befindet. Eine solche Situation kann auch dahingehend gedeutet werden, daß im Bereich um (x,y,z) ein Elektronenpaar mit α,β Spin lokalisiert ist. Tatsächlich findet man in Bindungen, einsamen Elektronenpaaren und Elektronenschalen die hohen ELF Werte.
Besonders für kristalline Stoffe ist ELF sehr attraktiv [3], da sie keine wellenvektorabhängige Größe darstellt und wie die Elektronendichte nur eine Funktion von den drei Ortskoordinaten (x,y,z) ist.
ELF wurde zur Analyse der Bindungsverhältnisse in aluminiumhaltigen intermetallischen Phasen und Zintl-Phasen verwendet. Aluminium ist in diesen Verbindungen an vielen Varianten der chemischen Bindung beteiligt und ELF unterscheidet deutlich zwischen metallischer Bindung, kovalenter Mehrzentrenbindung, sowie homo- und heteronuklearer Einfachbindung.

[1] A. Savin, A. D. Becke, J. Flad, R. Nesper, H. Preuß H. G. von Schnering, *Angew. Chem.* **1991**, 103, 421.
[2] A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, 92, 5397.
[3] A. Savin, O. Jepsen, J. Flad, O. K. Andersen, H. Preuß H. G. von Schnering, *Angew. Chem.* **1992**, 104, 186.

Computerunterstützte Chemie **154**

Eindeutige Wirkungsbereiche in Kristallstrukturen intermetallischer Aluminide

Ulrich Häußermann, Steffen Wengert, Reinhard Nesper
Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

Die Aufteilung des Raumes einer Kristallstruktur in sogenannte Wirkungsbereiche ihrer Bausteine (Atome, Ionen oder Moleküle) [1] ist ein nützliches Hilfsmittel für Verständnis und Klassifizierung von Strukturen. Die Raumteilung auf der Basis quantenmechanischer Größen hat gegenüber geometrischen und empirischen Raumteilungsmethoden den Vorteil, daß sie eindeutig definierte inkrementelle Größen liefern.
Die Analyse der Elektronendichte $\rho(x,y,z)$ und des Gradienten $\nabla\rho(x,y,x)$ nach Bader [2] führt zu geschlossenen Polyedern um Atomkerne, die den Raum der Elementarzelle lückenlos füllen und deshalb wohl die beste Definition von atomaren Wirkungsbereichen darstellen. Die Anwendung dieses Konzepts auf die von Becke und Edgecombe eingeführten Elektronen-Lokalisierungs-Funktion [3] führt ebenfalls zu einer eindeutigen Zerlegung des dreidimensionalen Raums. Die resultierenden Fragmente kann man als Wirkungsbereiche von Elektronen und Atomrümpfen bezeichnen. Beispiele für Wirkungsbereiche von Valenzelektronen sind Raumbereiche von Bindungselektronen oder einsamen Elektronenpaaren.
Neben dem Volumen eines Wirkungsbereichs kann hier auch die von den Polyedern jeweils eingeschlossene Elektronenzahl bestimmt werden. Mit dieser Definition von atomaren und elektronischen Wirkungsbereichen können interessante Relationen zwischen chemischer Bindung, Volumen und Elektronenzahl dieser Wirkungsbereichen bzw. deren Änderung bei Verbindungsbildung eindeutig quantifiziert werden, was am Beispiel intermetallischer Aluminide und Zintl-Phasen gezeigt wird.

[1] P. Niggli, *Z. Kristallogr.* **1927**, 65, 391; P. Niggli, *Z. Kristallogr.* **1928**, 68, 404.
[2] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, **1990**.
[3] A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.*, **1990**, 92, 5397.

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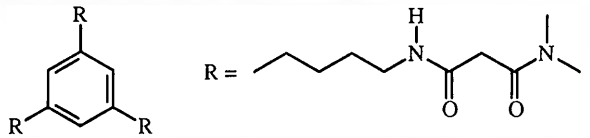
Computerunterstützte Chemie

Application of Genetic Algorithms in Molecular Modeling

T. Brodmeier, E. Pretsch

Department of Organic Chemistry, Swiss Federal Institute of Technology, CH - 8092 Zürich

A basic problem of molecular mechanics calculations is that the energy minimization has to be done on a complex hyper surface with many local minima. Therefore optimized structures can heavily depend on the chosen starting geometries. There is an inherent danger that the chemist finds the solutions which he had implicitly in his mind when he started the optimization.
Genetic algorithms (GAs), first described in 1975 by John H. Holland, are a new kind of optimization technique[1]. Fundamentally they can be seen as "intelligent" stochastic methods, designed in analogy to Darwin's evolution theory to perform the optimization.
In the present implementation[2] GAs are used to automatically find relevant starting points for a molecular mechanics optimization. For this reason only the torsion angles are encoded, the bond angles and bond lengths are kept constant. A population of different conformers is evolved using classic genetic operators like cross-over and mutation. The best conformers of the final population are then minimized using standard molecular mechanics techniques to adjust the bond lenghts and angles.



The application of the technique to model ionophor-cation complexes will be presented.

[1] J. Holland, *Adaptation in Natural and Artificial Systems*, Ann Arbor, University of Michigan Press, 1975
[2] T. Brodmeier, E. Pretsch, *J. Comput. Chem.* 1994, in print.

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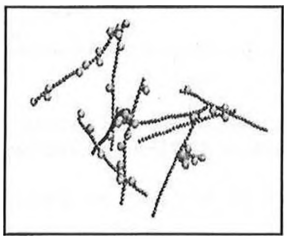
Chimie informatique

Computer simulation of bridging flocculation

S. Stoll and J. Buffle , Université de Genève,
Département de Chimie analytique, minérale et appliquée,
CH-1211 Genève 4.

In lakes, rivers and oceans a large fraction of submicron particles is bound to organic macromolecules. In cases where the size of the macromolecules is the same or larger then that of the colloids, bridging flocculation occurs leading to the formation of large aggregates. In spite of the importance of this situation in natural waters, little work has been done so far in simulating such systems. Using respectively a two and a three-dimensional model, we have simulated bridging flocculation between small colloids and large polymer chains to study the formation kinetics and the structural characteristics of aggregates under different physico-chemical conditions. Numerical data are presented to study the influence of (i) the reactivity of small aggregating particles with large polymer chains, (ii) the relative polymer/particle concentration ratio and (iii) the conformation of the chains on the evolution of aggregate size distribution. Three distinct successive modes of cluster growth are displayed. Although microcolloids react rapidly with polymers, the formation of large aggregates is slow, depending on the configurational properties of the polymer chains and on the concentration ratio of particles and chains. A typical three-dimensional structure using stiff polymer chains (10) and spherical particles (40) is presented below.



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Analytical chemistry

System peaks and retention mechanism in ion chromatography

G.Fóti, P.Hajós, G.Révész and E.sz.Kováts
Laboratoire de chimie technique, Swiss Federal Institute of Technology
CH–1015 Lausanne

Injection of a component into an ion chromatographic system perturbs the equilibrium in the column. The concentration perturbation results in one or more system peaks depending on the number of components of the eluent. The general retention equation given in ref [1] has been applied to a relatively simple system, where the eluent is a mixture of two strong electrolytes of unit charge and the stationary phase is a strong ion exchanger. The resulting equation predicts in such a system two system peaks, an early and a late system peak. Retention volumes of system peaks, of labelled eluent driving ions as well as of deuterium oxide have been related to the intereluent selectivity coefficient, to the column capacity and to the holdup volume of the column [2].

In order to prove the validity of the model a separation system fulfilling the limiting conditions of the model was taken. The binary eluent was a mixture of ethane and propane sulfonates as driving ions and analytes were strong electrolytes. The ion exchanger was a silicon dioxide preparation surface treated with a mixture of (3,3-dimethylbutyl)dimethyl-(dimethylamino)silane and [5-(dimethylamino)-3,3-dimethylpentyl]-dimethyl(dimethylamino)silane followed by quaternization of the exposed dimethylamino groups with methyl bromide. The resulting dense graft had a surface concentration of Γ_Q=0.62 μmol m^{-2} of quaternary ammonium exchange sites of unit charge. Retention volumes of water, deuterium oxide, labelled driving ions and some analytes of unit charge have been determined as a function of composition and concentration of the eluent. The resulting data base could be interpreted with the aid of the model.

[1] F. Riedo and E. sz. Kováts, *J. Chromatogr.*, **1982**, *239*, 1.
[2] G. Fóti, P. Hajós and E. sz. Kováts, *Talanta*, **1994**, in press.

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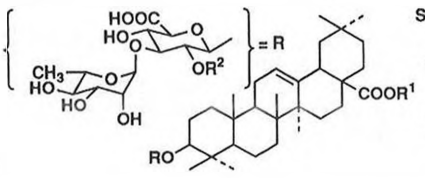
Analytical chemistry

Combined use of thermospray and continuous flow-FAB liquid chromatography-mass spectrometry for the analysis of glycosides in crude plant extracts.

J. -L. Wolfender and K. Hostettmann

Institut de Pharmacognosie et Phytochimie, Ecole de Pharmacie, Université de Lausanne, CH-1015 Lausanne, Switzerland

In crude plant extracts, some constituents of biological or pharmaceutical interest exist in the form of glycosides. As these compounds are usually labile and polar their off-line mass spectral investigation requires soft ionisation technique such as D/CI or FAB. When analysed on-line by LC-MS in crude extracts, they need equivalent ionisation techniques. In order to screen rapidly and efficiently compounds like saponins, cardenolides or secoiridoid glycosides by LC-MS, the use of two interfaces (TSP and CF-FAB) was investigated. An experimental set-up allowing the same standard HPLC conditions (1ml/min, 4 mm i.d. column) for both types of LC-MS ionisation techniques involving post-column addition of buffer or matrix and efficient splitting was used. Different extracts of Leguminosae, Apocynaceae and Gentianaceae were analysed by these methods. TSP LC-MS was found to provide good structural and molecular weight information on small glycosides (mono-, di- and sometimes triglycosides) [1]. CF-FAB provides mainly molecular weight information of these glycosides but allows the analysis of much larger metabolites such as octaglycosylated triterpenes. The complementary and the potential of these LC-MS techniques for the early recognition of glycosides in crude plant extracts is discussed.



Saponins		Ionisation	
R^1	R^2	TSP	CF-FAB
H	H	MW	MW
H	Glc	frag.	MW
Glc	Glc	frag.	MW

Fig: Di-, tri- and tetraglycosylated triterpenes analysed by LC-MS in the crude fruits water extract of *Swartzia madagascariensis* (Leguminoseae).

[1] J.-L. Wolfender, M.P. Maillard, K. Hostettmann, *J. Chrom.* **1993**, 647, 183.

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Analytische Chemie

Matrix Molecules: The Key for MALDI-MS Applications

K. O. Börnsen, E. Gassmann and H. M. Widmer
Corporate Analytical Research, Ciba-Geigy Ltd, CH-4002 Basel

After three years of its introduction, matrix assisted laser desorption and ionization mass spectrometry (MALDI-MS) [1] is already a well established analytical method in chemistry and biochemistry. The high sensitivity, the broad mass range, the absence of any fragmentation and the fast sample preparation are the main reasons for this success. However, the possibility of measuring complex sample mixtures, often without any sample pretreatment is one of the biggest advantages of this new method. Chemical classes such as polymers, additives, dyes, carbohydrates and oligonucleotides are now accessible to MALDI-MS. Additives to the matrix can strongly improve the resolution and the determination of molecular masses. New matrices with their main applications will be presented.

[1] M. Karas and F. Hillenkamp; Anal. Chem., **60**, 2299 (1988)

R. C. Beavis and B. T. Chait; Anal. Chem., **62**, 1836 (1990)

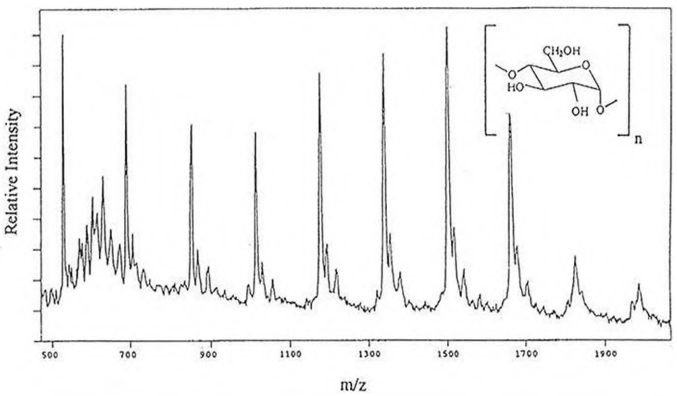
K. O. Börnsen, M. Schär, E. Gassmann, V. Steiner; Biol. Mass Spectrom. Vol. **20**, 471 (1991)

Analytische Chemie 160

Determination of Oligosaccharides in Soil Samples by Matrix-assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

S. Schuerch and U.P. Schlunegger
Department of Organic Chemistry, University of Bern, CH-3012 Bern

Soil samples, originating from fallow land of different age, have been analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). Sequences of hexoseoligosaccharides up to m/z = 4000 have been detected. Occurrence and distribution of the oligosaccharides are correlated with the peculiarities of soil genesis.



MALDI-TOF spectrum of a soil sample, showing hexoseoligosaccharides (hexose linear homologs H_3 through H_{12} with Δm = 162 Da). All signals originate from $[M + Na^+]$.

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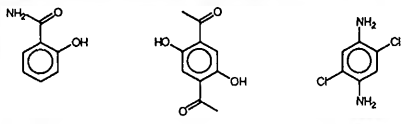
Analytische Chemie

New Matrix Compounds for Matrix Assisted Laser Desorption Ionization Mass Spectrometry.

J. Krause and U.P. Schlunegger
Institute of organic chemistry, University of Berne, CH - 3012 Berne Switzerland.

Since its introduction to analytic chemistry in 1988, Matrix Assisted Laser Desorption Ionization Mass Spectrometry (MALDI MS) has become an analytical tool of increasing importance.
Beside the instrumental technique, the choice of a good matrix compound is one of the most important problems of this method.
Until now, the most commonly used matrices are sinapinic acid (337 nm), 2,5 - dihydroxy-benzoic acid (337 nm) and nicotinic acid (266-290 nm) [1].
The main interest of this work was to find new matrix compounds and to get informations about the necessary functional groups in a matrix molecule.
More than 30 new compounds with different functional groups and combinations of functional groups have been tested as a MALDI matrix at 337 nm in both positive and negative ion mode. The results for bovine insulin are shown. Additionally, an UV-Vis spectrum was measured for each compound and the results are discussed.
Three compounds where found to be suitable as a MALDI matrix:

I.) Salicylamide
II.) 2,5 - Diacetyl - hydrochinone
III.) 2,5 - Dichloro - 1,4 - phenylenediamine



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[1] M. Karas, U. Bahr, A. Ingendoh, E. Nordhoff, B. Stahl, K. Strupat, F. Hillenkamp, Analytica Chimica Acta 4 (1990) 174-185.

Analytical chemistry 162

Analysis of Drugs and Drugs of Abuse by Micellar Electrokinetic Capillary Chromatography

O. Plaut and Ch. Staub
Institut universitaire de médecine légale, CH-1211 Genève 4

Micellar electrokinetic capillary chromatography (MECC, a subclass of capillary electrophoresis), associated with on-column, fast scanning, multi-wavelength detection is a powerful analysis technique. It is performed with the same apparatus as capillary electrophoresis (CE) although its separation principle is based on chromatography, that is, the difference in the distribution between solvent and micelles of ionic surfactants above their critical micelle concentration.

Attractive characteristics of MECC, such as high resolving power, ease of selectivity manipulation, automated injection system, small reagents amounts, tiny sample volumes, etc., make it a useful complement to traditional chromatographic techniques.

MECC also offers the possibility to directly inject aqueous mixtures as well as biological liquid samples after a simple filtration step, which is of greatest interest for forensic daily work.

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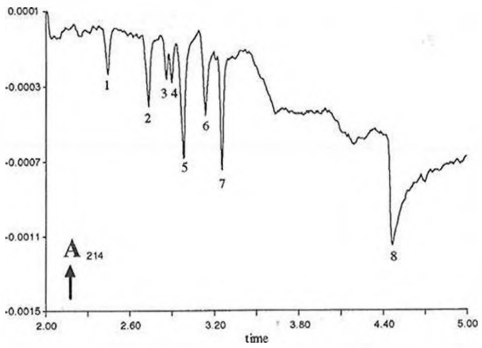
Analytische Chemie **163**

Capillary electrophoresis - a fast and universal tool in soil analysis

Markus Howald and Urs Peter Schlunegger
Institut für Organische Chemie, Universität Bern, CH-3012 Bern

Fast analysis of different species of molecules in soils by capillary electrophoresis is investigated. Several capillary electrophoresis techniques for the analysis of inorganic ions and carbohydrates has been checked. Respecting the intents of pedologues and the usually large number of soil analyses a bundle of capillary electrophoresis systems is proposed, capable of proceeding time-saving soil analyses. Examples of the application of these methods to soil samples are presented.



Simultaneously separation of alkali earth, transition metal cations and ammonium: Peak identities, concentrations and areas: (1) ammonium, 16 ppm, 108; (2) calcium, 20 ppm, 204; (3) magnesium, 6.5 ppm, 108; (4) manganese, 17 ppm, 103; (5) sodium, 16 ppm, 418; (6) aluminium, 11 ppm, 244; (7) potassium, 13.5 ppm, 322; (8) iron (III), 28 ppm, 1155.

[1] P. Jandik and G. Bonn, *Capillary Electrophoresis of Small Molecules and Ions*, VCH **1993**

Analytische Chemie **164**

Synchronized Cyclic Capillary Electrophoresis (SCCE)

Norbert Burggraf[1], Andreas Manz[1], Nico F. de Rooij[2], H. Michael Widmer[1]

[1]Ciba-Geigy Ltd., Corporate Analytical Research, CH-4002 Basel, Switzerland
[2]University of Neuchâtel, Institute of Microtechnology, Rue A.-L. Breguet 2, CH-2000 Neuchâtel, Switzerland

A cyclic capillary electrophoresis system can be achieved by arranging four capillaries of 20 mm length each into a square on a planar glass plate. With this arrangement fast separations of sample volumes (20 pL) with high separation efficiency is possible. Such a system enables us to simulate a conventional CE system with, for example a capillary of 800 mm length and 40 kV applied by using only 2 kV and moving the sample around ten cycles. Thus, the plate number per volt can be dramatically increased.

By synchronizing the system to the mobility of one of the separated compounds, a focusing on this compound can be achieved.
The sample may be detected using laser-induced fluorescence or other detection methods like refractive index detection or absorbance detection. Conceivable applications include solving difficult CE separation problems while applying low voltages. Different separations obtained with synchronized cyclic capillary electrophoresis will be presented and the specific characteristics of the system will be described.

Analytische Chemie **165**

Antisense Oligonucleotides and the Analytical Challenges for Capillary Gel Electrophoresis

Gerard J.M. Bruin[1], Iris Barmé[1], Dieter Hüsken[2], H. Michael Widmer[1] and Aran Paulus[1],

Ciba, [1] Corporate Analytical Research, and [2] Central Research Laboratories, CH-4002 Basel, Switzerland

Antisense compounds are chemically modified oligonucleotides of 12 to 30 bases in length, which are believed to inhibit the protein expression by specifically hybridizing with the messenger RNA. If, for example in a virus, an essential protein is suppressed, its proliferation is stopped. This methodology opens a new way to fight viral diseases with high specificity and is currently tested in clinical trails.

Size separation methods such as capillary gel electrophoresis (CGE) are most important for all aspects of antisense research, such as detection of failure sequences originating from the synthesis and degradation and metabolic products due to cellular nuclease activities. In this paper, we report on size separations of antisense oligonucleotides up to 30 bases with CE in polyacrylamide matrices.

Several compositions of the gel matrix with differing amounts of urea as denaturing agent and stabilizing additives such as PEG's were explored under various buffer and pH conditions. Fast CGE separations were carried out in 2 to 5 minutes with an applied filed of up to 1200 V/cm. Phosphorothioate oligonucleotides were base line resolved using 10 % T polyacrylamide gels. Optimal CGE conditions were used to examine the stability of antisense oligonucleotides against various endo- and exonucleases. The reaction kinetics of the oligonucleotide degradation could be studied by quantitation of the shortmers. This represents an easy assay to measure in an automated fashion under in vitro conditions enzymatic stability of antisense compounds.

Analytische Chemie **166**

Capillary Electrophoresis of ANTS labeled Oligosaccharide ladders Complex Carbohydrates

A. Klockow[1], R. Amadò[2], H.M. Widmer[1] and A. Paulus[1],
Ciba, Corporate Analytical Research, CH-4002 Basel, Switzerland[1]
Swiss Federal Institute of Technology (ETH Zürich), Institute of Food Science, CH-8092 Zürich, Switzerland[2]

In recent years carbohydrates are being recognized to play a vital role in a wide variety of scientific disciplines as well as in industrial areas. Studying complex carbohydrates has important implications in medical sciences and biotechnology, as a number of therapeutic proteins are produced by recombinant techniques. Often these proteins are expressed in mammalian cells with glycan moieties which affect their biological activity, lifetime and specificity. In food sciences polysaccharides such as starch, dextran and pectin are of special interest as they are important as nutrients and food additives.

Since complex carbohydrates are often present only in minute quantities in complex sample matrices, analytical techniques providing high resolution separations, for example capillary electrophoresis (CE), combined with sensitive detection are necessary. Several strategies for on-column detection of carbohydrates in CE have been discussed, including indirect photometric detection methods, direct amperometric or RI-detection and precolumn derivatization, which seems to be the most promising approach with respect to sensitivity and commercial availability.

8-aminonaphthalene-1,3,6-trisulfonic acid (ANTS) has been proposed as labeling reagent for electrophoretic separations since it carries negative charges over a wide pH range. The derivatization of polysaccharides and glycoprotein derived complex oligosaccharides allows fast CE separation with detection limits of $5*10^{-7}$ M or 8 femtomole for UV and $5*10^{-8}$ M or 400 attomole for LIF detection. Examples of high resolution separations of ANTS labeled polymeric carbohydrates such as dextran and polygalacturonic acid will be presented.

A protocol to derivatize as little as 50 picomole carbohydrate in a reaction volume of only 2 µl was worked out. To demonstrate the applicability of this ANTS labeling procedure to complex carbohydrate analysis, an oligosaccharide mixture derived from human Immunoglobuline G was labeled and separated within 5 min.

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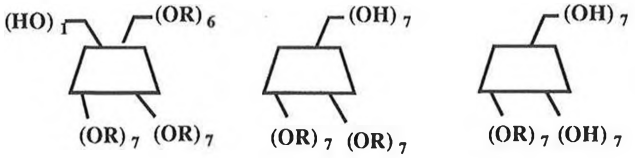
Chimie analytique

Synthèse de phases stationnaires HPLC pour séparations chirales

M.P. Vivarat-Perrin, S.G. Claude, R. Tabacchi
Institut de Chimie de l'Université de Neuchâtel, CH-2000 Neuchâtel

L'objectif de ce travail est la réalisation de phases stationnaires chirales pour la Chromatographie liquide haute performance (HPLC) afin d'obtenir des séparations de composés énantiomériques. Ces phases sont obtenues par greffage de β–cyclodextrines (βcyd) modifiées sur des billes de silice poreuse. Dans une première étape, après une protection sélective de fonctions alcools nous modifions les fonctions hydroxyle libres, primaires et secondaires, de la β-cyclodextrine par divers substituants (R = CH_3, CO-CH_3) tels que :



Tous ces produits sont isolés sur colonnes chromatographiques et totalement caractérisés par spectroscopie RMN 1D et 2D. L'obtention de produits d'une grande pureté est indispensable pour la reproductibilé des supports chromatographiques.

Analytische Chemie

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Direct Characterization of Supramolecular Complexes of Polypeptides and Proteins by Electrospray Mass Spectrometry

M. Przybylski, M.O. Glocker, C. Maier, C. Borchers, E. Dürr, W. Fiedler, H. Wendt*, H.R. Bosshard*
Fakultät für Chemie der Universität Konstanz, D-78434 Konstanz and *Biochemisches Institut der Universität Zürich, CH-8057 Zürich

The development of efficient "soft" desorption-ionization methods has led to a breakthrough in the direct mass spectrometric analysis of polypeptides and proteins, with fast atom bombardment (FABMS) and plasma desorption (PDMS) enabling the determination of smaller polypeptides (< 20 kD), while electrospray (ESMS) and laser desorption (LDMS) up to high molecular weight (> 100 kD) proteins. In combination with chemical or enzymatic fragmentations, these methods have been successfully applied in *primary structure* analyses, such as posttranslational modifications. Unlike the solid-phase MS methods, the recently discovered feasibility of ESMS to the direct analysis of specific *non-covalent biomacromolecular complexes* in solution is leading to new perspectives for supramolecular chemistry of polypeptides and proteins which lack analytical methods of high sensitivity *and* molecular specificity (M. Przybylski, et al., *Angew. Chem.* **1994**, in press). The range of hitherto successful studies in physiological-like solutions extends from specific enzyme-substrate/-cofactor complexes, to intact quarternary structures. Applications of ESMS to the identification of dimers and triplex forms of leucine zipper-type polypeptides and structural analogues, serine and cysteine protease-inhibitor complexes, and specific α-helical complexes of the lung surfactant protein SP-C will be reported. The characteristic charge distributions of multiply protonated ions not only provides the identification of supramolecular complexes, but also a differentiation of conformational states in solution. For more detailed structural characterization (e.g. surface topology), approaches have been developed by combining ESMS with selective chemical modification (*Proc. Natl. Acad. Sci. USA* **1992**, *89*, 5630), and H/D exchange reactions.

Analytical chemistry

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Systematic search for new xanthones in Gentianaceae species by LC-UV and LC-TSP-MS analysis.

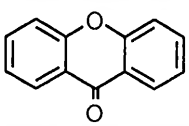
S. Rodriguez, J.-L. Wolfender, K. Hostettmann

Institut de Pharmacognosie et Phytochimie,Université de Lausanne, Ecole de Pharmacie, CH-1015 Lausanne, Switzerland

There has recently been an increasing interest in xanthones, a class of polyphenolic compounds, because some are known to be strong and selective inhibitors of monoamine oxidase (MAO) (hence potential antidepressive drugs) [1]. In order to discover new xanthones with potential MAO inhibitory activity, more than forty crude extracts of the Gentianaceae family have been routinely screened.

LC-UV and LC-TSP-MS are particularly efficient techniques for obtaining a rapid and precise idea of the phenolic constituents of crude plant extracts [2]. The systematic use of an in-house UV-spectra library and the corresponding MS data allow an *on-line* identification of known compounds, while isolation is performed for compounds which present new characteristics. This type of routine analysis permits an optimisation of the investigations and avoid unnecessary and costly isolations.

xanthone nucleus



Substituted groups on the xanthone nucleus in Gentianaceae species :

- sugars
- hydroxyl groups
- methoxy groups

The method does not replace other techniques of structure elucidation but permits a rapid identification of known compounds for chemotaxonomic investigations, and appears to be a powerful tool for targetting new molecules in crude plant extracts.

[1] O. Suzuki et al, *Planta Med.*, **1981**, 42, 17.
[2] J.-L. Wolfender, K. Hostettmann, *J. Chromatogr.*, **1993**, 647,191.

Chimie analytique

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Methoxyphenylpolysiloxanes. Polarizable stationary phases for Capillary Chromatography.

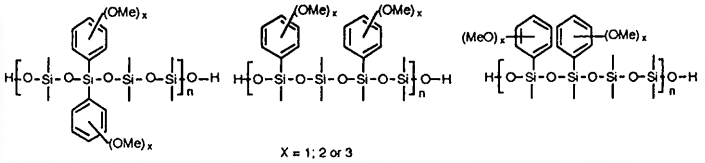
M. Monzione, S.G. Claude and R. Tabacchi

Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, CH-2000 Neuchâtel

Polarizable stationary phases have proven to be superior to polar stationary phases for the selective separations of position isomers. The soft dipole-induced-dipole interactions between the stationary phase and sample solutes give excellent resolution of isomeric pairs without excessive retention of these isomers.

The use of substituted phenyl functional groups provides a unique method of varying stationary phase selectivity. The resonating π electrons in the phenyl ring add polarizability to these phases.

A series of mono-, di-, and trimethoxyphenyl-substituted polysiloxanes (25% substitution) were synthesized and evaluated for use as stationary phases in capillary column gas chromatography.



The purpose of this work is two fold. Firstly, to investigate the influence of polymer properties concerning the positions of the methoxyphenyl groups on one or two silicon atoms and secondly the positions of the methoxy-groups on the aromatic ring.

These polymers have been coated on specially deactivated fused silica columns and their efficiency, activity, polarity and thermal stability was evaluated.

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Analytical chemistry

Monosized, silica based microspheres for chromatographic separations

L. Jelinek, R. Ohmacht, A. Pfenninger* and E.sz.Kováts
Laboratoire de Chimie Technique, Swiss Federal Institute of Technology
CH–1015 Lausanne
*Chemie Uetikon, CH-8707 Uetikon

Monosized, poly(silicic acid) (PSA) microspheres (d_p = 0.5 - 2.0 µm) were produced by continous introduction of tetraethoxysilane into an ammonia/water/ethanol mixture. The starting reaction mixture contained small silica particles as seed source. A secondary feed (ammonia/water mixture) was also introduced in order to keep composition of the reaction mixture constant during the controlled growth of the particles. After isolation the microporous PSA microspheres were calcined to give monosized, non-porous, compact SiO_2 microspheres. This product was silylated to produce reversed phase packing material for liquid chromatographic purposes. The final product was completely redispersable.

Chromatographic columns (33 x 4.6 mm) were packed with the silylated products. The hydrolytic stability of the products was excellent under acidic conditions and was satisfactory up to pH ≈ 9. The efficiency of the packing material was evaluated by separation of different protein and peptide mixtures to give high resolution power and rapid separations.

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Chimie analytique

Analyse par chromatographie gazeuse de racémates au moyen de cyclodextrines peralkylées

S.G. Claude, R. Tabacchi
Institut de Chimie de l'Université de Neuchâtel, CH-2000 Neuchâtel
A. Saxer
Institut für organische Chemie der Universität Bern, CH-3012 Bern

Les résultats obtenus à partir de β-cyclodextrines perméthylées et perpropylées, ainsi que de leur mélange [1], nous ont conduit à réaliser la synthèse de composés mixtes renfermant les substituants 6-méthyles et 2,3-propyles, respectivement 6-propyles et 2,3-méthyles.
Les composés examinés dans notre précédant travail [1] et d'autres, ont été chromatographiés en vue de mieux comprendre le mécanisme de la résolution.
Des conclusions intéressantes en découlent

[1] S. Claude, R.Tabacchi, A. Saxer, *Chimia* **1983**, *47*, 221

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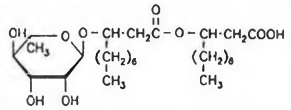
Analytische Chemie

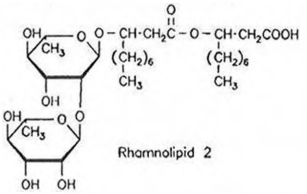
Development of a New HPLC Method for Monitoring Rhamnolipid Biosurfactants Excreted by *Pseudomonas* Species

T. Schenk, and B. Schmidt
Biologie V, RWTH Aachen, D-52056 Aachen, Germany

Bacteria of the species *Pseudomonas aeruginosa* are known to degrade n-alkanes. Biodegradation of the environmental contaminants is enhanced by glycolipids excreted by the microorganisms. The glycolipids of the strain *P. aeruginosa* DSM 2659 are rhamolipids RL1 & 2 of the following structure:



Rhamnolipid 1



Rhamnolipid 2

So far, RL concentrations were determined *via* F_{cmc} values or rhamnose after hydrolysis yielding only total amounts. The present method makes possible the determination of the individual RL, and allows a better understanding of laboratory and environmental processes. For that purpose, the RL were extracted from the culture media, and derivatized with p-bromoacetophenone. The resulting esters were chromatographed on a C_{18} RP column (250 mm x 4.6 mm) using a gradient of H_2O:CH_3CN (30:70 to 0:100, v:v); the column effluent was monitored at 265 and 320 nm. The method was applied for the determination of the RL concentrations in authentic culture media of *P. aeruginosa* during an entire cultivation cycle.

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Analytical chemistry

Analysis of cannabinoids by high performance liquid chromatography with electrochemical detection (HPLC/ED).

H. Lacalle and Ch. Staub
Institut Universitaire de Médecine Légale, CH-1211 Genève 4.

Cannabis, in its different forms (marijuana and hashish), remains the most popular drug of abuse in Switzerland. For forensic purposes, it is of most importance to be able to determine whether a person is under the influence of the drug in a particular moment. Therefore, the basic requirement is a very sensitive and selective analytical method allowing the simultaneous determination of the main psychoactive ingredient of cannabis (Δ⁹-tetrahydrocannabinol) and its major metabolites (11-hydroxy-Δ⁹-tetrahydrocannabinol and 11-nor-9-carboxy-Δ⁹-tetra-hydrocannabinol) in blood, where these compounds are found in the low ng/ml range.

The use of HPLC/ED for the detection of cannabinoids has been found to be a suitable alternative to gas chromatography/mass spectrometry (GC/MS), which is much more expensive and requires a derivatization of the phenolic group of the cannabinoids. Furthermore, some robotic systems currently available permit an on-line sample extraction and injection to HPLC, improving reproductibility and speed of the analytical procedure.

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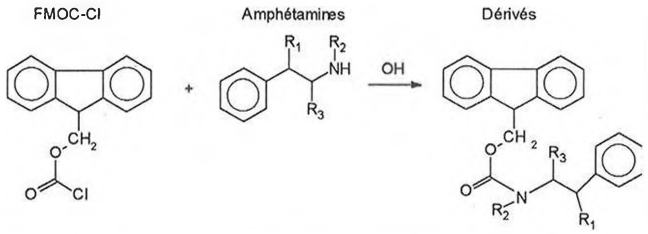
Chimie Analytique **175**

Dialyse, enrichissement et séparation par HPLC des amphétamines contenues dans le sérum après dérivatisation par FMOC-Cl

F. Sadeghipour, D. Bertin, J.-L. Veuthey
Laboratoire de chimie analytique pharmaceutique, Sciences II, Université de Genève, CH-1211 Genève 4

La consommation des amphétamines en tant que stupéfiants croît fortement dans les pays industrialisés. Une méthode analytique sensible et précise est donc nécessaire pour le dosage de ces composés dans les fluides biologiques. Nous présentons dans ce travail une méthode entièrement automatisée au moyen du système Gilson-ASTED, permettant de détecter les amphétamines contenues dans le sérum. Les amphétamines étudiées sont : la méthylène dioxyamphétamine (MDA), la méthylène dioxyméthamphétamine (MDMA, Adam, Ecstasy) et la méthylène dioxyéthamphétamine (MDEA, Eve).
Ces composés n'étant pas fortement absorbants, ils sont dérivés directement dans le sérum au moyen du 9-fluorenylméthylchloroformate (FMOC-Cl) selon la réaction :



Les dérivés formés sont fluorescents, permettant d'augmenter fortement la sensibilité et la sélectivité de l'analyse. Une partie de l'échantillon dérivé est alors dialysé au travers d'une membrane (dont le cut-off est de 15 kDaltons), puis enrichi sur une cartouche contenant un support C18. Après élution et chromatographie sur une silice C8, les amphétamines dérivées sont détectées au moyen d'un fluorimètre.
La méthode a été validée et appliquée à des cas réels de toxicomanes.

Analytische Chemie **176**

Screening for a Defence System in a Caterpillar by Tandem MS

H. Gfeller[1] U.P. Schlunegger[1], U. Schaffner[2] J.L. Boevé[2] I. Ujvary[2]
[1] Institut für organische Chemie, Universität Bern, Freiestrasse 3, 3012 Bern
[2] Zoologisches Institut, Universität Bern, Balzerstrasse 3, 3012 Bern

Due to the excellent sensitivity and the potential of mixture separation of tandem mass spectrometry a biological problem has been solved within a very short time and with very small amounts of biologically active material (one larva giving about 1 microliter of hemolymph only).
In contrast to the larvae of the generalist *Aglaostigma fulvipes* the larva of the sawfly *Rhadinocerea nodicornis* - a specialist living and feeding on the alpine plant *Veratrum album* - is never attacked by ants. Veratrum alkaloids are a particularly toxic group of steroidal alkaloids [1]. Crude preparation of some of these agents have even found practical application as insecticides. Nevertheless, *Veratrum album L.* possesses a herbivore community consisting of 29 insect species [2]. Yet, insects living on *Veratrum album* not only have to handle the toxic plant compounds, but are also exposed to ants. Here the question arises, how *R. nodicornis* manages predation pressure. In order to answer this question, leaves of the plant *Veratrum album*, hemolymph and excrements of the larvae of *R. nodicornis*, as well as those of other insects have been analyzed for veratrum alkaloids by mass spectrometry - EI and LSIMS ionisation - and tandem mass spectrometry.
We conclude, that the larvae of the specialist sawfly *Rhadinocerea nodicornis Konow* store in their hemolymph veratrum alkaloids originating from their host plant *Veratrum album L.* as detected directly by tandem mass spectrometry. 3-acetyl-zygadenine is the major alkaloid found in the hemolymph. Qualitative and quantitative data showed that the plant alkaloid 3-angeloyl-zygadenine is most probably metabolized in the larval gut to zygadenine and then acetylated. In contrast, no veratrum alkaloids were detected in the hemolymph and excrements of larvae of the generalist sawfly Aglaostigma fulvipes fed with *Veratrum album* leaves.

[1] I. Ujvary, et al *J. Agric. Food Chemistry* **1991** *39, 1875-1881*
[2] U. Schaffner,et al *J. Chem. Ecol. accepted*

The Investigation of "Single Event" Quality Deviation as a Contribution to Pharmaceutical Quality Assurance **177**

M. Wilkinson, Qualitätssicherung Pharma, Packmaterialkontrolle, SANDOZ AG, CH 4002, BASEL

In quality control the main class of data necessary to monitor quality standards is statistical data produced by routine analyses and other checks. Scatter may betray lack of control of the process, although the average may be within requirements. Data describing single or low frequency deviations can usefully be regarded as belonging to a separate category requiring different treatment. The usual response to a defective item is to attempt to reproduce the defect under laboratory conditions. It is often overlooked that the single reported event is typical of some general but unknown class of items, and that it will carry some, or even all, of the characteristics which identify the group and contain evidence suggesting the cause. A systematic approach to locate the exact nature of the problem is outlined in the poster:
The deviation statement must describe the deviation clearly. The Kepner Tregoe matrix (1) is used to assemble the facts in simple tabular form. The sample is examined using visual and analytical procedures. The following standardised questions are answered: What object is affected and also the trend (if still developing).
Comparison of the good sample with the complaint sample yields distinctions and changes, which highlight the differences between the complaint sample and the reference (good) samples. The cause must logically lie within the differences between the unaffected (good) item and the complaint sample
Having evaluated the available information one must convert this information into the form of a hypothesis. These ideas of the most probable cause can be checked against the facts. A good hypothesis will agree with the facts concerning both the complaint and the good sample and can then be looked upon as the most probable cause and meaningful action can be taken.

(1) Kepner H. and Tregoe B. The New Rational Manager, Kepner Tregoe Associates, Princeton N.J., 1981

Chimie Analytique **178**

I- Extraction en phase subcritique d'opiacés contenus dans une matrice liquide - application à l'urine

P. Edder, W. Haerdi, J.L. Veuthey, C. Staub
Département de chimie minérale, analytique et appliquée, Sciences II, Université de Genève, CH-1211 Genève 4.

L'extraction en phase supercritique (SFE) des liquides peut être envisagée selon deux approches différentes : soit directement au moyen d'une vaisselle spécialement conçue à cet effet, mais ne permettant pas l'adjonction d'un modificateur polaire; soit après adsorption préalable du liquide sur un support solide. En outre, cette dernière voie présente l'avantage d'introduire une sélectivité supplémentaire par le choix de ce support solide, c'est pourquoi nous l'avons appliquée aux analyses d'opiacés dans l'urine.
La méthodologie développée comprend une adsorption préalable de l'urine sur une silice très sélective, la Bond Elut Certify®, suivie d'une étape de lavage, puis d'une élution au moyen d'un fluide supercritique et enfin, après dérivation d'une analyse par GC-FID. L'aspect quantitatif de cette procédure (répétabilité, rendements d'extraction, linéarité,...) a été étudié pour quatre opiacés (codéine, éthylmorphine, 6-monoacétylmorphine et morphine) et comparé à la technique classique d'extraction liquide-solide. Même si les résultats obtenus sont relativement similaires, la SFE ne peut être considérée comme réellement avantageuse que si un couplage SFE-GC est envisagé, car l'extraction liquide-solide est dans ce cas précis plus aisée d'utilisation.

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Chimie Analytique

II- Extraction en phase subcritique d'opiacés contenus dans une matrice solide - application aux analyses des cheveux.

P. Edder, W. Haerdi, J.L. Veuthey, C. Staub
Département de chimie minérale, analytique et appliquée, Sciences II, Université de Genève, CH-1211 Genève 4.

En Toxicologie médico-légale, les analyses des cheveux sont devenus récemment un compléments fort utile aux analyses des fluides physiologiques comme l'urine et le sang, car elles permettent d'obtenir des informations sur plusieurs mois dans le passé du toxicomane. Toutefois, les méthodes d'extraction des stupéfiants dans les cheveux sont très longues (6-24h) et fastidieuses.
L'extraction de stupéfiants (opiacés) contenus dans les cheveux au moyen de fluide supercritique a permis de réduire considérablement le temps d'analyse. En effet, seulement 30 min. sont suffisantes pour obtenir une extraction quantitative et reproductible. L'aspect quantitatif de la méthodologie développée dans son ensemble, c'est-à-dire avec la SFE, la dérivation des opiacés (propionylation) et leur analyse par GC-MS de quatre opiacés est présenté. Notre méthode est alors comparée avec quatre procédures d'extraction classiques (extraction méthanolique, hydrolyse basique et acide, digestion enzymatique, suivies d'une extraction sur phase solide). Dans ce cas, la SFE s'est révélée plus rapide et parfois plus efficace que les techniques usuelles et démontre bien son potentiel vis-à-vis des matrices solides.

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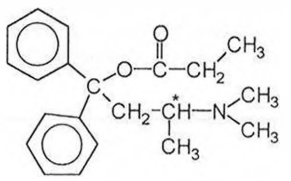
Chimie Analytique

Séparation chirale de la méthadone contenue dans le sérum.

S. Rudaz, J.L. Veuthey
Laboratoire de chimie analytique pharmaceutique, Science II, Université de Genève, CH-1211 Genève 4

La méthadone est maintenant utilisée dans de nombreux pays comme traitement de substitution à l'héroïne lors de thérapie de désintoxication. Ce composé possède un centre d'asymétrie et il est délivré en Suisse sous forme de mélange racémique alors qu'un seul isomère est efficace, la l-méthadone.



METHADONE

Il est nécessaire d'avoir à disposition une procédure analytique permettant de déterminer, dans le sérum par exemple, la proportion d'énantiomère présente. Après une étape de purification de l'échantillon au moyen de disques contenant une phase mixte de type C18-échangeur de cations, l'extrait est injecté sur une colonne chirale contenant une protéine (α-AGP). La résolution à la ligne de base des deux énantiomères est obtenue rapidement et avec une bonne répétabilité. Après avoir été validée, la procédure a été appliquée à l'analyse de cas réels.

Chimie bioanalytique

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Determination of the enantiomers of Zy 17617B in plasma by two-dimensional liquid chromatography with automated solid-phase extraction and column-switching

P. Fontannaz, M. Salanon, and D. Sallin
Preclinical Development and Drug Safety, Zyma SA, CH-1260 Nyon

A fully automated chromatographic system, combining solid-phase extraction with pre-column exchange and zone cutting with column-switching was developed for the routine analysis of the two enantiomers of Zy 17617B at the ng/ml level in plasma samples. Zy 17617B (Fig.1), is a pharmaceutical product with antidiarrhoeal properties. This compound is synthetized under its racemic form. A sensitive assay with chiral separation is thus required for the determination of pharmacokinetic data after oral intake of this drug.

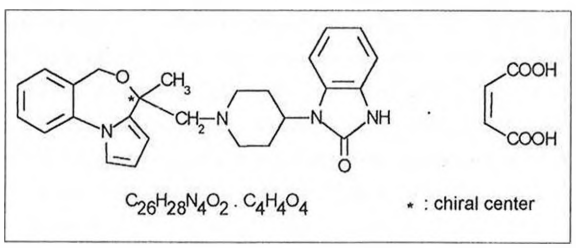

Fig. 1. Molecular sturcture of Zy 17617 B; mol. wt. 544.61

In a first step, the sample extraction and the elution were performed automatically using an on-line sample preparator and a reversed phase (RP-18) analytical column, respectively. In a second step, the peak of interest, previousely separated on the RP-18 column was pre-concentrated on a C-18 pre-column after zone-cutting. By column-switching, the trapped racemate was eluted onto a chiral column and each enantiomer was measured using a fluorescence detector. This fully automated system has been used for one-line analysis, which is an alternative to the time-consuming liquid-liquid extraction. The validation data demonstrated the reliability of the method.

Analytische Chemie

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Spurenanalyse von chlorierten Phenolen in komplexen Matrices

A. Ritter, EMPA St. Gallen, Abt. Produktanalytik, CH-9001 St. Gallen

Chlorierte Phenole sind Bestandteile von Desinfektionsmitteln, Holzschutzmitteln und Fungiziden, weshalb sie in erheblichen Mengen in die Umwelt gelangen. Im lebenden Organismus findet man sie als Abbaumetaboliten von Pentachlorphenol und Hexachlorbenzol. Durch Behandlung von Holzoberflächen mit chlorabspaltenden Desinfektionsmitteln entstehen chlororganische Verbindungen in Spuren aus Lignin. Ihr penetranter Geruch und die leichte mikrobielle Methylierbarkeit zu den ebenfalls geruchsintensiven Anisolen bewirkt, dass sie bei Kontakt Lebensmittel ungeniessbar machen.
Störfälle in Kläranlagen und belastetes Verpackungsmaterial aus Holz und Kunststoff für Lebensmittel waren der Anlass, eine möglichst empfindliche matrix-unabhängige Methode zur Spurenanalyse von chlorierten Phenolen zu entwickeln.

Die Wasserdampfflüchtigkeit der chlorierten Phenole erleichtert dabei das clean-up . In stark saurem Medium wird die Matrix (z.B. Abwasser, Holz, Papier, Verbundmaterial, Kunststoffe) in einer speziellen Umlaufapparatur mit Wasserdampf destilliert und das Kondensat kontinuierlich mit wenig Lösemittel extrahiert. Der alkalisch gestellte Extrakt wird mit Pentafluorbenzoylchlorid verestert und nach einer einfachen flüssig/-flüssig Extraktion die organische Phase direkt gaschromatographisch/-massenspektrometrisch mit negativer chemischer Ionisation (NCI) quantitativ analysiert. Dabei erreicht man je nach Isomerentyp durch den hohen Fluorierungsgrad der Derivate Nachweisgrenzen bis in den sub-ppb-Bereich. Je nach Säulentyp und gewähltem Temperaturprogramm lassen sich die Isomeren einzeln oder je Chlorierungsgrad als Summenparameter quantifizieren. Durch die Wahl grosser Destillationsblasen lassen sich auch auch Probenmengen bis 1 kg bequem zur Extraktion ohne weitere Probenvorbereitung einsetzen.

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Analytische Chemie **183**

Continuous Sample Pretreatment using a Silicon Free Flow Electrophoresis Device.

Daniel E. Raymond*, Andreas Manz, H. Michael Widmer
Ciba-Geigy Ltd., Corporate Analytical Research, CH-4002 Basel, Switzerland

In Free-Flow Electrophoresis (FFE) a thin rectangular bed is used through which a carrier buffer flows under laminar conditions. A narrow sample stream is continuously fed into this carrier solution. The application of an electric field perpendicular to the carrier flow results in separation of sample components via differences in their respective electrophoretic mobilities. In this manner a desired sample band can be selected and then directed to an analytical system for quantitation. Sample pretreatment may involve filtration of the sample from a particulate suspension, isolation of the component of interest, or derivatisation prior to analysis.

The channel system for free-flow electrophoresis has been fabricated onto a silicon wafer using micromachining technology. The overall dimensions are 3 cm wide and 6 cm long. However, the separation bed is 1 cm wide, 5 cm long, and 50 µm deep. The potential of the silicon FFE system for use as a continuous separation method is demonstrated by the continuous separation of rhodamine B isothiocyanate labelled lysine, glutamine and glutamic acid for over 20 minutes. Baseline separation of these species was achieved using only 50 V and half the separation bed length. The effect of flow from the side channel arrays, sample dilution, and the resolution as a function of the applied voltage have also been investigated.

Chimie analytique **184**

Application of Supported Liquid Membrane to Trace Metal Speciation Studies

N. Parthasarathy, R. Agraz, E. Haseroth, O. Keller, J. Buffle
Département de chimie minérale, analytique et appliquée, Sciences II, 30, quai E.-Ansermet, 1211 Genève 4

The transport of heavy metals, e.g. Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+}, through a 1,10-didecyldiaza-18-crown-6, fatty acid, phenylhexane-toluene supported liquid membrane (SLM), has been investigated for making speciation studies under natural water conditions. This novel method allows simultaneous separation and preconcentration of the target metals.
The transport of these metals in the presence of complexants such as Tiron and oxalate has also been studied.
A flat sheet membrane was used for optimizing the transport of metals across the designed membrane. Based on these studies, investigations with hollow fibers have been carried out to obtain higher preconcentration factors and faster response times.
By incorporating an electrochemical detector into the system, the sensitivity of the method can be extended to the picomole range.

Analytical Chemistry. **185**

DEVELOPMENT OF SENSORS FOR IN-SITU MEASUREMENTS IN NATURAL WATERS.

M.-L. Tercier, J. Buffle
Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, Sciences II, 30 Quai E.-Ansermet, 1211 GENEVA 4, Switzerland.

The understanding of physical-chemical processes occuring in natural water systems has become increasingly important owing to the greater need to safeguard the environment. The large number of possible physico-chemical interactions together with spatial and seasonal changes in the distrition of diverse elements makes mathematical modelling of processes difficult without access to large experimental data base. In addition, measurements have to be made without disturbing the media as the chemical forms of the elements are influenced by physical and chemical changes of the media.

Sensors allowing automatic, simultaneous and in-situ measurements of large number of parameters in a reasonable time would be ideal for this purpose. Electrochemical sensors seem to be potentially suitable for this application.

In this work a mercury-coated iridium-based microelectrode has been developed. Systematic studies to determine the utility of these sensors for in-situ trace metal determination in natural waters have been made. These microelectrodes were applied to lead and cadmium speciation studies directly in river waters by square wave anodic stripping voltammetry.

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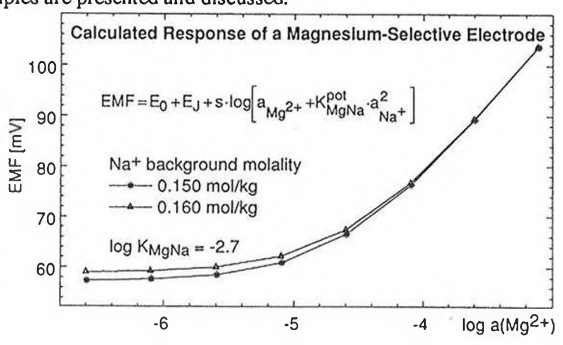
Quality Assessment of Magnesium-Selective Potentiometric Electrodes.

D.Citterio, C.Demuth, M.Linnhoff, S.Rasònyi, and U.E.Spichiger.
Centre of Chemical Sensors/Biosensors and (Bio-)Analytical Chemistry, Department of Pharmacy, ETH-Zürich, Technopark, Pfingstweidstr. 30, CH-8005 Zürich.

For clinical analysis a solvent polymeric membrane containing the magnesium-selective carrier ETH 7025 (N-Heptyl-N',N'-bis{8-[[3-(heptyl-methyl-amino)-1,3-dioxopropyl]amino]octyl}-N-methyl-propanediamide) was implemented in a commercially available instrument. Selectivity towards physiological background ions is an important factor for the quality of sample analysis. The performance of the sensor is often verified by standard addition of solutions containing the presumed interfering ions. However, the changing liquid junction potential, ionic strength and single ion activity coefficients upon standard addition of background ions have to be considered. Therefore, special emphasis is put on the calculation of activity coefficients in biological samples by using the Pitzer equations. This calculus allows for taking the interactions between ions in mixed elctrolyte solutions at a temperature of 310 K into account. Calculations are performed for aqueous calibration solutions with mean physiological molal activities of Na^+, K^+, Ca^{2+}, Cl^- and acetate representing anions with low mobility at pH 7.4 (see figure). Inaccuracies due to a lack in selectivity of a membrane may be corrected chemometrically by simultaneous measurement of the activity of interfering ions. This procedure shows some limitations, however. Models and examples are presented and discussed.



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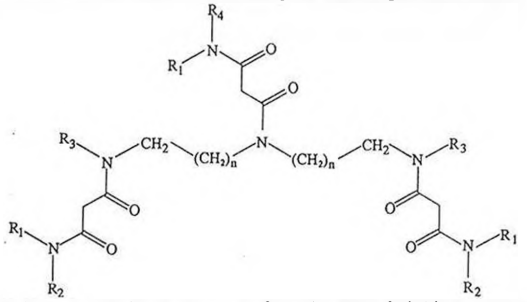
Analytische Chemie **187**

Quantitative Structure-Selectivity Relationship (QSSER) of "Magnesium-Selective" Neutral Carriers Incorporated in Solvent Polymeric Membranes.

U.E.Spichiger, D.Citterio, M.Nägele.
Centre of Chemical Sensors/Biosensors and (Bio-)Analytical Chemistry, D-Pharm, ETH-Zürich, Technopark, Pfingstweidstr. 30, CH-8005 Zürich.

More than 20 years of research in the group of Prof.W.Simon resulted in magnesium-selective, neutral ionophores providing useful discrimination of physiological cations when incorporated in solvent polymeric membranes. More than 44 structurally varied malondiamides were evaluated during the last few years. In many cases a small change in the structure resulted in a decisive variation of the selectivity pattern. The selectivity pattern is influenced by different factors like the lipophilicity of the membrane bulk, the dielectric constant and interactions between polymer, plasticizer and active membrane components. Apart from predictions of the optimum ligand sphere, the prediction of the selectivity pattern is scarcely feasible. The discrimination of background ions of biological samples was enhanced by optimizing the membrane composition, i.e. the type of plasticizer and the concentration of the ligand and anionic sites, carefully. Different procedures for the evaluation of the selectivity coefficients based on basically thermodynamic models and on more application near criteria, respectively, are relevant also [1].
Basic constitution of the discussed isologues of the ligand ETH 7025:



[1] R. Eugster, B. Rusterholz, A. Schmid, U.E. Spichiger, and W. Simon. Clin. Chem. **39**, 855-859, 1993.

Analytische Chemie **188**

Representative Sampling of inhomogeneous Riverwater

N. A. Corfù, U. Kettenring, M. Zehringer
Gewässerschutzamt Basel-Stadt, Hochbergerstrasse 158, CH-4019 Basel

For monitoring flowing surfacewaters in regard of compounds contained in river water (concentration and load) it is of great importance to take the inhomogeneity of the river water into account.
The conditions in the river Rhine were investigated at the Rhein-Überwachungs-Station (RÜS) [1] (Rhein-km 171.3) by tracer experiments [2]. On a stretch of 7 km above the RÜS the Rhine has 5 feeds and their waters are not completely mixed at the site of the RÜS (width 205 m, max. depth 11m). Thus the RÜS samples at 5 different points across the river section. The passing of the tracer at the RÜS was monitored by measuring 2 different sample types: 1. samples taken every 2 min. to get the tracer concentration as a function of time, 2. sample mixtures (continuously collected) representing the whole event; both sample types were collected for each sampling point.
To calculate the distribution of the tracer across the river section for both sample types and each sampling point, the results were fitted with a Gauss curve as a simple model, resulting in 2 sets each of 5 Gauss curves. The conformity of the parameters of all the 5 pairs of corresponding curves was excellent (0-15% deviation). Taking into account the time ratio of the 2 sample types the corresponding concentrations accorded well (2 - 12% deviation, 1 exception 48%). Thus, the concentrations of sample mixtures continuously collected reflect accurately an input of a compound into a river if the samples are taken at several important points across a river section.
To calculate the load correctly the following equation is valid:

$$F = \iiint c(x,y,t)v(x,y,t)dxdydt$$ (c = concentration, v = flowrate, x,y = point of the river cross section, t = time)

That equation cannot be solved in practice. The above mentioned results show that the time dependence of c(x,y,t) is not needed. But to calculate the average concentration of a compound in the whole river, the results of the different sample mixtures have to be weighted. There are 2 ways to get the weighting factors: either empirically from tracer experiments or by determing the flowrate profile across the river section. With both the total flowrate and the concentration of a sample - mixed over time and in the ratio based on the weighting factors - the total load can be calculated in an accurate way.

[1] Common project of the BUWAL and the Umweltministerium Stuttgart, N. A. Corfù, Abstract of the *Symposium on polar organic pollutants in the aquatic environment*, No. 5 (1993)
[2] Under direction of the Landeshydrologie und -geologie, Bern

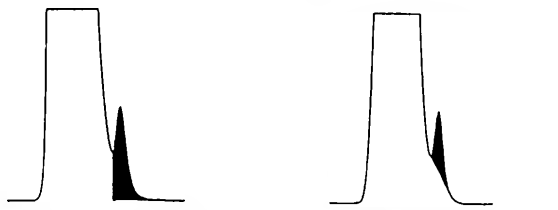
Analytische Chemie **189**

Quantitation of Second Eluted Small Chromatographic Peaks

Veronika R. Meyer
Institut für organische Chemie, Universität Bern, CH-3012 Bern

Computer simulations are used to show the problems and pitfalls associated with the quantitation of small chromatographic peaks which are eluted behind a much larger one. Depending on the size ratio and tailing of the peak pair a resolution of 2 or even 4 is necessary in order to obtain accurate quantitation; this is much higher than one would expect. The only favourable situation for integration is found when the peaks are truly Gaussian and of similar width. Then *height* determination down to the baseline should be used. If the peaks are tailed and are not resolved well enough no common integration technique (vertical drop separation or tangent skimming) gives accurate results. A special problem are narrow "rider" peaks which usually are quantitated by tangent skimming; however, this approach gives too low an area or height.

Example: Peak size ratio 100 : 1
Peak width ratio 2 : 1
Resolution 1.98
Tailing 1.5



135.5 % of true area
119.8 % of true height

58.8 % of true area
73.7 % of true height

Analytische Chemie **190**

Ion-Molecule Reactions with HCN in a Quadrupole-Quistor-Quadrupole Tandem Mass Spectrometer

S. König, P. Kofel and U.P. Schlunegger
Institut für organische Chemie, Universität Bern, CH-3012 Bern

Since on many planetary system and interstellar clouds the presence of methane, ethane, ethylene, ammonia, phosphine and hydrogen cyanide [1] has been indicated by infrared and radiometric measurements, the chemistry of these species is of considerable interest referring to the formation of prebiotic molecules. Produced by electrical discharges in the atmosphere even ionisation processes and following reaction products had been detected. The quadrupole, quistor, quadrupole tandem mass spectrometer [2] allows to explore ion-molecule reactions for both positive and negative ions. After formation in an external source, one ion species is selected by the first quadrupole and injected into the quistor for reaction with one or more neutral counterparts. The storage time and the reactant gas pressure in the quistor can be varied over a wide range. A series of experiments with these interstellar gases were performed on the quadrupole, quistor, quadrupole instrument. In particular the reactivity and reaction channels of HCN^+ and $HCNH^+$ will be discussed.

[1] V.G. Anicich, W.T. Huntress, M.J. McEwan, J. Phys. Chem, 1986, 90, 2446.
[2] P. Kofel, H. Reinhard U.P. Schlunegger, Organic Mass Spectrom., 1991, 26, 463.

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Analytische Chemie

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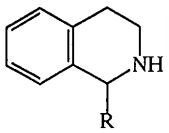
Collision-Induced Fragmentation Studies of 1-R-1,2,3,4-Tetrahydro-isochinolines and Benzaldehydoxime-O-(n)-R'-ethers

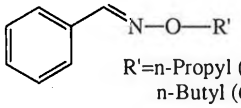
B. Pellascio, B. Aebi and U.P. Schlunegger
Institut für organische Chemie, Universität Bern, CH-3012 Bern

Mass-analysed ion kinetic energy (MIKE) experiments and the combination of MIKE experiments with collision induced dissociations (CID) are very powerful tools for the determination of molecular structures in mass spectrometry [1]. Especially the use of a floating collision cell leads to important additional structural informations.

The MIKE and the CID-MIKE fragmentations of four different 1-R-1,2,3,4-tetrahydroisochinolines and two benzaldehydoxime-O-(n)-R'-ethers have been investigated in detail experimentally in this work.



R=Methyl (1)
Ethyl (2)
Benzyl (3)
Allyl (4)



R'=n-Propyl (5)
n-Butyl (6)

As a result of this work we could show that for each chemical one fragmentation path leads to the same ion with m/z 132.

[1] R.G. Cooks, J.H. Beynon, R.M. Caprioli, G.R. Lester, Metastable Ions, Elsevier 1973

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USE OF THERMAL ANALYSIS FOR DESIGN OF THE SOLID STATE

D. Giron, Sandoz-Pharma, Analytical R&D, CH-4002 Basel

Most of the drugs are applied in the solid state. Since all the physico-chemical characteristics in the solid state are involved in the polymorphism or pseudo-polymorphism, pharmaceutical development is faced with this behaviour. Not only bioavailability differences may give rise to differences in activity or toxicity, but also stability, milling, storage and processing operations of the dosage form may be affected. Therefore the design of the desired polymorph has to be defined. With different analytical methods, thermodynamic relationships based on phase diagrams and kinetics have to be known in such a way that reproducible manufacturing procedures of raw materials may be developed and that storage or processing with excipients are controlled.
The study of polymorphism imply different crystallizations, melting, saturating experiments and selective and quick analytical methods. Thermal analysis, and combined techniques play an important role for the manufacture of single forms in situ and for the understanding of thermodynamics relationships and kinetics.
Some examples of problem solving - involving monotropy and enantiotropy as well as solvate or hydrate formation - will be given.
A scheme for design of solid state is proposed.

Analytische Chemie

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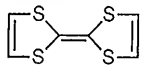
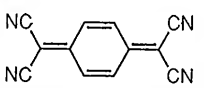
Amperometric Biosensors for Redox-Active Substrates.

J.Müller, U.Korell*, and U.E.Spichiger.
Centre of Chemical Sensors/Biosensors and (Bio-)Analytical Chemistry, D-Pharm, ETH-Zürich, Technopark, Pfingstweidstr. 30, CH-8005 Zürich.
* SANDOZ PHARMA LTD., Technical R&D, Analytical Research and Development, CH-4002 Basel.

Redox-active substrates can very generally be quantified by amperometric biosensors. The oxidation or reduction of a substrate like **hypoxanthine** or **hydrogen peroxide** is catalyzed by a specific enzyme like xanthine oxidase (E.C. 1.2.3.2.) or peroxidase (E.C. 1.11.1.7.). The selectivity of these electrodes, which discriminate even ascorbate, is determined by the low applied potential of ≈ -50mV. The electron transfer to the electrode is mediated by the organic salt tetrathiafulvalene-p-tetracyanoquinodimethane (TTF-TCNQ) (see figure).





tetrathiafulvalene (TTF) 7,7,8,8-tetracyanoquinodimethane (TCNQ)
redox couples at -100 to +300 mV vs. Ag/AgCl:
TTF^0/TTF^+; $TCNQ^-/TCNQ^0$; $TCNQ^{2-}/TCNQ^-$.

The components are not immobilized to a membrane but suspended in silicone oil. The analytical response of the electrode, the electrode current, is affected by several diffusion processes going on. However, due to the quick electron transfer induced by the mediator the chemical reaction is not governed by the diffusion of oxygen to the reactive zone. The TTF-TCNQ salt is non-toxic. The electrode acts like a reversible sensor due to the continuous, immediate regeneration of the mediator. A detection limit of 10 nM hypoxanthine or hydrogen peroxide with a response time of t_{95} ≈ 10 seconds were evaluated at a physiological pH between 6.1 to 8.8 for hypoxanthine and pH 6.0 for hydrogen peroxide. The low detection limit of the electrode provides a low substrate consumption. The lifetime of the sensors are limited by the lifetime of the enzymes. A second enzyme, purine-nucleoside-phosphorylase (EC 2.4.2.1.), was coupled to the the xanthine oxidase electrode to create a bienzymatic sensor for **phosphate**.

Analytical Chemistry

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Automated Wavelength Scanning in Two-Step Laser Mass Spectrometry: Application to Environmental Contaminants

Qiao Zhan, Pierre Voumard, and Renato Zenobi
LPAS (bâtiment de chimie), Ecole Polytechnique Fédérale, CH-1015 Lausanne

Two-step laser mass spectrometry (L2MS) is a modern analytical method that features intact vaporization and efficient soft ionization of high molecular weight compounds [1]. It utilizes a pulsed CO_2 laser for desorption of intact neutral molecules, a pulsed, tunable UV laser for resonance-enhanced multiphoton postionization, and a reflectron time-of-flight mass spectrometer for mass analysis. L2MS is a highly sensitive and optically selective surface analysis method. It can serve as a very powerful tool for the direct chemical analysis of selected compounds in complex sample mixtures, such as tissue matrices, polymer materials, environmental samples, and geo/cosmochemical materials. Because of the high sensitivity and optical selectivity of L2MS, virtually no sample preparation is needed, and spectra can be recorded in a very short time.

With increasing sample complexity, it is often necessary to obtain information in addition to the mass spectrum of the sample components, for example to distinguish isomers. Optical information can be obtained by scanning the ionization wavelength, and together with the mass spectral data, two-dimensional UV/MS spectra can be generated. This contribution describes a computer controlled system for variable wavelength L2MS. In particular, we present recent technological developments used to overcome problems with beam walk and laser power variation. We describe the application of this analytical method to the chemical analysis of polycyclic aromatic hydrocarbons (PAHs) adsorbed to aerosol particle surfaces.

[1] P. Voumard, Q. Zhan, R. Zenobi, *Rev. Sci. Instrum.* **1993**, 64(8), 2215.

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ANALYTICAL METHODS FOR QUANTITATIVE DETERMINATION OF POLYMORPHS

D.Giron, P.Piéchon, S.Pfeffer, Sandoz-Pharma, Analytical R&D, CH-4002 Basel

Polymorphism is the tendency of a substance to crystallise in different crystalline states. Polymorphs are different only in the solid state. Amorphous state is characterized by a non-ordered random system, related to the liquid state. Pseudo-polymorphs are solvates or hydrates and are correlated with phase diagrams of binary mixtures.
The progress of new methodologies allow to develop precise and sensitive analysis methods.
The contribution of different techniques including X-ray diffraction, IR, and microcalorimetry will be demonstrated.

Analytische Chemie

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Electrophoretically Mediated Microanalysis (EMMA) of Biological Extracts

Fred. E. Regnier
Department of Chemistry, Purdue University, Lafayette, IN 47907

Enzyme assays have been widely used in traditional chromatographic and electrophoretic systems to i) identify enzymes amoung the separated components, ii) establish that the three-dimensional structure of an enzyme is intact after fractionation, iii) quantify recovery and purification, iv) access the possibility of enzymatic isotypes in the sample, and v) obtain diagnostic evidence from the sample as in clinical and forensic analyses.

Studies will be reported in which enzyme activity was determined in a capillary electrophoretic system by continuously transporting substrate into the capillary during enzyme separations. Substrate transport and mixing were achieved through a combination of electroendoosmosis and differential electrophoresis in the reactants. Althoug the enzyme catalyzes product formation as it moves through the capillary, product does not accumulate. Under constant potential the enzyme and product are continuously separated. It will be shown that when the operating potential of the system is interrupted, product accumulates in the region of the enzyme. At zero potential, separation of product and enzyme ceases and product accumulates as in a batch reaction. When a detectable amount of product has accumulated, potential is again applied to the system and product transported to the detector. Through the use of laser induced fluorescence and a fluorogenic substrate it has been possible to detect 400 molecules of luecine amino peptidase. The fundamental principles of EMMA, control of separation selectivity, and application of the technique to a range of analytical problems including quantitation of enzymes in a single cell will be discussed.

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COLUMNA ANALYTICA

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HPLC'94 in Minneapolis

Veronika R. Meyer*

The motto of the 18th International Symposium on Column Liquid Chromatography, held from May 8 to 13, 1994, in Minneapolis, MN, USA, was 'Celebrating 30 Years of High Performance Liquid Chromatography'. In fact, the meeting even took place at the city where one of the earliest users of chromatography had been active decades ago. As mentioned in the opening ceremony, *Leroy Sheldon Palmer* had been professor at the University of Minnesota in Minneapolis-St. Paul from 1919 until his death in 1944. Grown up in St. Paul, the twin city of Minneapolis, *Palmer* used column liquid chromatography during his Ph.D. thesis work on the carotenoid content and composition of cattle fodder and milk. He could prove that the yellow pigments of milk (or butter) are not synthesized by the cow but have their origin in the grass; this work was performed from 1909 to 1913 at the University of Missouri in Columbia (L.S. Ettre, R.L. Wixom, *Chromatographia* **1993**, *37*, 659). In 1922, *Palmer* explained the technique of chromatography also in his book 'Carotenoids and Related Pigments. The Chromolipids'. As today's users of chromatography we should not forget that this method had a tough start and was not recognized as a valuable technique by the leading plant pigment scientists of the 1910's and even later.

**Correspondence*: Dr. V.R. Meyer
Institut für Organische Chemie
Universität Bern
Freiestrasse 3
CH–3012 Bern

These facts were briefly remembered by Prof. *Larry D. Bowers* (Indiana University, Indianapolis, IN, USA) and Prof. *Peter W. Carr* (University of Minnesota, Minneapolis) who both acted as chairmen of the symposium. They could welcome *ca.* 800 participants at the new Minneapolis convention center. The facilities rented for the symposium were large enough to allow the display of all the posters during the whole week; they were grouped around a 62-booth exhibition presenting the actual offer on instruments, columns, accessories and services in the field of chromatography. All together they gave a large show which joined research and commercial realization but regardless of this all walks were short and no poster was lost in a distant corner.

The scientific part of the meeting consisted of 5 plenary lectures, 105 lectures (which should also have been presented as a poster, but unfortunately many speakers did not use this opportunity of an additional display of their ideas) in triple sessions and 257 additional posters. This last number was planned to be higher but many (too many) poster walls remained empty. The participation in this symposium series seems to stagnate and it is still difficult to decide if this is a result of a harder economic situation or the increasing number of conferences and meetings. A HPLC symposium is no longer fancy although the topics have not lost their importance at all. The participants were rewarded with a richness on high-quality contributions which, as always, represented a good mixture of fundamental research and mature applications.

Structural Thinking

Maybe this was never expressed explicitly during the symposium, but as an observer I got the impression that concepts discussed in structural and supramolecular chemistry begin to occupy the minds of chromatographers. Of course the topic of structure-retention relationships was discussed in chromatography from the very beginning and molecular recognition models were always a driving force for the search after enantioselective separation systems. But it seemed as if these concepts have gained silently a higher level of importance and general acceptance, thus bringing a new, unspoken quality into discussions and considerations. An example was the lecture of Prof. *William H. Pirkle* who presented a deeper insight into the retention mechanisms on the chiral stationary phase Whelk-O 1 with dinitrobenzoyl-amido-tetrahydrophenanthren as selector [1]. The phase was published two years ago (W.H. Pirkle, C.J. Welch, *J. Liq. Chromatogr.* **1992**, *15*, 1947) and is commercially available for more than a year, but obviously a deeper understanding of how it works needs some time. The chiral selector of the phase is shown in *Fig. 1* and it can be seen that the dinitrobenzoyl (right) and the phenanthrene unit (left, upright) form a cleft which embraces the analyte. The better retained enantiomer of a chiral compound obviously undergoes simultaneously a face-to-edge and a face-to-face π–π interaction. As a result a wide range of aromatic compounds such as acids, amides, esters, epoxides, and sulfoxides including chiral drugs can be resolved.

Another striking example of how to create a highly selective environment for chromatographic differentiation was presented by Prof. *Fred E. Regnier*. Together with his coworkers he developed a technique for the preparation of completely synthetic affinity chromatography sorbents [2]. Molecular imprinting of a gel is not new but the selectivity and high performance obtained with *Regnier*'s approach seems to be extraordinary. A pro-

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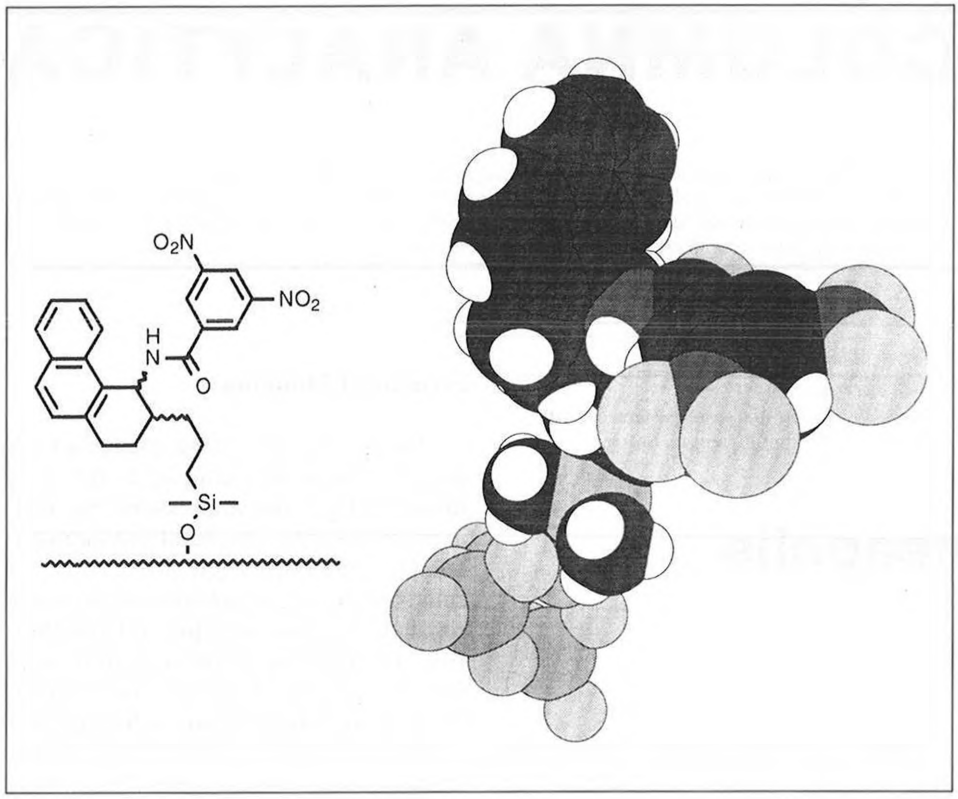

Fig. 1. *Structure of dinitrobenzoyl-amido-tetrahydro-phenanthren.* The chiral selector is bonded to silica and is commercially available as Whelk-O 1 [1].

tein is used as a template for the fabrication of a surface which is spatially complementary to the template species. Besides excellent affinity chromatographic selectivity these stationary phases are cheaper than immunosorbents and are prepared in much shorter time. Imaged surfaces have been prepared for a number of serum albumins from higher animals, lysozyme, ovalbumin, and transferrin; the latter compound could be isolated from serum in high purity. The only problem is the high price of the template protein, and *Regnier* does not yet know how to produce large amounts of a sorbent. On the other hand the procedure is so simple that it is planned to develop kits for the do-it-yourself preparation of sorbents with selectivity towards any protein the user is interested in. It is clear that the structure of the template molecule needs not to be known. The technique will be patented, so details were not disclosed.

New Approaches for Enantioselective Analysis

The use of macrocyclic antibiotics as chiral selectors has been studied and Prof. *Daniel W. Armstrong* presented them as a promising new class for the separation of enantiomers [3]. He used vancomycin, thiostrepton, and rifamycin with three, two, and one macrocyclic rings, respectively, as bonded stationary phases in HPLC and GC as well as mobile phase additive for capillary electrophoresis and thin layer or column liquid chromatography. More than hundred racemates could be resolved including some compounds which could not be separated so far. The macrocycles showed good chemical stability.

Mosbach's method for the preparation of chiral imprinted polymers was improved [4]. Polyacrylate-based stationary phases with a dipeptide imprint gave high separation factors together with remarkable chemical and mechanical stability. Excellent plate numbers, up to 40000 plates per meter for chiral separations, and high selectivity were found with polyacrylamides bonded to silica; the quality of these stationary phases depends on the preparation process, and best results were obtained by first co-polymerizing monomers (bearing functional groups which can bind to silica) together with acrylamides, then binding these polymers to silica [5]. A non-chromatographic approach for the separation of enantiomers is the use of micellar organogels which contain enzymes or any kind of chiral compound [6]. These gels are very easy to prepare and can act as enantioselective catalysts or as chiral membranes which enrich one optical isomer by a difference in transport rate through this mechanical barrier.

The importance of the capillary zone electrophoretic separation of enantiomers is growing due to the improved knowledge and increased number of chiral additives to the mobile phase. They include not only various cyclodextrins but also rifamycin and heparin [7]. A slightly different technique is the use of chiral surfactants such as *N*-dodecoxycarbonylvaline which form micelles [8]. Since both enantiomeric forms are available, the elution order can easily be adapted to the needs of a particular analysis.

The interaction between a cyclodextrin molecule which acts as a host and its chiral guest can be studied with NMR; together with capillary electrophoretic investigations it is possible to determine the relevant binding constants [9]. Similar studies of biological relevance can be performed by preparing a chiral stationary phase for HPLC which contains human serum albumin and α-acid glycoprotein in the same ratio as present in serum. Such a chromatographic system can act as a probe for serum protein binding of a great number of drugs [10].

Supercritical Fluid Chromatography

It seems as if at present SFC cannot expand its importance and range of applications although a number of highly developed instruments is on the market. (The really experienced users say that even the best instruments still suffer from technical problems.) I suppose there is not enough academic and industrial research in this

field because it is no longer 'en vogue' and many people prefer to play with capillary electrophoresis. New and promising applications are still presented in the field of enantioselective separations because SFC can yield high separation factors and short analysis time. An example is the resolution of camazepam (a benzodiazepine drug) and its metabolites by packed column SFC which was not possible by enantioselective single-column HPLC [11]. New developments allow to inject large sample volumes (up to 100 µl), including aqueous solutions, into capillary SFC which gives low detection limits and high analytical precision; also the coupling of HPLC, GC, and SFC is possible [12].

In contrast to SFC, supercritical fluid extraction is gaining popularity as a sample preparation technique. New reagents for the derivatization and thus extraction of certain compounds from a complex matrix have been developed, *e.g.* quaternary ammonium compounds which react with anionic surfactants in sewage sludge at high temperatures to give esters which can easily be extracted by supercritical fluids [13].

On the Search of Ultimate Sensitivity

Some research groups very successfully continue their efforts for ultratrace and single-cell analysis. As stated by Prof. *William S. Hancock* in his opening plenary lecture, capillary liquid chromatography can provide high sensitivity such as detection limits in the 5 ng or 200 fmol range [14]. Special techniques can make it possible to get even much lower sensitivities. Prof. *Edward S. Yeung* explained today's analytical goals by the example of blood cells [15]. A single red blood cell (erythrocyte) with a volume of 10^{-13} l contains:

potassium	8 fmol
lactate	1.3 fmol
sodium	1 fmol
pyruvate	800 amol
hemoglobin A	450 amol
glutathion	200 amol
carbonic anhydrase	7 amol
lactate dehydrogenase (LDH-1)	30 zmol
gluco-6-phosphate dehydrogenase (G6PDH)	20 zmol

The question is whether all cells are identical in their composition; the answer is no, mainly due to the differing age of the cells. Moreover, deviations from normal values can occur in the case of diseases. This gives the main stimulus for single-cell research: in an early stage of a disease only a few cells will be infected and their number is too low to show up in a normal blood test. As *Yeung* explained, the detection principle for very low concentrations is a fluorescence enzyme assay for enzymes (*e.g.* for LDH-1, but it should be possible to find appropriate substrates for all enzymes) or a particle immunoassay for other compounds (*e.g.* G6PDH). A LDH assay with a detection limit of 1.3 zmol has been published in April 1994 (Q. Xue, E.S. Yeung, *Anal. Chem.* **1994**, *66*, 1175). In Minneapolis the particle immunoassay for G6PDH with a detection limit of 1 zmol or 620 molecules was presented. The probes are antibody-coated latex particles which agglutinate in the presence of the antigen (*i.e.*, molecules of G6PDH) and the additional techniques necessary for a sensitive assay are capillary electrophoresis and laser-based particle counting. Single erythrocytes are injected into the capillary of 20 µm inner diameter and 40 cm effective length. They are lysed within 2 s, agglutination of the latex particles takes place and the aggregates (but not the single particles) are counted when they pass behind the detection window at the other end of the capillary. *Fig. 2* presents the results of the investigation of 25 erythrocytes; due to their different age the obtained counts vary between 45 and 632 per cell which corresponds to 2800 and 39000 molecules as was determined by a calibration curve.

The promising combination of chromatography (or capillary electrophoresis) with immunoassays, which is also studied intensively by *Regnier*, led to a first commercial instrument called 'Integral' by *Perceptive Biosystems* (*Paul Bucher*, Schützengraben 7, CH–4051 Basel). It

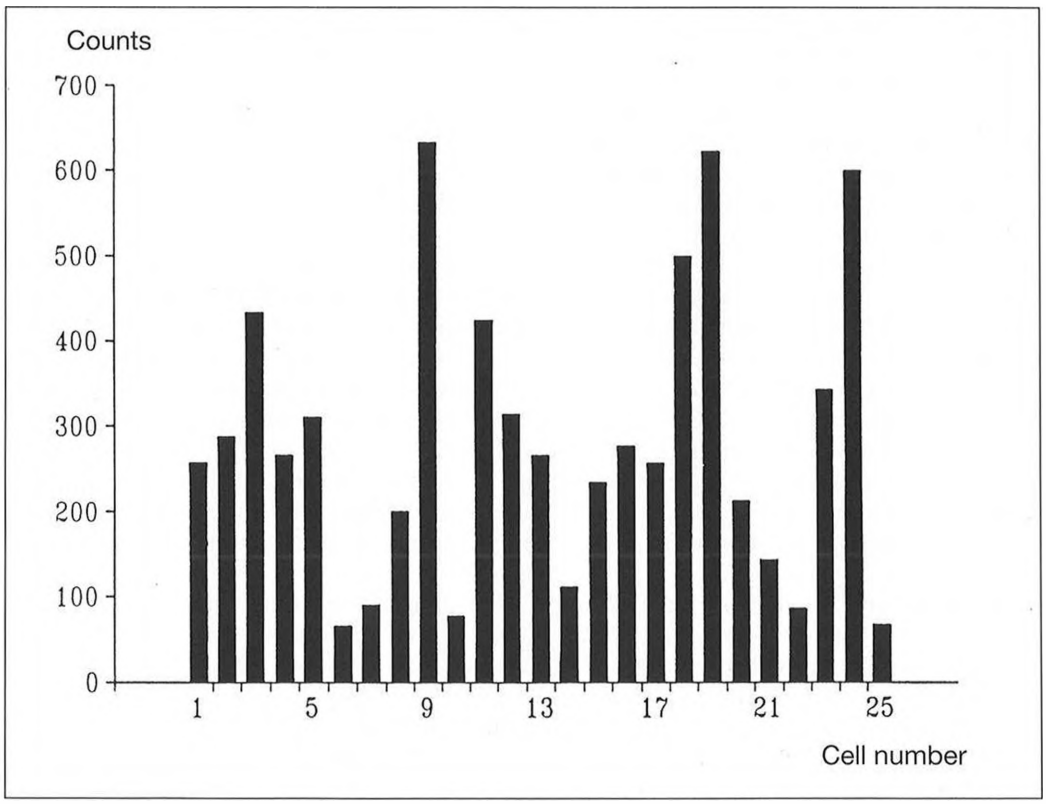

Fig. 2. *Micro particle immunoassay for gluco-6-phosphate dehydrogenase in erythrocytes.* The graph shows the number of latex agglutinates found by the analysis of 25 different single cells. 100 counts represent 6200 molecules of G6PDH, *i.e.* the oldest cells contain 2800 molecules, the youngest ones 39000 molecules [15].

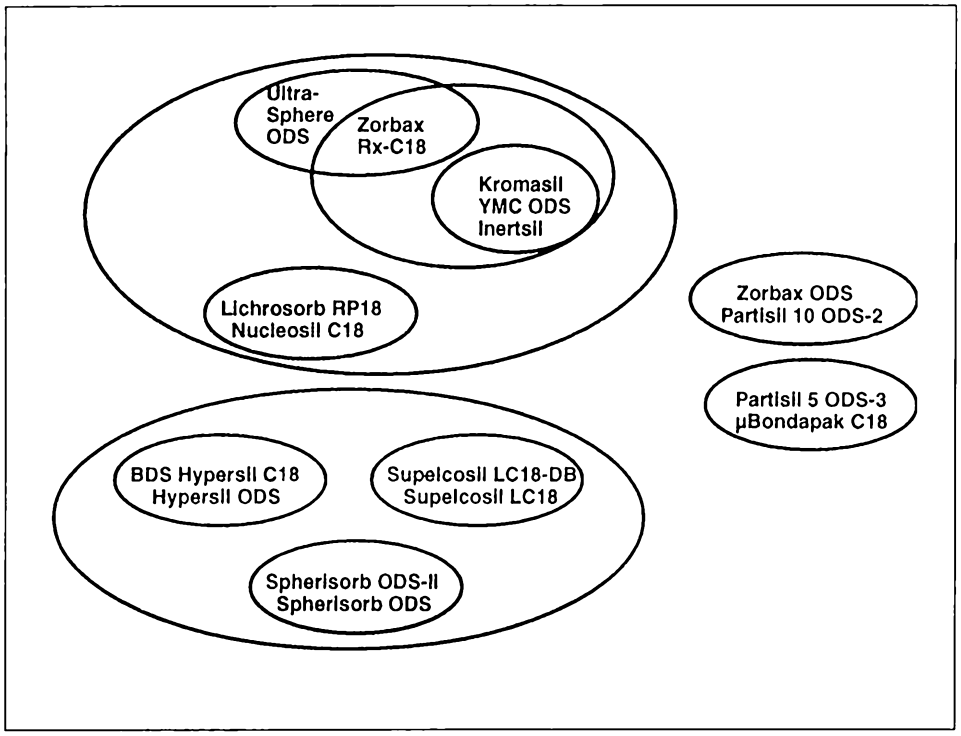

Fig. 3. *Grouping of commercially available octadecyl silica stationary phases by chemometric methods.* Phases which behave similarly are in close vicinity [21].

allows to use the two techniques individually or in combination whereby the immunoassay acts as a detection technique for the HPLC eluate.

The increasing demand for higher sensitivity coming from all fields of biology and medicine is the driving force behind the growing interest for micro packed HPLC capillaries (*LC Packings*, Dufourstrasse 30, CH–8008 Zürich). At present, it cannot be decided if the micro approach will also conquer other application fields, bringing better mass sensitivity also for less critical analyses, or if it will remain restricted to the biosciences. I hope the first scenario will come true. In a poster, very satifying conclusions could be drawn from a ten years experience with micro HPLC at *Dow Chemical Company* (Midland, MI, USA): lower solvent consumption (and costs for purchase and disposal), lower column costs, reduced maintenance requirements, excellent interfacing ability to a wide variety of detectors including the mass spectrometer, ease of coupling to multidimensional separations, and better column-to-column reproducibility [16]. Those who do not yet dare to go into the real microtechnique could try another promising approach, especially for the analysis of biomolecules:

Bischoff Analysentechnik (*Metrohm AG*, CH–9101 Herisau) just introduced well-packed columns with nonporous 1.5 μm particles. This technique combines high performance and high speed.

In the field of open HPLC capillaries Prof. *Hans Poppe* could report about his successful thick-layer concept [17]. It was possible to coat 5 μm capillaries with polyacrylate layers of 1–2 μm thickness, thus obtaining a high phase ratio. Such thick layers allow to inject larger samples which makes injection and detection problems easier to solve. The coating is stable up to pH 12.

The Contrary: Large-Scale Preparative Chromatography

All users of preparative HPLC will be grateful to learn that Prof. *Georges Guiochon* and coworkes have written a book about this topic which is published this year by Academic Press: G. Guiochon, S. Golshan-Shirazi, A. Katti, 'Fundamentals of Preparative and Nonlinear Chromatography'. This will make unnecessary the search after the numerous papers of these researchers since all their knowledge will now be found in this book. As *Guiochon* admitted in his lecture, some problems of preparative liquid chromatography are 'frustrating and interesting' at the same time [18] and the users of the technique can be grateful that excellent scientists are taking care of these problems in a superior manner.

The simulated moving bed technique is gaining importance which is documented by the fact that *Merck* (Rüchligstrasse 20, CH–8953 Dietikon) now sells an instrument of this type for use in large laboratory or pilot plant scale. In a lecture it was shown how the simulated moving bed approach cannot be only used for the preparation of commodity chemicals in the ton scale (this is already a reality in chemical industry) but also in a smaller scale for high-value specialty compounds [19]. As an example, steroid isomers (4% progesterone and 1,4% hydrocortisone in methanol) can be separated at a 32 times higher productivity than with elution chromatography; solvent usage is 16 times lower and the extract concentration is 19 times higher.

Computer-Assisted Chromatography

It is interesting to note that (at present) not much discussion is left on expert systems. It seems to be difficult to put so much knowledge into a computer that it really could replace a laboratory technician. An exception could be a specialized expert system for the troubleshooting of HPLC systems [20] which is commercially available (*LC Resources*, 2930 Camino Diablo, Walnut Creek, CA 94596, USA).

An important use of computer power is now firmly established in all kinds of data systems for chromatography. A modern data system not only controls the components of the HPLC instrument and performs the accurate integration of the chromatogram but it also includes a user-friendly and complete documentation for GLP, ISO, or EN requirements including audit trails.

Computers are also utilized for difficult detection problems, often in combina-

tion with a diode-array detector, and for a great variety of research based on chemometry. An example for the latter use is the attempt to classify the commercially octadecylsilica phases according to their similarity or dissimilarity [21]. Various test mixtures sensitive to silanol, hydrophobic, and trace metal activity as well as molecule shape selectivity were used to probe different aspects of phase behaviour. The results were investigated by principal components analysis and hierarchical cluster analysis and yielded the graph of *Fig. 3*. From this it is obvious which phases are very similar (and could be used as a substitute of each other if, *e.g.*, a certain material used in a published method is not at hand) and which ones show markedly different properties.

Thin Layer Chromatography as a Winner

Frequently HPLC and TLC are competitors and a certain analysis could be performed by both methods. Often TLC is used if sample preparation should be avoided because even a dirty sample can be spotted onto a plate which is used only once. In a forensic laboratory it turned out that TLC was favourable for other reasons. Although HPLC gave higher sensitivity in the analysis of reactive dye traces from natural fibres it is not used as a routine technique. TLC is less sensitive but it is simpler, thus it needs less staff training. But besides this TLC is preferred because TLC spots are easier to explain in courtroom situations than a more abstract HPLC curve [22]!

The Future

Again it was Prof. *Csaba Horváth* who could formulate his ideas on the present and future status of HPLC excellently in a plenary lecture (although 'prognosis is always difficult, especially if it concerns the future') [23]. He sees the nineties as an era of consolidation which also bring about a divergence of analytical and preparative/process chromatography. In *Horváth*'s opinion the milestones in chromatographic history always arose from the introduction of new column materials. The various 'silica ages' of HPLC were:

the paleolithic age with irregularly shaped mesoporous particles, the mesolithic age with spherical mesoporous particles, and now the neolithic age with gigaporous spherical particles.

Still a lot of research is done on new basic materials for HPLC (*e.g.* zirconia) and on new surface chemistries, and *ca.* 60 new commercially available stationary phases were introduced at Pittcon'94. The new surface chemistry research can also lead to membrane 'chromatography' where a single theoretical plate can be sufficient for a successful separation if the selectivity of the material is really high.

The symposium closed with an invitation to the 19th International Symposium on Column Liquid Chromatography which will be held from May 28 to June 2, 1995, in Innsbruck, Austria. Chairman is Prof. *W. Lindner* from the *Karl-Franzens*-Universität of Graz. Abstracts should be sent until Oct. 15, 1994 to HPLC'95 Secretariat, Tyrol Congress, Marktgraben 2, A–6020 Innsbruck.

[1] W.H. Pirkle, C.J. Welch, M.H. Hyun, S. Selness, 'Chiral selectors which utilize face to edge π–π interactions'.
[2] F.E. Regnier, S. Paliwal, T. Nadler, 'Molecular recognition of proteins based on surface imaged chromatographic media'.
[3] D.W. Armstrong, 'A new class of chiral selectors for LC, CE, and GC'.
[4] I.A. Nicholls, O. Ramström, K. Mosbach, 'Highly enantio-selective chiral stationary phases by molecular imprinting'.
[5] H. Engelhardt, W. Götzinger, 'Chiral polyacrylamides coated to silica for enantiomeric separation'.
[6] I. Uemasu, D. Fang, W.L. Hinze, 'Enantiomeric resolutions using «micellar» organogels'.
[7] T.J. Ward, A.J. Bell, W. Duncan, 'Chiral separations using capillary zone electrophoresis'.
[8] J.R. Mazzeo, E.R. Grover, M.E. Swartz, M. Merion, J.S. Petersen, 'Rational development of chiral separations: Theoretical aspects'.
[9] K B. Sentell, L.A. St. Pierre, 'NMR spectroscopy as a probe of inclusion complex interactions between cyclodextrins and chiral pharmaceutical compounds'.
[10] A.F. Aubry, N. Markoglou, G. Felix, I.W. Wainer, 'Evaluation of chiral stationary phases based on mixed immobilized proteins'.
[11] M.Z. Wang, M.S. Klee, S.K. Yangs, W.H. Wilson, 'Chiral resolution of camazepam and metabolites by packed column SFC'.
[12] H.J. Cortes, L.S. Green, R.M. Campbell, 'Large volume sample introduction for capillary SFC and trace analysis in complex samples using on-line coupled LC-GC-SFC'.
[13] J.A. Field, 'Chemical reagents and reactions for supercritical fluid extraction'.
[14] W.S. Hancock, J.E. Battersby, A. Guzzetta, R. Chloupek, M. Baumgardner, D.A. Lewis, 'The application of HPLC to metabolism and pharmacokinetics'.
[15] Z. Rosenzweig, E.S. Yeung, 'Laser-based particle counting microimmunoassay for the analysis of single human erythrocytes'.
[16] H.J. Cortes, C.D. Pfeiffer, J.M. Healy, K.M. Chritz, 'Microcolumn liquid chromatography: Technology for the present'.
[17] R. Swart, J.C. Kraak, H. Poppe, 'Prospects of open tubular liquid chromatography using 5 µm columns with a high phase ratio'.
[18] M. Sarker, G. Guiochon, 'Stability and efficiency of the bed packing in preparative columns operated under dynamic compression'.
[19] J.W. Priegnitz, B. McCulloch, A. Chandhok, 'Simulated moving bed adsorption as a preparative tool'.
[20] J.W. Dolan, R.W. Albrecht, L.R. Snyder, 'Expert system for troubleshooting LC problems'.
[21] B.A. Olsen, G.R. Sullivan, 'Chemometric categorization of octadecylsilyl bonded-phase silica columns using test mixtures and confirmation of results with pharmaceutical compound separations'.
[22] S.R. Crabtree, D.F. Rendle, K.G. Wiggins, M.T. Salter, 'The analysis of reactive dye derivatives from natural fibres'.
[23] C. Horváth, D. Farnan, D.D. Frey, 'Column technology in HPLC: From the first three decades to the next'.

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Chemieabteilung Ingenieurschule beider Basel, Muttenz
Zum 60. Geburtstag von Prof. Dr. *Dieter Jahn*

Lieber Dieter

Am 17. September 1994 feierst Du Deinen sechzigsten Geburtstag. Stellvertretend für Deine zahlreichen ehemaligen und derzeitigen Studierenden sowie Deine Kolleginnen und Kollegen der Ingenieurschule beider Basel gratuliere ich Dir dazu sehr herzlich und wünsche Dir weiterhin bei guter Gesundheit viel Freude an Deinem Unterricht und an Deinen vielseitigen Tätigkeiten in Deiner Freizeit!

Am 1. September sind 22 Jahre verflossen, seit Du als Dozent für Analytische und Physikalische Chemie an unsere Chemieabteilung gekommen bist. Nach der Matura in Dresden, dem Studium der Chemie in Bonn mit dem Abschluss als Diplom-Chemiker und der 1961 erfolgten Promotion in Physikalischer Chemie arbeitetest Du auf dem Gebiet von Ionenaustausch-Brennstoffzellen als Wissenschaftlicher Mitarbeiter bei der *Frauenhofer*-Gesellschaft in Bonn. 1963 führten Dich Deine beruflichen und persönlichen Interessen in die Schweiz. Als Gruppenleiter der Elektrochemie im Zentrallabor der Firma *Brown, Boveri & Co.* in Baden setztest Du Dich mit Elektrokatalyse, Brennstoffzellen und Halbleiter-Oberflächentechnologie auseinander. 1968 zog es Dich wieder nach Deutschland zurück, wo Du als Sektionsleiter Wissenschaft bei den *Langbein-Pfannhauser Werken* in Neuss die Galvanotechnische Forschung, die physikalisch-chemische Messtechnik und Analytik, die Materialprüfung und die Bereiche Physik und Chemie betreutest. Zahlreiche Publikationen und Vorträge zeugen von Deiner umfangreichen und breiten wissenschaftlichen und anwendungsorientierten Tätigkeit in der Industrie.

Dieser wissenschaftliche und technische Hintergrund, Dein angenehmer Umgang mit Menschen und Deine herausragende Begabung, komplizierte Sachverhalte, von den Prinzipien ausgehend einfach und klar darzustellen, machten es den damals Verantwortlichen leicht, Dich zum Dozenten für analytische und physikalische Chemie an unsere Schule zu wählen. Über fünfhundert Studierende konnten seither von Deinem umfangreichen Wissen, Deiner sehr sorgfältigen Unterrichtsvorbereitung, Deinem methodisch-didaktischen Geschick und Deinem individuellen und geduldigen Eingehen auf fachliche oder persönliche Probleme profitieren. Ausserhalb des Unterrichtes hast Du mit Umsicht und mit besorgtem Engagement den DECHEMA-Weiterbildungskurs in Formulierungstechnik für Industriechemiker geleitet und Dich mehrere Jahre als Mitglied des Advisory Board für den Bereich technische Chemie bei der CHIMIA zur Verfügung gestellt. Auch im Leitungsteam der Chemieabteilung, in dem Du nun 20 Jahre mitwirkst und das Du während einigen Jahren als Abteilungsvorsteher geleitet hast, schätzten wir Deine ruhige, kollegiale und gelegentlich auch von feinem Humor gewürzte Art. Lieber Dieter, alle, die Dich kennen, wünschen Dir zu Deinem sechzigsten Geburtstag viel Freude im Kreis Deiner geliebten Familie und neben der Erhaltung Deiner Freude am Unterricht möglichst viele gute Stunden beim Segelfliegen, entdeckungsvolle Reisen und eine gute Gesundheit!

Erich Flury

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Neuer Dozent für Physikalische Chemie an der Ingenieurschule Freiburg

Jean-Nicolas Aebischer*

En automne 1993, une des premières taches du doyen de la section de chimie, fut de nommer un nouveau professeur de Chimie Physique. Le choix du 'team' s'est porté sur la personne de *Jean-Nicolas Aebischer*. C'est avec plaisir que nous l'accueillons au sein de notre équipe et lui souhaitons plein succès dans son nouveau travail. Mais laissons le plutôt se présenter:
Les professeurs de chimie de l'EIF/Die Chemiedozenten der ISF

Nach dem unerwarteten und allzu frühen Tode des Dekans der Chemieabteilung und Dozenten für Physikalische Chemie Herr Prof. *Josef Portmann* habe ich im November 1993 nach einem 'Blitzaufenthalt' in der chemischen Industrie (*Ilford AG*) die Aufgabe als Lehrer für Physikalische Chemie hier an der Ingenieurschule Freiburg übernommen.

Nach der obligatorischen Schulzeit in Tafers (FR) besuchte ich das Gymnasium Heilig Kreuz in Freiburg, wo ich im Jahre 1983 die Matura Typus C ablegte. Im Herbst des selben Jahres begann ich an der Universität Freiburg mit dem Chemiestudium, welches ich im Dezember 1987 mit dem Diplom abschloss. Im Hauptfach belegte ich Physikalische Chemie und im Nebenfach Organische Chemie (Prof. *R. Neier*). Innerhalb der Diplomarbeit in Physikalischer Chemie befasste ich mich unter der Leitung von Prof. *T. Bally* und Prof. *E. Haselbach* mit der spektroskopischen Untersuchung der photochemischen Ringöffnung von Cyclobuten-Radikalkation zu Butatdien-Radikalkation in gefrorenen Gläsern bei 77 K.

**Korrespondenz*: Dr. J.-N. Aebischer
Ingenieurschule Fribourg
Sektion Chemie
4, rue du Musée
CH–1705 Fribourg

Anschliessend begann ich die Dissertation unter der Leitung von Prof. *E. Haselbach* mit dem Thema 'Mikrokalorimetrische Erfassung von intermolekularen Wechselwirkungen'. Es wurden dabei Fragestellungen aus den folgenden Themenkreisen behandelt: Kalorimetrische Erfassung von Enantioselektivität anhand der Messung von Bildungsenthalpien und Gleichgewichtskonstanten von diastereoisomeren Wasserstoffbrücken-Komplexen. Ebenso wurden die Enthalpien und die Gleichgewichtskonstanten für die Bildung von Elektronen-Donor-Akzeptor Molekülkomplexen gemessen. In einem dritten Teil der Dissertation wurde in Zusammenarbeit mit Prof. *R. Steiger* von der *Ilford AG* die Physisorption von Photosensibilisatoren (Cyaninfarbstoff) an, in Gelatine dispergierten, Silberhalogenid-Mikrokristallen untersucht. Dabei sollte vor allem auch der aus der Photographie bekannte aber mechanistisch wenig verstandene Effekt der 'Iodiddotierung' der Silberhalogenidkristalle auf die Aggregationstendenz der Farbstoffmoleküle untersucht werden. Diese Arbeit belegte, dass die Mikrokalorimetrie als komplementäre Oberflächen-Analysentechnik im Hinblich auf energetische und strukturelle Fragen einen wertvollen Beitrag zu leisten vermag.

Im Anschluss an die im Januar 1992 beendete Dissertation fing ich bei Prof. *M. S. Platz* an der Ohio-State University in Columbus als 'Postdoc' an. Während insgesamt 14 Monaten beschäftigte ich mich mit mechanistischen Aspekten der lichtinduzierten Inaktivierung von Viren. Das globale Ziel dieses Forschungsprojektes, welches eine Industriezusammenarbeit beinhaltet, ist die Inaktivierung von pathogenen Viren in Blutpräparaten. Auf der einen Seite interessierten wir uns für den Mechanismus der Reaktion des angeregten Sensibilisators mit dem vermuteten Zielmolekül, der viralen DNA. Dazu wurden 'Laser Flash Photolyse' Experimente zur Identifizierung charakteristischer Transienten durchgeführt. Andererseits interessierte uns die für die Selektivität der Methode unabdingbare Membranpenentration des Photosensibilisators. Diese Frage wurde anhand von spektroskopischen Experimenten mit Liposomen, die als Virusmembran-Modell dienten, untersucht.

In meiner neuen Funktion an der ISF geht es nun in erster Linie darum, die Ausbildung der Studenten sowohl in theoretischer als auch in praktischer Hinsicht auf einem entsprechenden Niveau sicherzustellen. Der Massstab, der diesbezüglich von meinem Vorgänger Prof. *J. Portmann* gesetzt wurde, gilt mir dabei als anstrebenswertes Ziel.

Was die spezielle Ausrichtung der Physikalischen Chemie unserer Sektion angeht, so möchte ich den Studenten die Gelegenheit geben, sich anhand von praxisorientierten Projekten mit Oberflächenphänomenen und schwachen intermolekularen Wechselwirkungen auseinanderzusetzen. Ich hoffe, mit dieser Orientierung nicht nur meinem pädagogischen Auftrag nachzukommen, sondern auch auf die Interessen der Industrie eingehen zu können. Es bleibt mir abschliessend meinen Kollegen hier an der ISF zu danken, die mir beim Einstieg in diese herausfordernde Tätigkeit mit ihrer Kompetenz und Hilfsbereitschaft beiseite standen und stehen.

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INFORMATION

29th Euchem Stereochemistry Conference Bürgenstock, May 1–7, 1994

The programme for the 29th Euchem Stereochemistry Conference covered an enormous range of chemistry, with an emphasis on the area of Molecular Recognition and Supramolecular Chemistry reflecting the Presidency of *D.N. Reinhoudt* (University of Twente, The Netherlands). This year, we were all especially pleased by the attendance of a former President, *J.D. Dunitz* (ETH-Zürich), as guest-of-honour. The participants, drawn from all over the world, were treated to lectures of the highest standard, and no-one can have left the Bürgenstock feeling anything but enthusiastic and refreshed. Support from the European Science Foundation and the Euroconferences Activity of the European Union allowed a number of younger scientists the opportunity to attend the conference and experience its unique atmosphere.

The first day of the conference was given a resounding start with the opening lecture given by *A.N. Hamilton* (University of Pittsburgh, USA), who spoke on the theme of 'The Design of Artificial Receptors for Complexation, Catalysis and Controlled Aggregation'. The main controlling feature of all the systems described was the hydrogen bond, augmented by carefully chosen use of guanidinium receptors to enhance the enthalpy of binding. Applications to the recognition of polypeptide α-helices and to the catalysis of the chorismate to prephenate rearrangement were then addressed. *R. Ungaro* (University of Parma, Italy) continued the theme of molecular recognition processes with an account of the use of versatile calixarenes. The importance of receptor conformation, and the controlling effects of metal-arene coordination, were nicely illustrated in the design of a caesium selective ligand with potential application for removal of radioactive material. Capping of calixarenes with amide linkers derived from alanine allowed the binding of D-alanine-D-alanine, the target of the antibiotic vancomycin.

The evening lecture was presented by *D.C. Wiley* (Harvard University, USA) who described structural studies on proteins important in the immune system, focusing on the interactions of these proteins with oligopeptides. The theme of the importance of protein conformation was then continued in a discussion of cell membrane fusion mediated by hemaglutinin, in which a significant change in tertiary structure is observed.

On the second day, *D.L. Boger* (*Scripps* Research Institute, La Jolla, USA) presented his recent work on the Duocarmycins, which bind to DNA in a reversible manner using an electrophilic cyclopropane as the warhead. Synthesis of a range of analogues of the natural compounds allowed a correlation between the stability of the compounds and their potency as DNA alkylators to be established. The detailed conformational preferences of the molecules, and the extent to which the cyclopropane was activated to nucleophilic attack, was shown to be crucial to their efficacy. *L.M. Gierasch* (University of Texas, USA) returned to the theme of protein structure, and particularly to the way in which polypeptide chains are transformed into their biologically active three-dimensional structure. The problem was illustrated by a discussion of Cellular Retinoic Acid Binding Protein, which possesses a significant proportion of β-sheet structure. The importance of molecular chaperones in controlling the folding process, in particular by disfavouring the formation of undesired structures by an ability to distinguish between native and non-native states, was then addressed.

The recent publication of a paper describing absolute asymmetric synthesis in a static magnetic field (*Angew. Chem.* **1994**, *106*, 460; *ibid. Int. Ed.* **1994**, *33*, 454) has generated great interest, and a discussion of these results was organised for the late afternoon of the second day. Although the principal author of the paper could not attend the discussion, we were pleased that *G. Zadel* (Universität Bonn, Germany), who had carried out a significant part of the experimental work, was able to be present. After a brief introduction to the area by *B. Feringa* (University of Groningen, The Netherlands), a lively discussion took place. The major concern of many in the audience was the lack of a clear explanation for the origin of the effect. The discussion was brought to a conclusion by *J.D. Dunitz,* who reminded the audience about the spontaneous resolution of sodium chlorate by crystallization during stirring reported by *D.I. Kondepundi* (*Science* **1990**, *250*, 975) and highlighted by *J.M. McBride* (*Angew. Chem.* **1991**, *103*, 298; *ibid. Int. Ed.* **1991**, *30*, 293) as an example of this sort of process in the solid-state. Further developments are awaited!

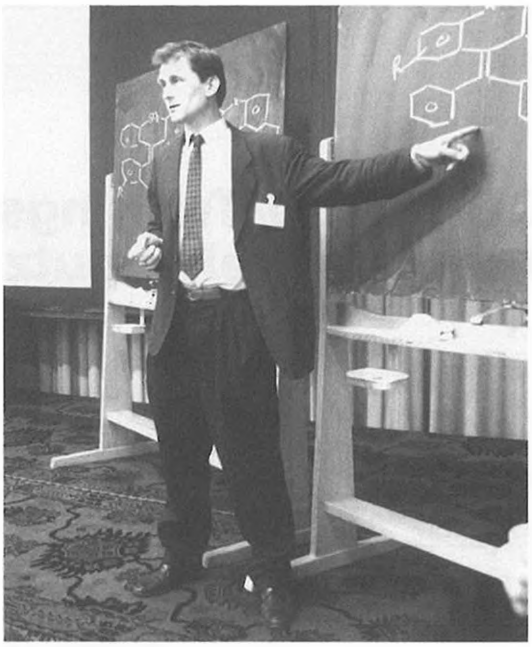
The second day was brought to a conclusion by *C.T. Walsh* (Harvard Medical School), who described studies on the two enzymes which mediate the formation of the lactate spacer which connects *N*-acetylglucosamine to the peptide chain in the peptidoglycan layer between the inner and outer membranes of bacteria. The first enzyme mediates the reaction between an *N*-acetylglucosamine unit and phosphoenol pyruvate with loss of phosphate to form an enolpyruvyl ether, while the second reduces this intermediate in a stereospecific fashion to stabilise the linker.

On the morning of the third day, the glorious weather which had been enjoyed by all the participants thus far had disappeared, and it was left to the speakers to raise our spirits. The first presentation by *V. Sniekkus* (University of Waterloo, Canada) led us on a tour through the two-dimensional world of aromatic chemistry. The audience was well-entertained, and convinced of the value of directed-metalation of a range of aromatic systems as well as the additional synthetic scope provided by subsequent transition metal-catalysed cross-coupling reactions. Recent results on the extension of the directed metalation process to remote sites were presented,

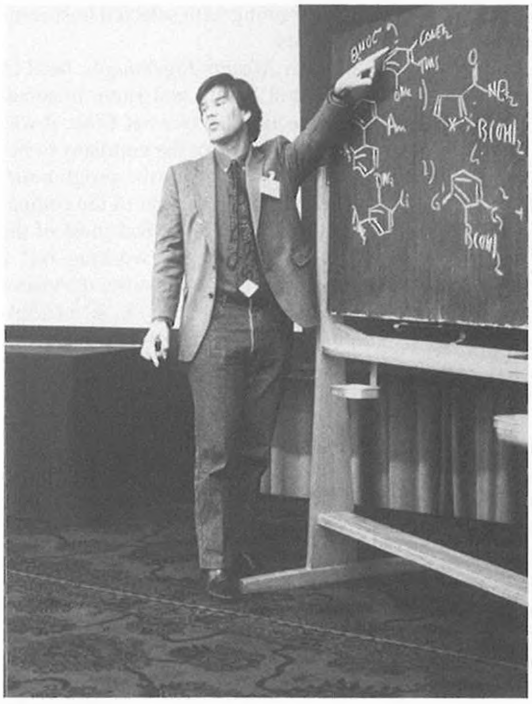
D.N. Reinhoudt (the president)

D.L. Boger

L.M. Gierasch



B.L. Feringa



V. Snieckus

S.V. Ley

amply demonstrating that this classical area is very much alive and well. The next speaker, *J.K.M. Sanders* (University of Cambridge, U.K.), returned to the central theme of the meeting with a very well-argued account of the design of synthetic enzyme mimics based on cyclooligomerization of porphyrins. Control of this process was elegantly achieved using templates which bind selectively to the desired macrocyclic host. Two examples of the use of cyclic porphyrin trimers as enzyme like catalysts were presented, including the control of the *Diels-Alder* reaction to give the thermodynamically more stable product, and the catalysis of acyl group transfer reactions. A final comparison of the relative merits of synthetic enzyme mimics and catalytic antibodies was then presented.

After a rather grey afternoon, the weather improved slightly for the traditional concert organised by *K. Müller* (*F. Hoffmann-La Roche AG*, Basel), which featured music for flute and string trio by *Rossini* and *Mozart*, either side of a *Beethoven* string trio piece.

On Thursday, *B.L. Feringa* (University of Groningen, The Netherlands) presented his work on 'Chiroptical Molecular Switches'. The key materials, highly hindered alkenes which due to distortion exist as chiral entities, can be switched between the two enantiomeric states photochemically. The second talk of the day was presented by *J. de Mendoza* (Universidad Autonoma de Madrid, Spain) who returned to the main theme of the meeting with a lecture entitled 'Self-Assembly, Molecular Recognition and Chiral Discrimination through Hydrogen Bonds'. Chiral recognition of amino acids was achieved by a linked combination of a guanidinium group and a crown ether to bind the carboxylate and ammonium groups, respectively, with additional binding using a hydrophobic aromatic system. A discussion of nucleotide receptors based on *Kemp*'s acid, and a self-assembly system which dimerises into the same arrangement as is found in a tennis ball brought the presentation to a conclusion.

The theme of the evening lecture by *G. Wegner* (*Max-Planck*-Institute für Polymerforschung, Mainz) was the use of rigid polymeric systems, in which the backbone was decorated with flexible side chains. These materials are able to self-assemble, whilst maintaining liquid-like properties in the volume were the side-chains intermesh. Applications of these materials for the preparation of semiconductors on the Ångstrom scale, and for the preparation of molecular sieves, indicated their potential uses.

The final day of the meeting began with a discussion of 'Stereognostic Coordination Chemistry' from *K.N. Raymond* (University of California, Berkeley, USA), who convinced us that he had not invented the word stereognostic, but had used the ideas of coordination chemistry to design excellent ligands for the coordination of toxic metal ions such as plutonium and lead, and also for the effective coordination of metal oxo ions by introducing hydrogen bond sites for the oxygen atoms. The metallic flavour of this session was continued with a discussion by *E. Kimura* (Hiroshima University, Japan) of the unique role of zinc cations in biological processes, in which the acidity of water molecules bound to polyamine coordinated zinc was significantly raised. The consequences of this for the mechanism of action of enzymes as carbonic anhydrase was then addressed. An example of the use of a zinc complex coordinated by a macrocyclic polyamine as a selective three-point receptor for deoxythymidine concluded the talk.

On the final evening, *S.V. Ley* (University of Cambridge, U.K.) presented a *tour de force* of synthetic chemistry in which the humble dimer of dihydropyran formed a basis for a plethora of new synthetic methods. These ranged from the stereoselective alkylation of α-hydroxyacids, to the one-pot assembly of a trisaccharide in a most impressive overall yield. The symposium was then brought to a close by *K. Müller* (*F. Hoffmann-La Roche AG*, Basel) with a masterly summary of the proceedings, which left no-one in the audience unmoved.

The 30th Euchem Conference on Stereochemistry will take place from April 30th to May 6th, 1995, at the Bürgenstock. The president will be Prof. *H. Schwarz* (Technische Universität, Berlin, Germany).

Richard F.W. Jackson, University of Newcastle upon Tyne, U.K.

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IUPAC
International Union of Pure and Applied Chemistry

IUPAC-UNESCO-UNIDO-Trainings-Programm für Sicherheit und Umweltschutz

IUPAC: International Union of Pure and Applied Chemistry

UNESCO: United Nations Educational, Scientific and Cultural Organization

UNIDO: United Nations Industrial Development Organization

Catching up on safety standards

Thai Chemist gets rundown on S+E at *Roche* Basel

IUPAC-Vizepräsident Prof. *Albert Fischli* über das Trainings-Programm

Warum hat die IUPAC dieses Ausbildungsprogramm ins Leben gerufen?

Sicherheit und Umweltschutz sind in der chemischen Industrie von globalem Interesse. Für multinationale Unternehmen gilt überall derselbe Standard. Sie wollen auch in Entwicklungsländern sicher produzieren und den Belangen der Umwelt gerecht werden. Ziel des Trainings-Programms ist es, Leute aus Dritt-Welt-Ländern auszubilden und für diese Probleme zu sensibilisieren. Dabei können uns Kongresse und Meetings, bei denen in erster Linie theoretisches Wissen vermittelt wird, nur in sehr beschränktem Masse weiterhelfen. Vielmehr braucht es weltweit Spezialisten, Zentren und Institute, die sich mit Sicherheit und Umweltschutz befassen. Um deren Ausbildung und Aufbau zu fördern, bieten wir Leuten aus Dritt-Welt-Ländern ein wirkliches Training an, Anschauungsunterricht in Unternehmen, in denen Sicherheit und Umweltschutz schon heute einen höheren Stellenwert geniessen. Sie können bei ihrem Aufenthalt den Alltag der entsprechenden Fachabteilungen kennenlernen, blicken hinter die Kulissen und kehren dann wieder zurück, um das Gelernte in ihrem Land anzuwenden.

Wie werden die Praktikanten ausgewählt? Müssen sie spezielle Qualifikationen mitbringen?

Die Länderorganisationen der UNESCO und UNIDO machen eine Art 'Vorscreening' und schlagen dann den drei internationalen Gremien einige Kandidaten zur endgültigen Auswahl vor. Bei diesem Vorscreening kommt eine Reihe von Kriterien zum Tragen: Im Vordergrund stehen das *Curriculum Vitae* und die Expertise zum anderen. Das heisst, die Bewerber müssen beruflich mit dem Bereich Sicherheit und Umweltschutz innerhalb der chemischen Produktion zu tun haben; sie müssen z.B. über eine gute Vorbildung und selbstverständlich auch über englische Sprachkenntnisse verfügen. Hauptsächlich nach diesen Kriterien werden die Praktikantinnen und Praktikanten ausgewählt. Bei der Suche nach geeigneten Gastfirmen kann dann auf persönliche Wünsche der Teilnehmerfirmen wie auch der Kandidaten eingegangen werden.

Wieviele Sicherheit- und Umweltschutzexperten aus Entwicklungsländern werden in den Genuss eines derartigen Ausbildungskurses kommen?

Etwa zehn bis zwölf pro Jahr. Die allererste Runde hat Anfang dieses Jahres begonnen. Nach Abschluss ihres Aufenthaltes werden die Leistungen der Teilnehmerinnen und Teilnehmer beurteilt. Die besonders Erfolgreichen erhalten die Gelegenheit, noch ein zweites Mal eine andere Firma zu besuchen. Diesen zweiten Kurs können sie dann, falls wiederum sehr positiv beurteilt, mit einem Zertifikat beenden.

Sinn und Zweck muss es ja sein, das Gesehene und Gelernte zu Hause in die Praxis umzusetzen. Werden die Praktikanten dabei auch über ihren Aufenthalt in einer Gastfirma hinaus unterstützt?

Verpflichtet sind die Gastfirmen dazu nicht. Die UNESCO beziehungsweise die UNIDO übernehmen die Reisespesen und die Unternehmen finanzieren den Aufenthalt. Ich bin aber überzeugt, dass die Praktikanten während ihres Aufenthaltes ihre Chance nützen und entsprechende Kontakte knüpfen. So sollten sie nach ihrer Rückkehr, wenn fachliche Probleme auftauchen, über kompetente Anlaufstellen verfügen. In diesem Zusammenhang sollte man vielleicht auch ein Projekt erwähnen, das die UNIDO in Angriff genommen hat. Sie bauen zurzeit ein sogenanntes *Global Network of Safety* auf. Im Rahmen dieses Programmes werden Schulungszentren für Sicherheit und Umweltschutz in Entwicklungsländern aufgebaut. In Indien, Indonesien und Thailand hat man schon konkrete Pläne. Und für diese Schulungszentren sollen die Teilnehmer des Trainings-Programmes als Lehrkräfte herangezogen werden.

Was kann ein Praktikant oder eine Praktikantin zum Beispiel von einem vierwöchigen Aufenthalt bei Roche *Basel mit nach Hause nehmen?*

Sie haben ein Unternehmen gesehen, das mitten in der Stadt steht und hier eine chemische Produktion unterhält. Sie haben die Einstellung der Mitarbeiterinnen und Mitarbeiter kennengelernt, das Klima in der Firma. Sie haben etwas über den hohen Stellenwert von Sicherheit und Umweltschutz in Industrieländern allgemein und speziell bei *Roche* Basel erfahren. Darüberhinaus konnten sie sich mit technischen und für sie besonders interessanten Einzelproblemen auseinandersetzen und spezifische Kontakte zu Schlüsselpersönlichkeiten knüpfen. All das wird ihnen bei der Arbeit in ihrem Lande ein gehöriges Stück weiterhelfen.

Catching up on safety standards

Polish chemist *Tadeusz Piotrowski* has just completed a one-month training and work-experience visit with *Ciba*'s Safety and Environmental Protection Department in Basel. Though the time went by much too fast, he says his hands-on look inside a modern production facility was very rewarding.

As part of a training programme initiated by the International Union of Pure and Applied Chemistry (IUPAC) in cooperation with UNESCO and UNIDO, Mr. *Piotrowski*, who works at a public institute in Warsaw, was in Basel to learn about the latest explosion prevention and process safety techniques. Aimed at safety and environment specialists from countries with development needs in this area, the programme offers visits and in-service training with selected host companies.

For *Kaspar Eigenmann*, head of Central Safety and Environmental Protection Services at *Ciba*, it was only natural for the company to become involved in the programme. *Martin Glor*, another of the company's S&E experts, had most of the responsibility for working out a schedule that would offer the visitor more than just a brief look at *Ciba*'s prevention and protection systems. 'Among other things, in the short time available Mr. *Piotrowski* had to lend a hand in our S&E lab,' says *Glor*. 'Afterwards, he was able to see the effects of the various calculations and lab experiments when we ran full-scale tests at our test site in Zeglingen.'

One of the main things the *Ciba* experts wanted to show their guest was how S&E measures are implemented. Key topics here were the use of decision trees and the standard methods and procedures employed at *Ciba* for risk analysis.

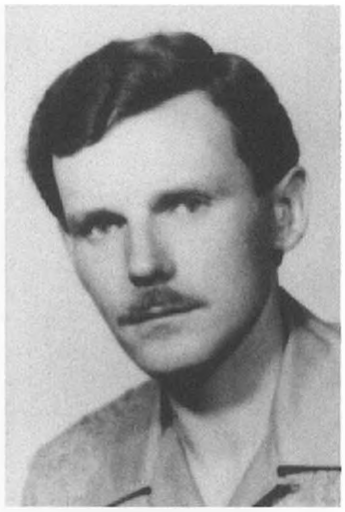
For *Piotrowski*, the electrostatic measurement of dust and solids was one of the most interesting topics. In addition, he received training in identifying and classifying risks related to static electricity in powders and other materials. The programme also included visits to companies that manufacture process equipment and machinery.

In his report to IUPAC about his stay in Basel, *Piotrowski* said that he was returning to Poland with some excellent impressions and many ideas that he would be able to apply in his work. In particular, he said, he had learned a great deal about new measurement techniques for dust explosions. He was also impressed

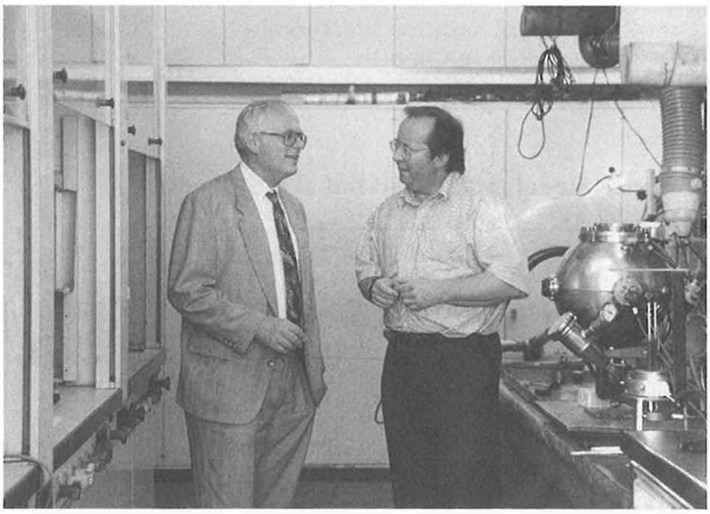
by computer methods for analysing experimental data and sees several possibilities for putting his new knowledge to practical use.

This is exactly what *Eigenmann* and *Glor* are hoping for. 'Actually, the training programme was developed with specialists from developing countries in mind', says *Eigenmann*, 'but it's also proved useful for colleagues from Eastern Europe. For many years, safety and environmental protection did not exactly have top priority there.' He believes that if training programmes like this can help them close the gap, the effort and expense involved is worthwhile for both sides of the partnership, especially in terms of safety in the chemical industry and environmental quality.

For *Martin Glor*, there is also another issue. Research-based companies in the West use, state-of-the-art equipment, and this was certainly something new for their trainee. But, says *Glor*, 'let's hope he will try to persuade the people at home to buy the same equipment, in the interests of the environment'.



Tadeusz Piotrowski



Dr. Eigenmann, *corporate safety officer* (left) *and Dr.* Glor, *both from* Ciba-Geigy AG, *Basel, Switzerland in one of the company's safety research laboratories*

Prof. Albert E. Fischli (IUPAC Vice-President, left) *and Dr.* Louis Schnurrenberger, *both from* F. Hoffmann-La Roche Ltd., *Switzerland, in front of one of the company buildings*

Dr. Marisa Arunchaiya, *head of the analytical laboratory of the Ministry for Science and the Environment in Bangkok, Thailand*

Thai chemist gets rundown on S+E at *Roche* Basel

The schedule this young lady received was pretty impressive: a crowded four-week training programme at *Roche* Basel, where she was the guest of the Department of Safety and Environmental Protection. During her stay, she got to know nearly every section of the CSE and PSU departments, *e.g.*, special areas such as plant safety, the incident task force and technical safety, the environmental protection laboratories, and the units for safety and health safeguards at the workplace.

Dr. *Marisa Arunchaiya* is from Thailand; she heads the analytical laboratory of the Ministry for Science and the Environment in Bangkok. Her work there is mainly concerned with the study of industrial chemicals. She was the second person to take part in a course jointly sponsored by two United Nations agencies, UNESCO and UNIDO, in collaboration with IUPAC (International Union of Pure and Applied Chemistry). The training programme offers safety and environmental protection experts from developing countries the opportunity of receiving continuing education in their specialist field, as guests of selected companies.

Dr. *Louis Schnurrenberger* developed the programme for the young scientist and oversaw her stay at *Roche*. Dr. *Arunchaiya* demonstrated her eagerness to learn by following up particular questions and setting priorities of her own. She was especially interested in the waste recycling and waste analysis units, risk analysis in chemical production and industrial hygiene, as well as gaining a deeper insight into the field of *Good Laboratory Practices* (GLP). The introduction of this internationally accepted standard for determining the properties of chemical substances is currently high on the agenda in Thailand. However, putting the guidelines into practice is still fraught with problems.

During her stay in Basel, Dr. *Arunchaiya* lived in an apartment in the 'Spalen' quarter. This gave her an opportunity to learn something of the other sides of city life, apart from its chemical industry. Her programme included a religious service each Sunday. This is how she summed up the visit: 'The stay in Basel more than lived up to expectations. I have become more aware of and knowledgeable about the environmental protection and safety problems we face in Thailand. *E.g.*, I have realized that, to solve certain problems, it generally needs several well-coordinated organizations. I also got ideas and inspiration about where to start making changes. I hope that everything I learned during this visit will contribute to progress in this field in Thailand.'

Louis Schnurrenberger also gives an upbeat assessment: '*Marisa Arunchaiya* was highly competent and already familiar with some aspects of the subject. In my view, that is the key to getting the most out of an educational visit of this nature. Otherwise, we could have done little more than convey the briefest of overviews. Dr. *Arunchaiya* was able to gain a valuable insight into the work of our Safety and Environmental Protection Department and take comprehensive documentation back with her. She made numerous contacts and saw – for example – how important it is for industry and the authorities to cooperate closely. My colleagues and I have also benefited from this visit: we have had a glimpse into world of industry in Thailand. *E.g.*, we were surprised to learn how modern the analytical laboratories in Thailand are, though there are often problems getting equipment properly serviced.'

Once back home, Dr. *Arunchaiya* will first be getting back into her normal work routine. But she is keen, in the very near future, to put what she has learned into practice. One definite result of her stay is that *Marisa Arunchaiya* now has lines of communication to experts in Basel: 'All the specialists I met did everything possible to explain things to me, but they also offered advice about how to deal with particular problems which might crop up in the future.'

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Schweizerisches Komitee für Chemie
Comité Suisse de la Chimie

A Bronze Medal for Switzerland at the Chemistry Olympiad 1994

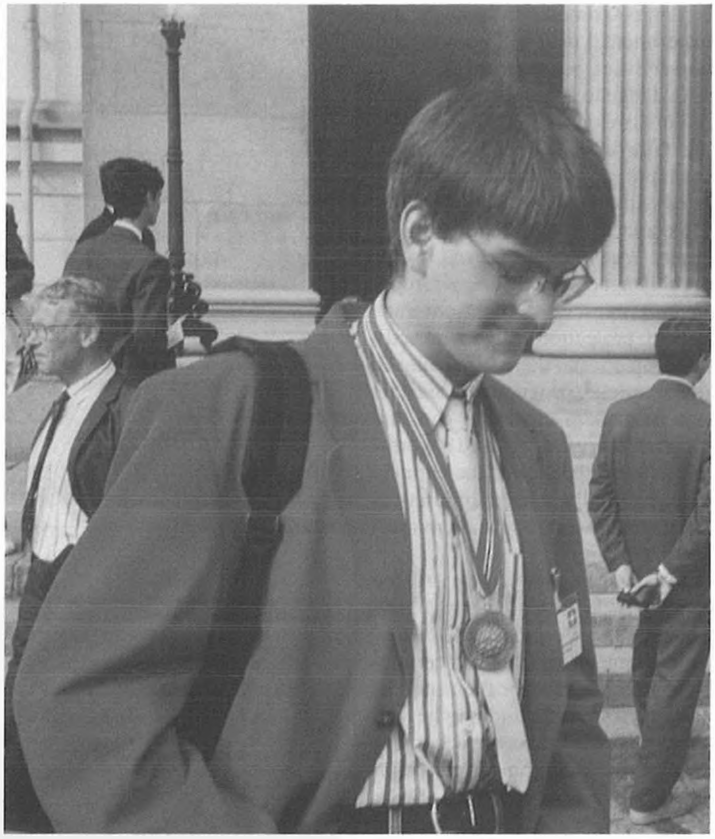
Yes, we got it! Switzerland has obtained a bronze medal at the 26th International Chemistry Olympiad in July 1994, thanks to *Wendelin Stark*, a 18-years old student from the Gymnasium Rychenberg in Winterthur. And *Simon Brugger*, from Salins VS, has obtained a honorable mention.

The 26th International Chemistry Olympiad took place from July 3rd to July 11th in Oslo, Norway. Forty-one countries sent a delegation of their four best students, coming from a pre-university level. After tough theoretical and practical competitions, the best students were rewarded by gold, silver, and bronze medals. The first 10% get gold medals, the next 20% silver, and the next 30% bronze medals. Honorable mentions were delivered to those students having solved at least one theoretical problem without any mistake. But they had all the opportunity of exchanging ideas with young people from all over the world during sport activities and sightseeing trips. This meeting of young people with a common interest in chemistry is one of the aims of the Olympiads.

The best results went to a Russian (83.9 points out of a maximum of 100), a Lituanian, and Korean student. Thanks to *Wendelin Stark* (66.7 points), Switzerland has obtained a bronze medal, at a drastic difference from 1992 results, where we got no medals at all. Whatever his achievement, it must be stressed that *Wendelin Stark* is not a good image of a 'bright student': he is more. He is even a remarkable exception in our country, since he has developed a nice private laboratory at home, where he can carry out difficult organic synthesis, even under nitrogen pressure. He is already working with professors from Zürich University and chemists from *Firmenich*; he has even obtained organic compounds that have never been synthesized before. Without his unique performance, Switzerland would have been deprived of medals, like Belgium, Cyprus, Finland, Greece, Kuwait, Slovenia, and Venezuela.

If Switzerland wants to get olympic medals in the future, more intense preparation has to be carried out. In all countries national delegates are trained by the Ministry of Education in official preparation camps during about two weeks. In Switzerland more extensive training should be done in the future for preparing the following Olympiads: Beijing 1995, Moscow 1996, Montreal 1997, Melbourne 1998. And more teachers should be involved in the whole operation.

The members of the Swiss olympic team 1994 were:
- *Simon Brugger*, *1975, 1991 Salins.
- *Rita Mayer-Sommer*, *1976, 8053 Zürich.
- *Philippe Nihan*, *1976, 1028 Préverenges.
- *Wendelin Stark*, *1976, 8400 Winterthur.



Wendelin Stark

From left to right: Rita Mayer, Simon Brugger, Maurice Cosandey, *the guide*, Wendelin Stark

The problems to be solved by the candidates were the following:

Problem 1 (8 points)

Lactic acid is produced in the organism by the muscular metabolism. But it is neutralized in the blood by the hydrogenocarbonate ions HCO_3^-, as will be shown later on. Dissociation constant for lactic acid HL is $K_{a\,HL} = 1.4 \cdot 10^{-4}$ and for carbonic acid: $K_{a1} = 4.5 \cdot 10^{-7}$ and $K_{a2} = 4.7 \cdot 10^{-11}$. In the following questions, carbonic acid is assumed to be entirely dissolved (no gas).

a) Calculate the pH of a HL soln. $3.00 \cdot 10^{-3}$ M.

b) Calculate the equilibrium constant for the reaction between HL and hydrogenocarbonate HCO_3^-.

c) $3.00 \cdot 10^{-3}$ mol HL is added to 1 l of a 0.024M $NaHCO_3$ soln., so that HL is totally neutralized. Determine the pH of the $NaHCO_3$ soln. before and after addition of HL.

d) Suppose that the pH changes in the blood from 7.40 to 7.00 due to lactic acid production after a given muscular activity. If blood is treated as a simple 0.022M hydrogenocarbonate soln. with pH = 7.40, how many moles of lactic acid HL are to be added to 1.00 l of this soln. to cause the same pH change?

e) A sat. $CaCO_3$ soln. has a pH 9.95. Determine the solubility of $CaCO_3$ in water and show that its solubility product is $K_s = 5 \cdot 10^{-9}$.

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f) Determine the maximum concentration of free Ca ions at pH 7.40 and with $[HCO_3^-]$ = 0.022M as studied in *d*).

Problem 2 (6 points)

Nitrogen content in food is usually determined by the following *Kjeldahl* method. The food sample is digested in hot H_2SO_4, where all N atoms are converted into ammonium ions. Then NaOH is added and ammonia NH_3 is produced, then transported and collected in an excess of HCl soln. This partially neutralized HCl soln. is titrated by a standardized NaOH soln., so that the initial amount of nitrogen can be calculated.

a) 0.2515 g of a cereal is digested with H_2SO_4. NaOH is added and ammonia is absorbed in 50.00 ml of 0.1010M HCl. 19.30 ml of 0.1050M NaOH is needed to neutralize the excess of HCl. What is the amount of nitrogen in the sample in % mass?

b) What is the pH in the soln. in a) after addition of 0 ml, 9.65, 19.30, and 28.95 ml of NaOH? The acidity constant K_a for the ammonium ion is $5.7 \cdot 10^{-10}$.

c) Draw the titration curve.

d) What should be the limits of the pH domain for an indicator suitable for this titration?

e) The same *Kjeldahl* method is used to determine the molecular mass of amino acids. Suppose that 0.2345 g of the amino acids **A** is digested so that the ammonia produced is collected in 50.00 ml of 0.1010M HCl. And back-titration is done using 17.50 ml of 0.1050M NaOH. What is the molecular mass of this amino acid **A**?

Problem 3 (9 points)

a) Draw the *Lewis* structure of the following compounds: SCl_2, SO_3, SO_2ClF, SF_4, and $SBrF_5$.

b) Draw carefully their geometrical structures.

c) Consider one compound X containing one sulphur atom, oxygen and one or several halogens. In water this compound X is destroyed without oxidation, reduction, precipitation or gas formation. The resulting soln. is tested with reagents in 0.1M concentration. Which ions can be detected with the following tests?

i) addition of HNO_3 and $AgNO_3$
ii) addition of $Ba(NO_3)_2$
iii) addition of NH_3 up to pH 7, then addition of $Ca(NO_3)_2$
iv) addition of $KMnO_4$, then $Ba(NO_3)_2$
v) addition of $Cu(NO_3)_2$

d) Tests described in *c*) with the aq. soln. from X give a yellowish precipitate in *i*), no precipitate in *ii*), *iii*), and *v*). In *iv*) the color of $KMnO_4$ disappears, and a white precipitate is produced after addition of $Ba(NO_3)_2$. What are the possible formulas for X?

e) 7.190 g of X is dissolved in 250.0 ml of water. To 25.00 ml of this soln. some nitric acid is added and enough $AgNO_3$ to get full precipitation: 1.452 g of precipitate is obtained. What is the formula X?

f) What is the equation of the reaction between X and water? If no value has been obtained in *e*), assume that X is SOClF.

Problem 4 (8 points)

Platinum(IV) oxide is a solid that can be prepared in the laboratory, knowing that it is in equilibrium with Pt metal and pure oxygen at 650° at the pressure of 1 atm (= $1.01325 \cdot 10^5$ Pa).

a) As no platinum(IV) oxide has been found naturally on earth, what can you infer about the conditions existing on earth during its formation? Was the oxygen pressure bigger, equal, or smaller than 1 atm? Was the temperature higher, equal or smaller than 650°?

b) What are the ΔG and K_p values for the formation of platinum(IV) oxide at 650° if the oxygen pressure is 1 atm?

c) Platinum(IV) oxide can be obtained by heating a soln. containing hexachloroplatinate(IV) ions in the presence of sodium carbonate. The obtained precipitate $PtO_2 \cdot nH_2O$ can be transformed into platinum(IV) oxide at higher temperature. Later on, it will be assumed that n = 4. Write the equations for the preparation of platinum (IV) oxide.

d) $PtO_2 \cdot 4H_2O$ (or $Pt(OH)_4 \cdot 2H_2O$) is soluble in both basic and acidic solns. Write the equations of these dissolutions in HCl and NaOH.

e) Platinum can be dissolved in aqua regia with formation of hexachloroplatinate(IV) ions. Aqua regia is a mixture of conc. HCl and HNO_3 in the ratio of 3:1; it contains nitrosyl chloride (NOCl) and atomic chlorine formed during the mixing. This atom is supposed to be responsible for the dissolution of Pt. Write the equation for the formation of aqua regia, and of its action on platinum.

f) The hexachloroplatinate(IV) ion can be precipitated from its soln. as ammonium hexachloroplatinate (IV). Pyrolysis of this compound yields platinum powder and gaseous products. What is the equation for this pyrolysis?

g) Ammonium hexachloroplatinate (IV) can be transformed into $Pt(NH_3)_2Cl_2$ which may have two different structures:

- a *cis*-structure ΔH_f° = −467.4 kJ/mol, ΔG_f° = −228.7 kJ/mol)
- a *trans*-structure ΔH_f° = −480.3 kJ/mol, ΔG_f° = −222.8 kJ/mol).

Is the geometrical structure of $Pt(NH_3)_2Cl_2$ linear, planar, tetrahedral, or octahedral?

h) What is the most stable form, the *cis* or the *trans* one?

i) Platinum can be used as a catalyst to help transforming CO ΔH_f° = −110 5 kJ/mol, ΔG_f° = −137.3 kJ/mol) and oxygen into CO_2 ΔH_f° = −393.5 kJ/mol, ΔG_f° = −394.4 kJ/mol). Is the reaction spontaneous at 25°? Is it exothermic? Calculate ΔS° for this reaction. Does the entropy increase or decrease in this reaction?

j) Plot the equilibrium constant *vs.* temperature.

Problem 5 (8 points)

a) What is the IUPAC name for $(CH_3)_2CHCH(CH_2CH_3)(CH_2CH_2CH_3)$?

b) How many isomers including stereoisomers are there for C_5H_{10}?

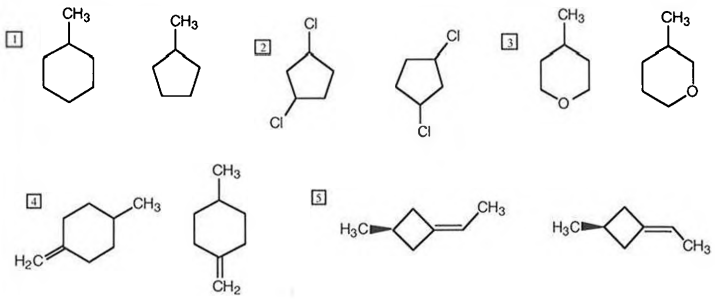
c) Which of the following compounds have a dipole moment different from zero?

g) Which of the following neutral molecules have no formal positive or negative charges: $(CH_3)_3N-B(CH_3)_3$; $(CH_3)_2N-O-CH_3$; $CH_2=N=N$; $(CH_3)_3N-O$; $F_3B-O(CH_3)_2$?

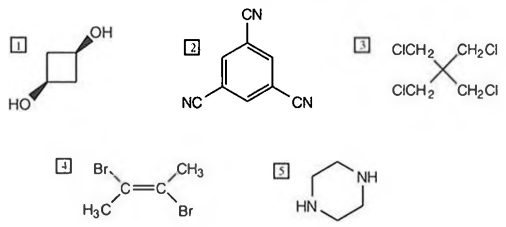
Problem 6 (9 points)

A compound **A** ($C_{12}H_{16}O$) is optically active and displays a strong IR absorption between 3000 and 3500 cm^{-1} and two middle absorptions at 1580 and 1500 cm^{-1}. **A** does not react with 2,4-dinitrophenylhydrazine (2,4-DNPH). However, mixed with I_2/NaOH, **A** is oxidized and reacts positively with the iodoform test. Ozonolysis of **A** (O_3, than Zn/H^+) yields **B** ($C_9H_{10}O$) and **C** ($C_3H_6O_2$). Both **B** and **C** produce a precipitate with 2,4-DNPH, but only **C** reacts with *Tollens*' reagent. Two mononitrated derivatives **D** and **E** can be written from **B** but the nitration of **B** (HNO_3/H_2SO_4) produces only **D**. The product obtained from **C** with *Tollens* reagent is acidified and heated. It yields **F** ($C_6H_8O_4$) which displays no absorption in the infrared above 3100 cm^{-1}.

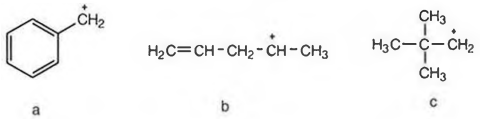
a) Draw the formulas for **A** to **F** and describe all the previous reactions



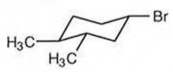
d) Which of the following pairs are structural isomers?



e) Group the following structures by order of increasing stability.



f) What is the correct description for the following compound .



1*R*,3*R*,4*R*, 1*R*,3*R*,4*S*, 1*R*,3*S*,4*R*, 1*S*,3*S*,4*R*, or 1*S*,3*S*,4*S*?

including the iodoform test, with 2,4-DNPH and *Tollens* reagent.

b) Draw the structure of compound **C** in the (*R*)-configuration using a *Fischer* projection. Is it D or L?

Problem 7 (5 points)

a) Determine the work done by one mole of ideal gas in an isothermal expansion from $V_1 = 1.00$ dm^3 to $V_2 = 20.0$ dm^3 at $T = 300.0$ K.

b) Determine the heat transferred to the gas in this expansion.

c) In an adiabatic expansion the work produced by the gas is smaller than in an isothermal process. Which of the three following sentences explains best this peculiarity? 1. The volume of the gas is maintained constant; 2. The expansion is always irreversible; 3. No heat is provided to the gas.

Problem 8 (7 points)

a) ^{238}U undergoes many α- and β-disintegrations before being transformed into stable ^{206}Pb.

i) How many α- and how many β-disintegrations does it undergo before becoming stable?

ii) Which is the only one of these nuclides which appears in the chain of disintegrations of ^{238}U: ^{235}U, ^{234}U, ^{228}Ac, ^{224}Ra, ^{224}Rn, ^{220}Rn, ^{215}Po, ^{212}Po, ^{212}Pb, ^{211}Pb?

b) What is the fragment X produced in the following fission process? $^{235}U + n \rightarrow {}^{137}Te + X + 2n$

c) Natural uranium is formed by 99.28% ^{238}U and 0.72% ^{235}U. Half-lifes of ^{238}U and ^{235}U, respectively, are $4.5 \cdot 10^9$ and $7.0 \cdot 10^8$ years.

i) What is the ratio of their activities in natural uranium?

ii) A mineral contains 50% in mass of uranium. Determine the activity due to ^{238}U in 1.0 kg of this mineral.

d) Consider the radioactive filiation: $^{97}Ru \rightarrow {}^{97}Tc \rightarrow {}^{97}Mo$ (stable), whose half-lifes are: for ^{97}Ru 2.7 d, for ^{97}Tc $2.6 \cdot 10^6$ years. At t = 0, a ^{97}Ru source has an activity of $1.0 \cdot 10^9$ Bq. What is its activity at t = 6.0 d and at t = 6000 years?

Practical problem 1 (2.5 h)

The sample to be analyzed is a 12 ml soln. containing some EtOH and 6 g of an unknown oily mixture made of fatty acids and ethyl esters of these fatty acids.

1. *Determination of the acidity index*. Transfer 2.00 ml of the unknown soln. into a 250 ml flask. Add 100 ml of EtOH/ether 1:1 and 5 drops of indicator. Titrate with an 0.10M alcoholic soln. of KOH. Calculate the acidity index, *i.e.*, the mass of KOH in mg required to neutralize 1 g of the oily acid/ester mixture.

2. *Determination of the saponification index*. Transfer 2.00 ml of the unknown soln. into a 250 ml flask. Add 25.0 ml of an 0.50M alcoholic KOH soln. Heat under reflux for 30 min. Cool with tap water. Transfer the soln. into a 50 ml calibrated flask, and fill it up with EtOH/H_2O 1:1. Pick up 10 ml of this soln., and titrate with 0.1M HCl and phenolphthalein. Calculate the saponification index, *i.e.*, the mass of KOH in mg required to saponify 1 g of the oily acid/ester mixture.

3. *Determination of the iodine number*. In this operation IBr undergoes a simple addition to the C=C double bonds of the oil. IBr is used as a 0.2M soln. in AcOH (*Hanus*' reagent). As IBr is used in excess all unsat. molecules are consumed. The remaining IBr is then transformed into I_2 by adding I^- ions according to:

$$IBr + I^- \rightarrow I_2 + Br^-$$

The iodine I_2 produced is titrated by a thiosulfate soln.

Transfer 1.00 ml of the unknown soln. into a 500 ml flask. Add 10 ml CH_2Cl_2 and 25.0 ml of *Hanus*' soln. Cover with aluminium foil. After 30 min, add 10 ml of a 15% KI soln. Stir vigorously and add 100 ml of H_2O. Titrate with 0.20M sodium thiosulfate. When the soln. is pale yellow, add 3 ml of a starch soln. Titrate up to total discoloration. Determine the iodine number, *i.e.*, the mass of iodine I in g that could react by addition of IBr with 100 g of the oily ester/acid mixture.

4. *Final analysis*. Calculate the number of moles of ester contained in 1.00 g of the oily acid/ester mixture.

Practical problem 2 (2.5 h)

The concentration of bromide ions in an aq soln. is determined by adding an excess of silver ions which produces a pale green-yellowish precipitate of AgBr. The silver ions in excess are titrated by slowly adding a soln. of thiocyanate, which produces a white precipitate of silver thiocyanate.

$$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$$
$$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(s)$$

The end of the AgSCN precipitation is determined by the interaction of ions Fe(III) which produces an intense red color with thiocyanate ions according to the equation:

$$Fe^{3+}(aq) + SCN^-(aq) \rightarrow FeSCN^{2+}(aq)$$

i) *Titration of bromide in an unknown solution*. Transfer 25.00 ml of the unknown bromide soln. into a 250 ml flask. Add 5 ml of 6M nitric acid, then 25 ml of 0.100M silver nitrate, and 1 ml of Fe(III) soln. as indicator. Titrate the excess of silver ions with a soln. of *ca.* 0.08 M KSCN. The end-point is defined by the appearance of a faint but stable brownish color in the soln. (containing also the precipitate).

ii) *Standardization of the thiocyanate*. Transfer 25.00 ml of the silver nitrate soln. into a flask. Add 5 ml of 6M nitric acid, 1 ml of indicator (Fe(III) soln.) and *ca.* 25 ml of water. Titrate this silver soln. with the same KSCN soln. and determine the end-point by the same method.

Calculate the concentration of the KSCN soln. and then the concentration of the bromide soln.

iii) *Final theoretical calculations*. At the end-point of the double titration of bromide and thiocyanate, the soln. is saturated in both AgBr and AgSCN. Determine the concentration in free bromide ions in the soln., taking into account the following solubility products: K_s (AgBr) = $5.00 \cdot 10^{-13}$ and K_s (AgSCN) = $1.00 \cdot 10^{-12}$.

Dr. *Maurice Cosandey*
Committee on the Teaching of Chemistry (IUPAC)

Neue Schweizerische Chemische Gesellschaft Sektion Medizinische Chemie (SMC)

5th Annual Meeting, Institute of Organic Chemistry, Basel, May 26, 1994

Prof. *Jonathan A. Ellman*, University of California at Berkeley, succeeded to attract more than one hundred medicinal and organic chemists to his lecture on 'Combinatorial Synthesis and Evaluation of Compound Libraries Based upon Pharmacophore Structures'. Prof. *Ellman* has won instant recognition for his 'seminal work on the solid phase synthesis of 1,4-benzodiazepines (*J. Am. Chem. Soc.* **1992**, *114*, 10997), which layed the ground for the creation of a small-molecule library of one of medicinal chemistry's most notable pharmacophores and represents one of the first examples of the application of combinatorial organic synthesis to nonpolymeric organic compounds' (E.M. Gordon et al., *J. Med. Chem.* **1994**, *37*, 1385). He dissected 1,4-benzodiazepines into three components, aminobenzophenones bound to a solid support, commercially available protected α-aminoacids and a plentitude of alkylating agents. After working out an expedient synthesis for substituted aminobenzophenones by coupling *o*-nitroarylstannyl derivatives bound onto solid support with substituted benzoic acid chlorides using *Stille* chemistry, he was able to set up >100 aminobenzophenones on solid support. Combinatorial synthesis with >40 protected α-aminoacids and >50 commercially available alkylating agents permit >20000 permutations. Because of problems encountered with arginine- and histidine-derivatives, *Ellman* succeeded to synthesize 10800 compounds – on pins. The final products were liberated into 96 well microtiter plates, ready for testing in various binding and enzyme assays (CCK, HIV Tat, Ras farnesyltransferase, tyrosine kinases). In the meantime Prof. *Ellman* has expanded his approach to β-turn mimics (3220 compounds) as mimetics for somatostatine. Furthermore, he synthesized antiinflammatory α-alkylarylacetic acids by firstly selectively mono-alkylating a trisanion of substituted *p*-halophenylacetic acids – attached on solid support – in α-position and secondly by alkylating the *para*-position using the *Suzuki* coupling reaction with alkylboranes and palladium catalysts. More recently, he applied the combinatorial library concept to the synthesis of large numbers of prostaglandine derivatives: 4α-hydroxycyclopentenones were fixed on solid support *via* a tetrahydropyranyl-ether linkage. Organozincate conjugate addition, followed by alkylation of the intermediate enolate, provided both PG side chains.

In the following administrative part of the meeting the members of the SMC accepted the report of the cashier (Dr. *A. Storni*) and a minor amendment of the regulations (Article 8: the term of the SMC committee was extended from two to three years in accordance with the three years term of the NSCG committee). The chairman, Dr. *E. Kyburz*, announced that two members of the board, Drs. *J. Kalvoda* and *A. Storni*, will no longer be available for a next term. He expressed his thanks for their much appreciated contributions and extended a cordial invitation to our colleagues to propose their candidacy for the impending election in fall for the next three year period 1995–1997.

Dr. *Wolfgang Fröstl*, Ciba

CHIMIA 48 (1994) Nr. 7/8 (Juli/August)

Tagungen, Veranstaltungen, Weiterbildung

European Federation of Biotechnology

ECB 7 and BIOEXPO 95

The two major events of European Biotechnology held together for the first time

Nice (France), February 19–23, 1995

ECB7, 7th European Congress on Biotechnology, and BIOEXPO 95, 6th Exhibition of Biotechnology Applied to Research, Industry and Agriculture, will be held together at the Acropolis Center, Nice (France), from February 19 to 23, 1995.

For the first time, on the occasion of the *Pasteur* commemoration year, these two major venues will be united in a single event, linking science and technology, which will be a milestone in the sphere of biotechnologies.

ECB7: A complete panorama of the state of the art of biotechnologies worldwide

Since 1978, the European Congress on Biotechnology brings together regularly over 2000 participants representing the European and world elite of specialists in the biotechnologies: researchers, academics, industrialists, members of national and European Union administrations...

After Switzerland, United Kingdom, Germany, The Netherlands, Denmark, and Italy, it is now the turn of France to welcome the 7th edition of the Congress (ECB 7) in the year commemorating the centenary of the death of *Pasteur*.

Over five days (February 19–23), ECB 7 will offer a complete panorama of the recent acquisitions as well as of the prospects in the field of the biotechnologies through 10 plenary conferences, 60 parallel sessions (symposia, workshops, roundtables), and some 1500 poster communications.

The Congress will naturally cover recent discoveries in all the basic disciplines of the biotechnologies, but also new breakthroughs in applications, current and potential markets, the socio-economic and regulatory context.

BIOEXPO 95:

The showcase of technological innovation

Since its creation in 1985, BIOEXPO is, every two years in Paris, the showcase of innovation devoted exclusively to the 'life sciences' techniques constituted by the biotechnologies.

Addressing primarily professionals, BIOEXPO is a privileged setting for generating new collaboration ventures and exchange of technologies, services, products stemming from biotechnologies or necessary for their implementation.

In Nice, at the very core of ECB 7, BIOEXPO 95 will present during four days (February 20–23) over an exhibition area of 4.000 m² the latest innovations already on the market or pending commercialization in sectors as diverse as engineering, human and animal health, chemistry, antipollution, minerals, agriculture, agrifood, energy...

Over 150 exhibitors, of whom a third from abroad, are expected, including equipment manufacturers and distributors, service companies, consultancy and engineering firms, government organizations, public and private research institutes, professional organizations, training services, financial bodies...

Information and registration:

ECB 7: Société de Chimie Industrielle, 28, rue Saint-Dominique, F–75007 Paris
Tel.: (33-1) 45 55 69 46
Fax: (33-1) 45 55 40 33

BIOEXPO 95: SEPFI TECHNOEXPO, Blenheim Group, 70, rue Rivay, F–92532 Levallois-Perret Cedex
Tel.: (33-1) 47 56 21 15
Fax: (33-1) 47 56 21 10

Energietage 94 am *Paul Scherrer* Institut

10.–12. November 199

Thema: Energie und nachhaltige Entwicklung

- Energienutzung und Energiebereitstellung – Umweltaspekte
- Energieforschung und Internationalisierung externer Kosten

Programm und Anmeldung:

Paul Scherrer Institut
Mrs. *Ursula Grütter*
CH–5232 Villigen PSI
Tel. +41-56-99 29 19
Fax +41-56-99 21 99

Ankündigung der Swiss Tissue Culture Society:

STCS
SWISS TISSUE CULTURE SOCIETY
A BRANCH OF THE EUROPEAN TISSUE CULTURE SOCIETY

Im August 1993 wurde die Schweizer Gesellschaft für Zell- und Gewebekultur (Swiss Tissue Culture Society, STCS) in Anlehnung an den Europäischen Verband 'European Tissue Culture Society' (ETCS) gegründet. Das Ziel der Vereinigung ist, den Fortschritt der Zell- und Molekularbiologie und damit auch der *in vitro*-Systeme zu fördern. Als Verbindungsglied zwischen den Mitgliedern will man Erfahrungsaustausch und Zusammenarbeit fördern- und über Neuigkeiten und Entwicklungen auf dem Gebiet der Zell- und Gewebekultur zu informieren. Darüberhinaus wird die Förderung junger Mitglieder in Trainingskursen und Seminaren ein wichtiges Anliegen von STCS sein. Die Gründungsmitglieder und bisher neu dazugestossenen Mitglieder sind an universitären, industriellen und anderen Forschungseinrichtungen tätig, sodass ein breites Erfahrungsfeld vertreten ist, welches auch zur Information von wissenschaftlichen Organisationen, Industrie, Legislative und Exekutive über Fragen der Zell- und Gewebezüchtung sowie der damit verbundenen Anwendung und Validierung zur Verfügung steht.

Auskünfte über STCS kann die Sekretärin des Vereins erteilen:
Dr. *Anke-Peggy Holtorf, Ciba-Geigy AG*, K681.1.02, CH–4002 Basel
(Fax: 061 696 40 69, E-Mail: INTERNET ANKE-PEGGY.HOLTORF@ DM.RS.CH)

Ankündigung des ersten Treffens der Swiss Tissue Culture Society:

Am 2. Dezember 1994 wird das erste eintägige Treffen der Schweizer Gesellschaft für Zell- und Gewebekultur (Swiss Tissue Culture Society, STCS) in Basel statfinden. Unter dem Titel

'New Technologies in Cell & Tissue Culture' werden die Teilnehmer nach einem Einführungsvortrag Gelegenheit haben, neueste Forschungsergebnisse und Techniken in Kurzvorträgen oder Postern darzustellen und mit ihren Kollegen zu diskutieren. Die Ziele des Treffens sind:

- die Bildung eines kompetenten Forums für universitäre, industrielle und klinische Forschung
- und die Bildung eines Anknüpfungspunktes für spätere Zusammenarbeiten,
- Informations- und Wissensaustausch
- und die Unterstützung und Förderung junger Wissenschafter.

Die Teilnahme ist allen offen, die sich für die neuesten wissenschaftlichen Methoden der Zell- und Gewebekultur interessieren. Nähere Informationen zu den aktiven und passiven Teilnahmekonditionen stehen von der Sekretärin zur Verfügung:
Dr. *Anke-Peggy Holtorf, Ciba-Geigy AG*, K681.1.02, CH–4002 Basel
(Fax: 061 696 40 69, E-Mail: INTERNET ANKE-PEGGY.HOLTORF@ DM.RS.CH)

Praxisorientierte EAWAG-Kurse PEAK

Weiterbildung in Umweltwissenschaften

Unter dem Namen PEAK bietet die EAWAG eine neue Serie von Weiterbildungsveranstaltungen für Fachleute aus der Praxis an. Die Kurse basieren auf eigenen Forschungsarbeiten und Erfahrungen und widerspiegeln die aktuellen Arbeitsgebiete. Jährlich werden *ca.* 5 Kurse durchgeführt.

Die PEAK vermitteln Wissen und Technik für die praktische Tätigkeit. Dabei sollen der gesamtheitliche Umweltschutz und die Zusammenarbeit über die Grenzen von Disziplinen und Institutionen hinaus gefördert werden. Die Veranstaltungen dienen nicht nur der Wissensvermittlung, sondern bilden auch ein Forum für den Meinungsaustausch; unter den Teilnehmern, zwischen Forschung und Praxis.

Jeder Kurs bildet eine Einheit und kann unabhängig von anderen absolviert werden. Zu allen Kursen werden Unterlagen abgegeben. Die Kurskosten sind in der Grössenordnung von *ca.* Fr. 200.– pro Tag (inkl. Mittagessen, Kaffee, Dokumentation).

Die Teilnehmer/innen sollen aktiv an den Kursen mitwirken und einen Leistungsnachweis erbringen können. Sie erhalten eine Teilnahmebestätigung. Bei erfolgreicher Absolvierung des Leistungsnachweises werden Krediteinheiten vergeben, die einen Vergleich mit anderen Studiengängen erlauben und aufsummiert werden können.

Programm 1994

20. Sept. 1994	Umweltarchive – Ordnung und Chaos
Infotag 1994	Natürliche und vom Menschen verursachte Ablagerungen als Grundlage für umweltverträgliche Entwicklungen Leitung: *Theresa Buesser, Michael Sturm*
6.–8. Sept.1994	Organische Schadstoffe in der Umwelt
PEAK-Vertiefungskurs V3/94	Transport- und Umwandlungsprozesse in Gewässersystemen werden am Beispiel organischer Chemikalien illustriert und die ökotoxikologischen Effekte erläutert Kursleitung: *Werner Angst, Hanspeter Kohler*
19.–21. Okt. 1994	Chemische Umweltanalytik: Konzepte und Methoden
PEAK-Anwendungskurs A2'/94	(1. Wiederholung des Kurses A2/94 vom 23.–25. März 1994) Moderne Konzepte und Fortschritte der chemischen Analytik von Wasser, Boden und Luft; von der Probenahme bis zur Dateninterpretation Kursleitung: *Walter Giger, Christoph Moor, Marc Suter*

Anmeldung/Information
Heidi Gruber, EAWAG, Überlandstr. 133, CH–8600 Dübendorf, Tel. 01/823 53 93, Fax 01/823 53 98

Grenzüberschreitende Hochschulstudiengänge

14. REGIO-SYMPOSIUM

über
Interface between Biology and Synthesis

'IBIS'

14.–16. September 1994
im Centre protestant de Rencontre in Sornetan, Berner Jura

veranstaltet von den Universitäten Basel, Freiburg i.Br. und Mulhouse für Doktoranden und Mitarbeiter aus den chemischen Hochschulinstituten und für Chemiker aus der Industrie des REGIO-Gebiets.

Wissenschaftliches Komitee

Prof. *W. Eberbach*	Freiburg i.Br.
Prof. *B. Giese*	Basel, Organisator
Prof. *A. Pfaltz*	Basel, Organisator
Prof. *P. Schiess*	Basel, Organisator
Prof. *J. Streith*	Mulhouse

Das REGIO-Symposium wird unterstützt durch einen Beitrag der folgenden Institution: – COMETT Community Action Program in Education and Training for Technology – UETP EUCOR – Chemipharm.

Programm

Mittwoch, 14. September 1994
11.00 Prof. *St.A. Benner* (ETH-Zentrum, Zürich)
'Protein Conformation'
14.30 Prof. *W. Arber* (Biozentrum, Universität Basel)
'Limits of Fidelity of Enzymes and Determinism'
16.00 Prof. *D. Hilvert* (*Scripps* Research Institute, La Jolla) 'Structural Basis of Antibody Catalysis'
20.00 Poster-Präsentation

Donnerstag, 15. September 1994
09.00 Prof. *G. v. Kiedrowski* (Universität Freiburg i.Br.)
'Minimal Models of Self Replicating Molecules, I'
11.00 Prof. *S.A. Benner* (ETH-Zentrum, Zürich)
'Redesigning Nucleic Acids'
16.30 Prof. *D. Hilvert* (*Scripps* Research Institute, La Jolla) 'Controlling Chemical Reactivity and Selectivity with Catalytic Antibodies'
20.00 Prof. *J. Seelig* (Biozentrum, Universität Basel)
'Lipid Model Membranes and Biosensors'

Freitag, 16. September 1994
09.00 Prof. *Ch. Leumann* (Universität Bern)
'Sequence Specific Molecular Recognition of Nucleic Acids'
11.00 Prof. *G. v. Kiedrowski* (Universität Freiburg i.Br.)
'Minimal Models of Self Replicating Molecules, II'
12.15 Poster-Preisverteilung

Einschreibegebühr
– für Universitätsangehörige SFr. 130.–
– für Teilnehmer aus der Industrie SFr. 400.–

Die Einschreibegebühr ist bis zum 2. September 1994 zu entrichten.
Entweder: per Postcheckzahlung an: Basler Kantonalbank, 4002 Basel, PC 40-61-4
Mit dem Vermerk: Konto Nr. 16-534.502.96
Prof. Dr. *P. Schiess*, REGIO-Symposium
oder: per internationalen Check (Eurocheck) zahlbar an: Prof. Dr. *P. Schiess*, REGIO-Symposium (bitte auf der Rückseite die Eurocheckkarten-Nr. angeben).
Anmeldung und Checks sind zu senden an: Sekretariat (Frau *Rieser*), Institut für Organische Chemie, St. Johanns-Ring 19, CH–4056 Basel.

Poster
Die Teilnehmer sind eingeladen, eigene Forschungsergebnisse in Form eines Posters vorzustellen (140 x 100 cm). Die Poster sollen anlässlich der Posterpräsentation am Mittwoch abend um 20.00 Uhr anhand von 2–3 Dias oder Folien kurz vorgestellt werden. Die beste Posterpräsentation wird mit einem Preis belohnt!

Unterkunft und Verpflegung
Im Centre protestant de Rencontre, CH–2716 Sornetan, Tel. 032/91 95 35. Unterkunft im Einzel- oder Doppelzimmer, bzw. im Schlafsaal zu 8 Betten. Unterkunft und Verpflegung sind in der Einschreibegebühr inbegriffen, Getränke extra.

Sornetan liegt in einer malerischen Umgebung auf 850 Meter Höhe inmitten des Berner Juras. Es empfiehlt sich, Wanderschuhe mitzubringen.
Es wird erwartet, dass die Teilnehmer während des ganzen Symposiums anwesend sind.

Sicherheit in chemischen und verfahrenstechnischen Anlagen

ETH – ESCIS – Fortbildungskurs an der ETH-Zürich vom 17.–20. Oktober 1994

Das Institut für Verfahrens- und Kältetechnik der ETH-Zürich organisiert zusammen mit der Expertenkommission für Sicherheit in der Chemischen Industrie der Schweiz (ESCIS) einen viertägigen Fortbildungskurs:

Basismodul	17.10.1994 'Risikoanalyse' Dr. *F. Schmalz*
Fachmodul 1	18.10.1994 'Thermische Gefahren' Dr. *F. Stoessel*
Fachmodul 2	19.10.1994 'Gasausbreitung' Prof. Dr. *T. Fanneløp*
Fachmodul 3	20.10.1994 'Explosionsschutz' Dr. *R. Ott* und Dr. *M. Glor*

Der Kurs richtet sich an Ingenieure und Naturwissenschaftler, die in Forschung, Projektierung und Betrieb von verfahrentechnischen und chemischen Anlagen mit Sicherheitsfragen konfrontiert sind, sowie an ETHZ-Doktoranden in Verfahrenstechnik und Chemieingenieurwesen. Die Teilnehmerzahl ist infolge der Gruppenarbeiten beschränkt. Das Kursprogramm mit allen weiteren Angaben ist erhältlich von: Institut für Verfahrens- und Kältetechnik, *Ch. Heinzen* (01 632 25 03), ETH-Zentrum, CH–8092 Zürich.

11th (Montreux) Symposium Liquid Chromatography/Mass Spectrometry (LC/MS; SFC/MS; CE/MS; MS/MS)

This symposium is organized by the International Association of Environmental Analytical Chemistry

November 9–11, 1994
Short Course on LC/MS, SFC/MS, and CE/MS
November 7–8, 1994
Convention and Exhibition Center Montreux (Switzerland)

The symposium on LC/MS, SFC/MS, CE/MS, and MS/MS will deal with all qualitative and quantitative areas of this topic including technical developments, considerations, validation with on-line and off-line aspects, theoretical considerations and applications of the techniques in environmental clinical and pharmaceutical analysis and other fields.

Subtopics will be introduced by plenary lectures and invited research lectures followed by brief research presentations and posters.
Address before and after the Symposium and short course:

Workshop Office IAEAC,
M. Frei-Häusler
Postfach 46
CH–4123 Allschwil 2
Tel. (004161) 481 27 89
Fax (004161) 482 08 05

'Probleme des Chemikers im Zusammenhang mit der Registrierung von Wirkstoffen'

behandelt eine Fachtagung am 22. September 1994 (9.00–17.00 Uhr) bei der *Sandoz AG*, Basel. Die Fachtagung wird in deutsch und englisch (mit Simultanübersetzung) durchgeführt und von der 'Schweizerischen Vereinigung dipl. Chemiker HTL (SVCT)' in Zusammenarbeit mit der 'Neuen Schweizerischen Chemischen Gesellschaft (NSCG)' organisiert.
Auskünfte:
Herr *J. Brocher*, *Sandoz Pharma AG*, Bau 507/151, CH–4002 Basel, Telefon (+41-61-324 11 11; Telefax (+41)-61-324 58 14.

News

Zur Gründung der *Verlag HCA AG*

Die *Neue Schweizerische Chemische Gesellschaft (NSCG)* hat beschlossen, ihre Verlagsaktivitäten aus der Gesellschaft auszugliedern und sie rückwirkend zum 1. Juli 1994 auf eine eigenständige Firma, die *Verlag Helvetica Chimica Acta AG (Verlag HCA)* mit Sitz in Basel, zu übertragen. Die künftige enge Zusammenarbeit zwischen der NSCG und dem neuen Verlag widerspiegelt sich in den Besitzverhältnissen: Mit 52% der Anteile ist die NSCG Mehrheitsaktionär; die *VCH Verlagsgesellschaft*, Weinheim, und *Birkhäuser+GBC Grafische Unternehmen*, Basel, beteiligen sich zu je 24% am Verlag HCA.

Geschäftsführer des Verlags HCA ist *M. Volkan Kisakürek*, der weiterhin auch als Chefredakteur der Helvetica Chimica Acta tätig sein wird. Diese 1917 gegründete, international renommierte Fachzeitschrift veröffentlicht Primärliteratur auf allen Gebieten der Chemie und kann einen eindrucksvollen 'Impact Factor' aufweisen. Präsident des Verwaltungsrates des neuen Verlages ist *Luigi M. Venanzi*. Unter dem Vorsitz des Geschäftsführers wird ausserdem ein Verlagsbeirat, dessen weitere Mitglieder prominente Wissenschaftler mit internationalem Ansehen sind (*Richard R. Ernst*, *Nobel*-Preisträger in Chemie 1991, *Albert Eschenmoser*, *Hans-Jürgen Hansen* und *Gerhard Quinkert*), für die Programmpolitik und verlegerische Fragen zuständig sein.

Die Zusammenarbeit mit VCH ist für die NSCG nichts Neues: Bereits seit fast zwei Jahren bestehen Kopublikationsaktivitäten. Von der künftigen Kooperation mit VCH, die weltweit für Marketing und Vertrieb verantwortlich sein wird, verspricht sich der Verlag HCA eine Optimierung seiner Marktposition – dank der langjährigen Verlagserfahrung und dem internationalen Vertriebsnetz von VCH. Da VCH vor allem auf dem Gebiet der Chemie tätig ist, werden von dieser Kooperation deutliche Synergieeffekte erwartet.

Mit dem Birkhäuser+GBC Grafische Unternehmen, das seit deren Gründung die Zeitschrift Helvetica Chimica Acta setzt und druckt, steht für die technische Seite und die Produktion ein erfahrener Partner bereit.

Roche AIDS-Medikament erhält in der Schweiz erweiterte Zulassung

Das *Roche* AIDS-Medikament *Hivid*® (Dideoxycytidin) ist seit Dezember 1992 in der Schweiz für die Kombinationstherapie mit *Zidovudin* (*Retrovir*®) bei AIDS-Patienten zugelassen. Die Interkantonale Kontrollstelle für Heilmittel (IKS) in Bern hat *Hivid* auch für die Monotherapie bei AIDS-Patienten gutgeheissen. Das Medikament kann nun bei erwachsenen Patienten mit fortgeschrittener HIV-Infektion als Alternative zur *Zidovudin*-Therapie eingesetzt werden, falls Patienten *Zidovudin* nicht vertragen oder auf *Zidovudin* nicht mehr ansprechen. Eine aktuelle Studie hat gezeigt, dass *Hivid* mit dem AIDS-Medikament *Didanosin* (*Videx*®) in der Wirkung vergleichbar ist.

Das Bundesamt für Sozialversicherungen hat *Hivid* am 15. März 1994 in die Liste der kassenzulässigen Medikamente aufgenommen. Mit dieser Indikationserweiterung und der Rückvergütung durch die Krankenkassen steht den HIV-Patienten nun eine weitere Behandlungsmöglichkeit zur Verfügung.

Anorganische und Organische Chemie in Deutschland

Aktuelle Tagungen, neue Vereinigungen

Die klassischen Gebiete der Chemie, die Anorganische und die Organische Chemie, werden mit ihren modernen Forschungsrichtungen auf zwei Tagungen der Gesellschaft Deutscher Chemiker (GDCh) im Oktober vorgestellt: Die Organiker tagen in Erfurt vom 6.–8. Oktober 1994 auf der ORCHEM '94, die Anorganiker treffen sich vom 13. bis 15. Oktober 1994 in Potsdam.

Beide Fachrichtungen der Chemie werden in der GDCh künftig stärkeres Gewicht erhalten. Der GDCh-Vorstand hat die Gründung der '*Liebig*-Vereinigung für Organische Chemie' und der '*Wöhler*-Vereinigung für Anorganische Chemie' beschlossen.

Orientation about research involving genetically modified organisms in Switzerland in 1993

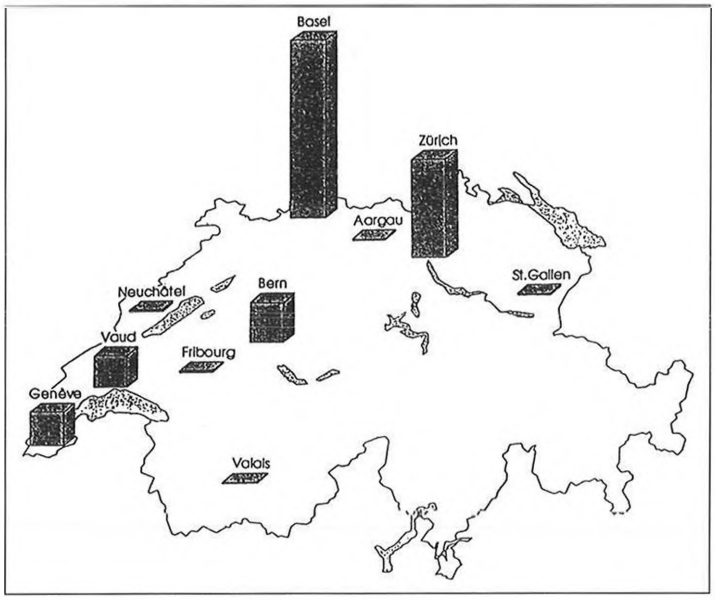
Swiss Interdisciplinary Committee for Biosafety in Research and Technology (SCBS)

The SCBS, founded in 1986, is supported by the three Swiss Academies of Sciences, of Medical Sciences, and of Technical Sciences. In addition, in accordance with to the new Ordinance on Protection against Major Accidents (StFV), in spring 1992 an agreement was made between the Swiss Federal Office of Environment, Forests and Landscape (BUWAL) and the SCBS. According to this agreement, the secretariat of the SCBS continues to serve as the office for the registration of projects involving genetically modified organisms; in addition, it informs the cantonal executive authorities regularly on the registered projects and serves as an information office. The SCBS consists of 23 full members (11 from universities, 5 from industry, and 7 from federal and cantonal offices) and of 8 associate members. It is divided into the three sections 'Experimental Genetics', 'Technology,' and 'Ecology', and an executive committee directs its activities.

The SCBS deals with questions of biosafety arising in projects with biological material that is able to replicate autonomously. The majority of questions arise from work with genetically modified organisms. Moreover, the committee evaluates recombinant DNA products to the extent that these are not already dealt with by established commissions and procedures. The SCBS also is available to assess projects involving natural oganisms.

In January 1992 the 'Guidelines for Work with Genetically Modified Organisms' of the SGBS formulated in collaboration with the BUWAL came into force. These *Guidelines* are based on the German Law on Gene Technology, the Council Directives of the European Community and on the *NIH Guidelines*. The *SCBS Guidelines* will be adapted regularly in line with any new directives of the EC. They can be obtained in German, French, and in English through the SCBS-Secretariat (c/o Dr. *Karoline Dorsch-Häsler*, Apfelbaumstrasse 43, CH–8050 Zürich Tel./Fax. 01/312 08 40).

No special obligations exist for work with well investigated host-vector systems and donor organisms. In the case of small scale safety level 1 projects notification by the institution is sufficient. A total ot 501



project leaders in ten cantons (AG, BE, BS, FR, NE GE, SG, VD, VS, ZH) were engaged in recombinant DNA research of safety levels 1–3 in 1993 (see *Fig.*)

The SCBS has to be notified about every large scale project of safety level 1, while projects of safety levels 2–4 have to be registered with the SCBS. These projects are listed by canton in the *Table* shown below. Neither large-scale projects of safety levels 2–4 nor small scale projects of safety level 4 were registered with the SCBS in 1993.

As in previous years, the number of research groups in Switzerland working with genetically modified organisms has increased, *i.e.*, from 364 in 1992 to 501 in 1993. The number of projects of risk category 2 has increased, too, from 57 in 1992 to 81 in 1993. This is due to the increasing use of viral vectors developed to produce large amounts of proteins in animal cells.

The SCBS was contacted by several research groups regarding gene therapy in Swiss hospitals. Members of the SCBS and additional experts have discussed the requirements for proposals for gene therapy and for the procedure for assessing gene therapy protocols. Consequently, the 'Guidelines for the Submission of Human Gene Therapy Protocols' were compiled and published. In short, the 'Points to Consider in the Design and Submission of Protocols for the Transfer of Recombinant DNA into the Genome of Human Subjects' published in the 'NIH-Guidelines for Research Involving Recombinant DNA Molecules' have to be dealt with. In addition the proposals have to be submitted to the local ethical committees.

There is great interest worldwide in the development of safe and efficient vaccines against dysentery caused by bacterial pathogens of the genus *Shigella*. Oral vaccination with live avirulent strains currently appears to be the most promising approach. The Swiss Serum and Vaccine Institute in Bern constructed a recombinant derivative of a well characterized, safe, and immunogenic cholera vaccine strain. This strain expresses the main *Shigella sonnei* surface antigen. After approval of the protocol by the SCBS, a phase I clinical study involving 11 volunteers was conducted in Summer 1993 in the Swiss Serum and Vaccine Institute. The volunteers were administered a single oral dose of the recombinant vaccine. All of the vaccinees described the general acceptability of the vaccine to be very good. Excretion of the vaccine strain was very low. The vaccine was able to confer a certain degree of primary immunity to some of the volunteers.

In 1993, the SCBS has not received any applications for field trials of genetically modified plants.

The SCBS would like to thank all researchers concerned for following the Guidelines and for carefully observing the required safety measures.

Dr. Karoline Dorsch-Häsler
Prof. Dr. Heidi Diggelmann
President SCBS
Zürich, July 1994

	Number of projects		
	Small scale		Large scale
Canton	Level 2	Level 3	Level 1
Basel-Stadt	17	3	26
Bern	12	1	
Fribourg			1
Genève	8		
Neuchâtel	1		
St. Gallen	3		
Valais			2
Vaud	15	1	4
Zurich	25		1
Switzerland	81	5	34

Schweizer Polyethylen-Industrie

Kunststoff-Unternehmen bilden neue Interessengemeinschaft

Die Kunststoff-Unternehmen der Schweizer Polyethylen-Industrie haben sich zu einer neuen Interessengemeinschaft zusammengeschlossen, welche Öffentlichkeit und Anwender über die weitreichenden Einsatzmöglichkeiten und Herstellungsverfahren von Polyethylen informieren möchte. Als Fachgruppe im Kunststoffverband Schweiz (KVS) gehören zur neuen Interessengemeinschaft zusätzlich zu den bis anhin vertretenen Folienherstellern auch PE-Hersteller/-Importeure sowie Verarbeiter und Wiederaufbereitungsunternehmen aus der ganzen Schweiz. Damit ist der gesamte Produktionskreislauf der Schweizer Polyethylen-Industrie in der Interessengemeinschaft vertreten.

Die aktive Kommunikationspolitik seitens der PE-Industrie soll zur Verbesserung des Informationsstandes der Öffentlichkeit beitragen und die ökonomische und ökologische Bedeutung von Polyethylen in der Schweiz aufzeigen. Insbesondere sollen die verschiedenen Kunststoffarten, welche heute im allgemeinen Sprachgebrauch unter den Sammelbegriff 'Plastik' fallen, als eigenständige Materialien positioniert werden, wie dies beispielsweise auch bei den Metallen erfolgt.

Polyethylen wird heute in allen Lebensbereichen eingesetzt und leistet oft direkt oder indirekt einen sinnvollen Beitrag zum Umweltschutz. Gerade im Bereich Umweltverträglichkeit geniesst Polyethylen hohes Ansehen, das durch Fachkreise, Behörden und unabhängige Untersuchungsanstalten mit zahlreichen Studien und Ökobilanzen immer wieder unterstrichen wird.

In diesem Zusammenhang will die Interessengemeinschaft unter Einbezug der Öffentlichkeit, mit Hilfe eines konstruktiven Dialoges sowie kontinuierlicher Forschung und Entwicklung und einem sinnvollen Recycling einen Beitrag zur Reduktion des Abfallproblems und der damit verbundenen Belastung der Umwelt leisten.

Die Unternehmen der Schweizer Polyethylen-Industrie sind sowohl national als auch international tätig. In ihren Regionen nehmen sie als Arbeitgeber wichtige Funktionen ein und stellen insgesamt über 12 000 Arbeitsplätze, welche direkt mit der PE-Verarbeitung im Zusammenhang stehen.

Als Werkstoff ist Polyethylen, das wie auch Holz und andere natürliche Materialien aus Wasserstoff und Kohlenstoff besteht, besonders umweltverträglich, weil sowohl beim Recycling als auch bei der Verbrennung keine belastenden Nebenprodukte oder Verbindungen entstehen.

Polyethylen macht bereits heute in seinen beiden Ausführungen HDPE (hohe Dichte) und LDPE (niedrige Dichte) etwa 28% des gesamten Kunststoffverbrauchs in der Schweiz aus und gewinnt anteilsmässig zunehmend an Bedeutung. Der Rohstoff, das Polyethylengranulat, der zur Herstellung der verschiedenen Produkte dient, wird entweder aus dem Ausland importiert oder aus dem Recycling gewonnen, da in der Schweiz kein neues Granulat produziert wird.

Die Hauptlieferanten unseres Marktes sind die Nachbarländer Deutschland, Frankreich und Italien, wo Polyethylen mit einem Crack-

verfahren, ein chemisch-thermischer Spaltprozess, aus Rohbenzin gewonnen wird. Erstaunlich ist, dass trotz des allgemein hohen Kunststoffbedarfs unserer Zeit nur rund 2–4% des Primärrohstoffs Erdöl in die gesamte weltweite Kunststoffindustrie fliessen.

Für weitere Informationen wenden Sie sich bitte an:
Informationsstelle der
Schweizer Polyethylen-Industrie
Postfach 17
CH–8702 Zollikon-Station
Telefon 01 392 02 08

Preise

Fluka-Preis an *Eric N. Jacobsen*

Zum achten Mal wurde jetzt der mit 10000 SFr. dotierte *Fluka*-Preis für das Reagens des Jahres vergeben. Die Auszeichnung erhält in diesem Jahr Prof. Dr. *Eric N. Jacobsen*, Harvard/MA, USA, für eine Arbeit auf dem Gebiet der synthetischen organischen Chemie.

Das Reagens des Jahres 1994 ist ein chiraler, nicht racemischer Übergangsmetallkatalysator, der eine wichtige, schon sehr lange bekannte und oft eingesetzte präparative Transformation, die Epoxidierung von nicht funktionalisierten Alkenen, nun auf neuartige Weise enantioselektiv führt. Die Enantiomerenüberschüsse erreichen 98%, und die vielseitig reaktive Epoxidfunktion eröffnet in der Folge extrem kurze Wege zu pharmakologisch aktiven Verbindungen.

Der Katalysator, ein Mangan(III)-Salen-Komplex, zielt also mitten in das Zentrum der modernen Wirkstoff-Forschung: auf die effektive, preiswerte, ökologische Herstellung enantiomerenreiner Pharmaka durch katalytische enantioselektive Synthese. Hier setzt das Reagens des Jahres ein Zeichen; binnen kurzem hat sich das Verfahren in der noch immer kleinen Gruppe von katalytischen enantioselektiven Verfahren mit industrieller Bedeutung etabliert; ein Aspekt, der von der Jury bei der Preisvergabe besonders gewürdigt wurde.

Der von der Schweizer Feinchemikalienfirma *Fluka* gestiftete Preis wird jährlich von einem unabhängigen Komitee für ein wichtiges neues Reagens auf chemischem, biochemischem oder analytischem Anwendungsgebiet vergeben.

Neue Mitglieder

Neue Schweizerische Chemische Gesellschaft

Bucher, Christoph, 8037 Zürich

Eigenmann, Kaspar,
4114 Hofstetten

Engeloch, Thomas, 2000 Neuchâtel

Falter, Ralf,
D–69483 Wald-Michelbach 1

Franz, Andreas, 2000 Neuchâtel

Henz, Matthias, 2000 Neuchâtel

Karvas, Milan, Dr.,
81109 Bratislava, Slovakia

Korell, Ulrich, Dr., 4123 Allschwil

Lübbers, Thomas, Dr.,
D–79415 Bad Bellingen

Rutsch, W., Dr., 1723 Marly 1

Spichiger, J., Dr., 8820 Wädenswil

Teranol AG, Lalden, 3930 Visp

Tóth, Gyula, Prof. Dr.,
H-7601 Szigeti

Waldmeier, Pius, 4434 Hölstein

Vorträge

Institut de Chimie, Université de Neuchâtel

Avenue de Bellevaux 51, Neuchâtel

Jeudi 22.9.94 Petit Auditoire (3e Cycle) 16.00 h	Prof. *Sir A. Battersby* University Chemical Laboratory, Cambridge 'Biosynthesis of Vitamen B_{12}: Part I'
Vendredi 23.9.94 Petit Auditoire (3e Cycle) 16.00 h	Prof. *Sir A. Battersby* University Chemical Laboratory, Cambridge 'Biosynthesis of Vitamen B_{12}: Part II'

EMPA Dübendorf

Öffentliches Seminar
Kontakt/Auskunft: Frau M. Boll
Telefon 01 823 42 30 oder 01 823 45 99

Montag 19. September 1994	Luftfremdstoffe, Umwelttechnik *A. Herzog* 'Messung organischer Immissionen'

Ehrungen

Prof. Dr. *Arnold Brossi*, NHI Scientist Emeritus und gegenwärtig Visiting Research Professor an der Georgetown Universität in Washington, D.C., hat anlässlich seines 70. Geburtstages verschiedene Ehrungen erhalten: die Ehrendoktorwürde der *Adam Wickiewicz* Universität in Poznan, Polen; die *Pro Merito* Medaille der *Palacky* Universität in Olomouc, Czech Republic; das 15. Symposium über 'Natural Products and Medicinal Chemistry', 3.–7. Januar 1994 in Mona, Jamaica, wurde ihm gewidmet; Vol. 39 von *Heterocycles* wird seine Verdienste ehren.

Prof. Dr. *François Diederich*, Professor der ETH-Zürich für Organische Chemie, hat die folgenden mit Preisen verbundenen 'Name-Lectureships' gehalten: 1. *Abbott*-Lectureship an der University of Chicago, 2. *Barré*-Lectureship an der University of Montreal und 3. *Steinhofer*-Lecture an der Universität Freiburg/Breisgau.

Bücher

Bei der Redaktion eingetroffene Bücher

M. Gerloch, E.C. Constable
'Transition Metal Chemistry'
VCH, Weinheim – New York – Basel – Cambridge – Tokyo, 1994

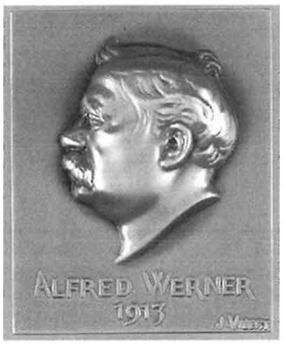
CHIMIA 48 (1994) Nr. 7/8 (Juli/August)

Wissenschaftliche Auszeichnungen der NEUEN SCHWEIZERISCHEN CHEMISCHEN GESELLSCHAFT

Ausschreibung für die Verleihung 1995/96

Distinctions scientifiques de la NOUVELLE SOCIÉTÉ SUISSE DE CHIMIE

Mise au concours pour 1995/96



***Werner*-Preis**
Der *Werner*-Preis wird an schweizerische oder in der Schweiz tätige Nachwuchswissenschafter für ausgezeichnete Forschungsarbeiten auf dem Gebiet der Chemie verliehen. Die Auswahl umfasst Kandidaten und Kandidatinnen aus Hochschulen und Industrie.
Die Preisverleihung findet im Frühjahr 1995 statt.
Einreichefrist: 31. Oktober 1994

Prix *Werner*
Le prix *Werner* sera attribué à un jeune chercheur suisse ou un jeune chercheur exerçant son activité en Suisse, pour un travail de haute qualité dans le domaine de la chimie. Les candidats et candidates peuvent être issus d'une Haute École ou de l'industrie.
La remise du prix aura lieu au printemps 1995.
Délai de présentation: 31 octobre 1994.

***Sandmeyer*-Preis**
Der *Sandmeyer*-Preis wird für hervorragende Arbeiten auf einem Gebiet der industriellen oder angewandten Chemie an ein Arbeitsteam oder einen Einzelnen verliehen. Die Arbeit soll in der Regel in der Schweiz oder im Ausland von einem Arbeitsteam mit Beteiligung von Schweizer Bürgern und Bürgerinnen ausgeführt worden sein.
Die Preisverleihung findet im Frühjahr 1995 statt.
Einreichefrist: 31. Oktober 1994

Prix *Sandmeyer*
Le prix *Sandmeyer* sera attribué à un groupe de travail ou à un candidat unique pour un travail de haute qualité dans le domaine de la chimie industrielle ou appliquée. Le travail doit avoir été réalisé en Suisse ou à l'étranger par un groupe de travail comprenant des citoyens et citoyennes suisses.
La remise du prix aura lieu au printemps 1995.
Délai de présentation: 31 octobre 1994.

Dr.-*Max-Lüthi*-Preis
Die Dr.-*Max-Lüthi*-Auszeichnung wird für ausgezeichnete Diplomarbeiten verliehen, die an Chemieabteilungen von höheren technischen Lehranstalten der Schweiz ausgeführt werden.
Anträge der Abteilungsvorsteher der Chemieabteilungen müssen bis Ende Dezember 1994 an den Geschäftsführer der NSCG eingereicht werden.
Die Preisverleihung findet im Frühjahr 1995 statt.

Prix Dr.-*Max-Lüthi*
Le prix Dr.-*Max-Lüthi* est attribué à l'auteur d'un travail de diplôme de qualité exceptionelle effectué dans le département de chimie d'une école technique supérieure suisse.
Les propositions des directeurs des départements de chimie des écoles techniques supérieures suisses doivent être soumises à l'administrateur de la NSSC avant la fin décembre 1994.
La remise du prix aura lieu au printemps 1995.

***Paracelsus*-Preis**
Der *Paracelsus*-Preis wird im Turnus von 2 Jahren verliehen, das nächste Mal im Frühjahr 1996.
Einreichefrist: 31. Oktober 1995.

Prix *Paracelse*
Le prix *Paracelse* sera remis tout les 2 ans, la prochaine fois au printemps 1996.
Délai de présentation: 31 octobre 1995.

Vorschläge und Bewerbungen sind mit den notwendigen Unterlagen an den Geschäftsführer der NSCG einzureichen.

Propositions et candidatures doivent être adressées à l'administrateur de la NSSC avec un dossier complet.

NEUE SCHWEIZERISCHE CHEMISCHE GESELLSCHAFT
NOUVELLE SOCIÉTÉ SUISSE DE CHIMIE

Dr. K. Heusler
Präsident/Président
Dr. K. Gubler
Geschäftsführer/Administrateur

Adresse: c/o Ciba, K-25.5.02
CH–4002 Basel

CHIMIA 48 (1994) Nr. 7/8 (Juli/August)

CHIMIA-REPORT

Sehr geehrte Inserenten

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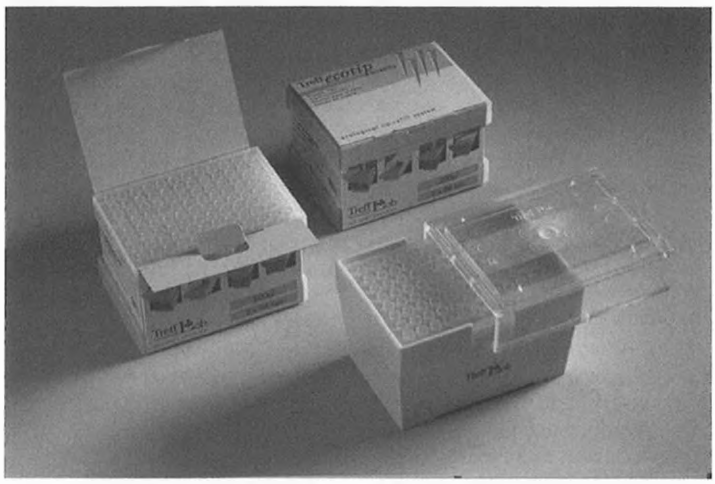
Besten Dank!

Treff Ecotip – ein umweltfreundliches Nachfüllsystem für Pipetten-Spitzen



Treff Ecotip-Set ist ein umweltfreundliches Nachfüllsystem für palettierte RL-Spitzen, welches den Kunststoff-Abfall stark reduziert und weniger Platz für die Aufbewahrung von Spitzen beansprucht. Das System ist einfach und praktisch in der Anwendung und ist umweltfreundlich verpackt. Die Ecotip-Box aus Polycarbonat hält ein Rack mit 8 x 12 Spitzen und ist mehrfach autoklavierbar. Mit dem transparenten Schiebedeckel kann die Box jeweils für nur eine Reihe von 8 Spitzen geöffnet werden, die anderen Spitzen werden dadurch vor Kontamination besser geschützt. Die Ecotip-Box eignet sich vorzüglich für Arbeiten mit 8-Kanal- und 12-Kanal-Pipetten. Ein Ecotip-Refill (Nachfüllpackung) besteht aus zwei Rack mit je 96 Spitzen. Treff Ecotip-Spitzen passen auf Treff Pipetten und alle anderen, bekannten Einkanal-und Mehrkanal-Pipetten.

- TreffLab
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Alarmwerte: zwischen 0,1–0 l/min Wasser
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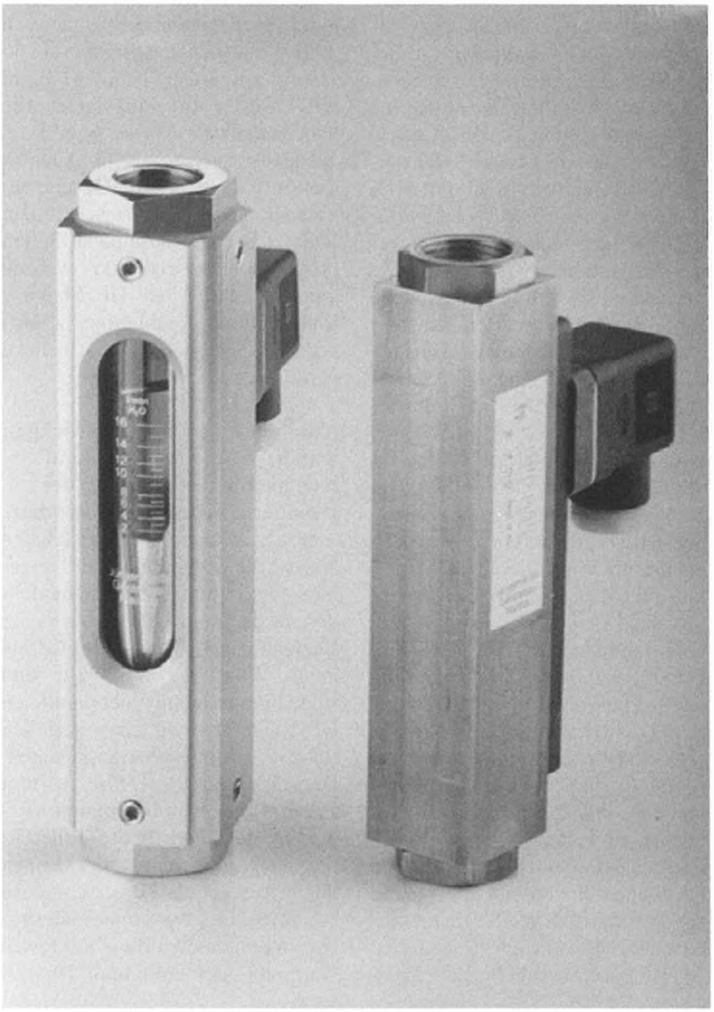


CHIMIA 48 (1994) Nr. 7/8 (Juli/August)

Der HP LaserJet 4 Plus stellt einen neuen Leistungsstandard für den Laserdruck auf: Höchstgeschwindigkeit mit scharfen Ecken und Kanten

Den schnellen Netzwerken mit einer Vielzahl von angeschlossenen Benützern gehört die Zukunft. Zur Nervensäge werden Netzwerke dann, wenn das zu druckende Dokument im Flaschenhals des gemeinsam genutzten Druckers stecken bleibt. Der neue Laserdrucker HP LaserJet 4 Plus des Markführers Hewlett-Packard löst dieses Problem. Dabei signalisiert das 'Plus' eine wesentliche Leistungssteigerung zum bisherigen Preis. So bietet die neue Generation der marktführenden HP LaserJet 4-Familie bezüglich Druckleistung und -qualität, Netzwerkintegration, Papierhandhabung, ökonomischem Einsatz und Grafikfähigkeit wesentliche Vorteile. Die herausragendsten Leistungsmerkmale sind: Druckgeschwindigkeit von 12 Seiten/min, problemlose Integration in Standardnetzwerke und Multinetzwerk-Protokoll-Umgebungen, unter anderem dank bidirektionaler paralleler- und serieller Schnittstelle sowie der brandneuen HP JetDirect-Karte, auf der Anschlüsse für Ethernet, BNC und Localtalk bereits vorhanden sind. Weiter eine hervorragende, zusätzlich verbesserte Druckqualität, eine äusserst flexible Papierhandhabung mit der ab Herbst verfügbare Option für den Zweiseitendruck, der HP EconoMode, welcher den Tonerverbrauch um 50% senkt sowie die HP MEt-Technologie, die den nutzbaren Speicher nahezu verdoppelt. Die Plus-Serie besteht aus zwei, für verschiedene Bedürfnisse konzipierten Drucker. Das Basismodell, der HP LaserJet 4 Plus ist speziell für PC-Arbeitsgruppen ausgelegt. Beim HP LaserJet 4M handelt es sich um einen vorkonfigurierten Netzwerkdrucker, der speziell für den Einsatz in Multivendor-Umgebungen ausgelegt ist. Die HP JetDirect-Karte ist bei diesem Printer bereits vorinstalliert und er verfügt über Postscript Level 2. Der HP LaserJet 4 Plus kann modular aufgerüstet werden. Der Energieverbrauch entspricht den Normen des Bundesprogramms E2000 und des amerikanischen Energy Star-Programms. Die beiden, für ein monatliches Druckvolumen von 20 000 Seiten ausgelegten Geräte, sind ab sofort über den HP Fachhandel erhältlich. Der für den Fachhandel unverbindliche Listenpreis beträgt inkl. WUST für den HP LaserJet 4 Plus Fr. 2795.– und für den HP LaserJet 4M Plus Fr. 3750.–

Hohe Druckgeschwindigkeit ohne lange Wartezeiten

Hohe Druckgeschwindigkeit ist die eine Seite der Medaille. Oft wird sie jedoch von langen Wartezeiten beim Seitenaufbau zunichte gemacht. Beim HP LaserJet 4 Plus erfolgt die Ausgabe der ersten Seite bereits nach 17 s. Dies vor allem dank eines 25 MHz Intel i960 RISC-Prozessors, der eine schnelle Verarbeitung der Daten garantiert. Einen Beitrag zur Geschwindigkeitserhöhung leistet auch die sogenannte Resource Saving-Funktion, welche dafür sorgt, dass bei einem Sprachwechsel von PCL auf PostScript einmal geladene Schriften, Macros und Logos nicht neu geladen werden müssen. Unter PostScript laufen zudem die Verarbeitung und das Ausdrucken simultan ab. Das heisst, während eine Seite gedruckt wird, verarbeitet der Drucker bereits die nächste.

Aus eins mach zwei – Druck komplexer Seiten mit Standardspeicher

Der HP LaserJet 4 Plus ist standardmässig mit einem Speicher von 2 MByte ausgerüstet. Er kann auf 66 MByte aufgerüstet werden. Beim HP LaserJet 4M Plus lauten die entsprechenden Werte 6 MByte, aufrüstbar auf 38 MByte. Auch in diesem Fall sorgt eine HP-eigene-Technik dafür, dass selbst mit dem Standardspeicher komplexe Seiten problemlos ausgedruckt werden können. Mittels der HP Memory Enhancement Technology (MEt) wird die Speicherkapazität nahezu verdoppelt.

Anschlussfreudig und sprachgewandt: Woher der Druckauftrag auch immer kommt, der Drucker erkennt den Absender

In der offenen Welt der lokalen Netzwerke ist die Frage der Umgebungsflexibilität von entscheidender Bedeutung. Auch in dieser Beziehung lassen die beiden Geräte keine Wünsche offen. Sie sind standardmässig mit einer parallelen HP BiTronics und einer seriellen RS-232 Schnittstelle ausgestattet. Der HP LaserJet 4 Plus verfügt zudem über einen modularen MIO 5.1 E/ASteckplatz für die HP JetDirect-Netzwerkschnittstelle. Er ist damit in mehr als 12 verschiedene Netzwerkbetriebssysteme integrierbar und unterstützt die wichtigsten Netzwerk-Protokolle und -Topologien.

Der HP LaserJet 4M Plus besitzt bereits eine vorinstallierte HP JetDirect-Karte der neuesten Generation für den Anschluss an Ethernet-, LocalTalk- und Token Ring-Netzwerke. Er ist damit multiprotokollfähig und unterstützt gleichzeitig 11 Netzwerkbetriebssysteme. Alle Schnittstellen können gleichzeitig aktiv sein.

Neben der Anschlussfreudigkeit sind die neuen Maschinen auch äusserst sprachgewandt. So arbeitet der HP LaserJet 4 Plus mit der erweiterten HP PCL 5 Druckersprache mit HP GU2. Er kann optional mit PostScript ausgerüstet werden. Auch der HP LaserJet 4M Plus ist mit HP PCL 5 ausgerüstet. Darüber hinaus verfügt er über Adobe PostScript Level 2. Die Spracherkennung und -Umschaltung erfolgen automatisch.

- Hewlett-Packard (Schweiz) AG
  Frau Susanne Bättig
  In der Luberzen 29
  CH–8902 Urdorf
  Telefon 01 735 71 11
  Telefax 01 735 77 00

Leserdienst Nr. 82

Die neue UV-Serie von ATI Unicam

Am 29. Juli 1949 verkaufte Unicam den ersten Spektralphotometer, einen SP500, an die Universität von Glasgow. Beinahe fünf Jahrzente später finden sich die Spektralphotometer von ATI Unicam in vielen Laboratorien und Firmen wieder. ATI Unicam hat es sich zur Aufgabe gemacht, stets Produkte von höchster Qualität kombiniert mit einfachster Bedienung herzustellen.

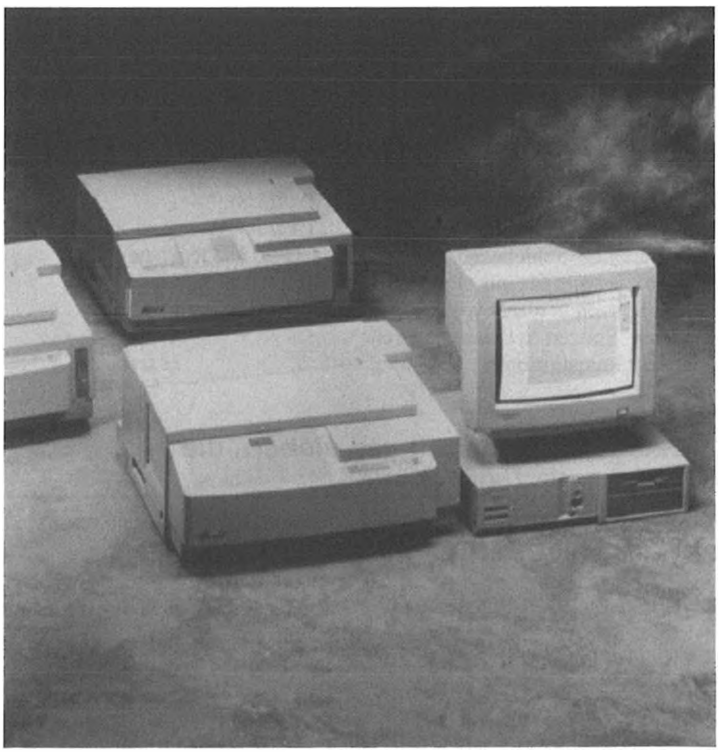
Unter diesen Gesichtspunkten entstanden auch die neuen Doppelstrahl-Spektralphotometer der UV-Serie (UV2, UV3 und UV4).

Holographische Gitter (Master Interferometric Gratings) sind ein Garant für beste Streulichtwerte. Quarz beschichtete Optik mit über 90% Reflexion kombiniert mit einem selbstoptimierenden Lampenumschaltspiegel ergeben beste Signal-Rauschwerte. Die hohe Scangeschwindigkeit (3800 nm*min^{-1}) erlaubt eine effiziente Arbeitsweise. Für stark absorbierende Lösungen steht zudem der Intelliscan-Mode zur Verfügung, welcher das bestmögliche Spektrum in kürzester Zeit ergibt. Zur Gerätesteuerung steht wahlweise die eingebaute PRISM-Software oder die auf WINDOWS basierende Vision-Software zur Verfügung.

Wenn höchste Leistung verlangt wird, lohnt es sich, die Spektralphotometer der ATI Unicam UV-Serie zu prüfen.

- Henry Sarasin AG
  Laborgeräte
  Postfach
  CH–4010 Basel
  Telefon 061 272 52 10
  Telefax 061 272 52 53

Leserdienst Nr. 83



Reagent of the Year 1994

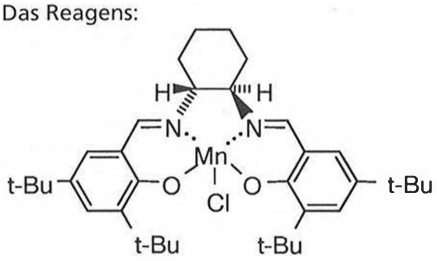
14715 (R,R)-(-)-N,N'-Bis(3,5-di-tert.butyl-salicyliden)-1,2-cyclohexan-diamino-mangan-chlorid, [(R,R)-Jacobsen Katalysator I].
Packungsgrössen: 1 and 5 g

14717 (S,S)-(+)-N,N'-Bis(3,5-di-tert.-butyl-salicyliden)-1,2-cyclohexan-diamino-mangan-chlorid;[(S,S)-Jacobsen Katalysator I]
Packungsgrössen: 1 and 5 g

The Preisträger 1994:
Prof. Dr. E.N. Jacobsen

E.N. Jacobsen, geboren 1960 in New York, beendete sein Studium an der University of California, Berkeley, bei Prof.R.G. Bergman. Zu einem Postdoctorat schloss er sich der Gruppe von Prof.K.B. Sharpless an, und ging dann als Assistant Professor, später Associate Professor, an die University of Illinois, Urbana-Champaign. Seit 1993 ist er Professor an der Harvard University, Cambridge, MA.

Das Reagens:



1994 und ent-1994

Enantiomer hoch angereicherte Epoxide aus nicht funktionalisierten Alkenen – das ist die Essenz einer aufregenden Chemie um das Reagens des Jahres 1994 oder ent-1994, eines chiralen nicht racemischen, katalytisch wirkenden Uebergangsmetall-komplexes.
Ein recht breites Substratspektrum ist schon untersucht worden; die Enantiomerenüberschüsse erreichen in der Regel 90%; manchmal sogar 98% [1,2]. Das ganze Potential des methodischen Konzeptes wird gerade ausgelotet: die Feinabstimmung der Liganden [3] , die Erprobung von Dienen und En-inen als Substraten [4] , die enantioselektive Oxidation von Sulfiden zu Sulfonen [5], und die Herstellung von Aziridinen [6]. Die Bemühungen um enantioselektive Additionen an nicht funktionalisierte Doppelbindungen sind weiterhin sehr intensiv [7]; hier ist das Reagens des Jahres 1994 ein echtes Highlight. Die Epoxid-funktion eröffnet durch die vielseitig mögliche Folgechemie extrem kurze Wege zu pharmakologisch aktiven Verbindungen, wie zu enantiomerenreinen Antihypertensiva aus Dimethylchromenen [8]. Auch eine Synthese der Taxol-Seitenkette ist schon beschrieben [9].

Mit der diesjährigen Preisvergabe zeichnet die Jury eine wichtige Entdeckung auf einem aktuellen Schlüsselgebiet der organischen Synthese aus. Das Preiskomitee würdigt aber nicht nur ein Reagens, sondern ausdrücklich auch eine Methode: die leichte Zugänglichkeit beider Enantiomere sowie eine sehr leichte Reaktionsführung machen das Verfahren ideal für die Anwendung im multi-kg Massstab. So hat die Reaktion schon jetzt ihren Platz gefunden in der immer noch sehr kleinen Gruppe von enantioselektiven, katalytischen Verfahren von industrieller Bedeutung.

Literatur:

[1] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, J.Am.Chem.Soc. 1990,**112**, 2801. [2] (a) W. Zhang, E.N. Jacobsen, J.Org.Chem. 1991,**56**,2296; (b) E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker, L. Deng, J.Am.Chem.Soc. 1991,**113** 7063. [3] S.Chang, R.M.Heid, E.N. Jacobsen, Tetrahedron Letters, 1994, **35**,669. [4] N.H. Lee, E.N. Jacobsen, Tetrahedron Letters 1991, **32**, 6533. [5] M. Palucki, P.E. Hanson, E.N. Jacobsen, Tetrahedron Letters, 1992, **33**, 7111. [6l Z. Li, K.R. Conser, E.N. Jacobsen, J.Am.Chem. Soc. 1993,**115**,5326. [7] See literature cited in [6]. [8] N.H. Lee, A.R. Muci. E.N. Jacobsen, Tetrahedron Letters 1991, **32**, 5055. [9] L. Deng, E.N. Jacobsen, J.Org. Chem.1992, **57**, 4320.

Preiskomitee 1994:

Prof. Dr. D. Enders, Aachen
Prof. Dr. H.J. Hansen, Zürich
Prof. Dr. G. Helmchen, Heidelberg
Prof. Dr. G. Simchen, Stuttgart und
Dr. W. Keller, Buchs

Der Fluka Preis:

Mit dem Fluka Preis "Reagent of the Year" werden seit 1987 alljährlich Forschungsarbeiten ausgezeichnet, die erstmals aufzeigen, dass einer neuen Verbindung der Rang eines wichtigen Reagens in der organischen Chemie, in der Biochemie oder in der analytischen Chemie Verwendung finden kann. Für den Preis können Wissenschaftler aus Hochschule, Industrie und aus behördlichen oder privaten Lehr- und Forschungsanstalten nominiert werden. Die Preissumme beträgt sFr. 10'000.-. Vorschläge für den Fluka Preis "Reagent of the Year" senden Sie bitte bis jeweils 30.September an das Preiskomitee c/o Fluka Chemie AG, CH-9470 Buchs/Schweiz. Die vollständigen Statuten stellen wir Ihnen auf Wunsch gerne zu.

Fluka

Fluka Chemie AG
Industriestrasse 25
CH-9470 Buchs/Switzerland

CHIMIA 48 (1994) Nr. 7/8 (Juli/August)

Miniaturisiertes Dispergiergerät Neuer ULTRA-TURRAX® T 8 für Kleinstmengen

In allen naturwissenschaftlichen Bereichen ist die Miniaturisierung in vollem Gange. Um entsprechend arbeiten und reproduzierbare Ergebnisse erzielen zu können, ist die Herabsetzung der Korngrösse und die Homogenität von den zu bearbeitenden Proben von grösster Bedeutung.

Zum Homogenisieren, Dispergieren, Suspendieren und Emulgieren von Kleinstmengen ab 0,1 ml wurde der ULTRA-TURRAX® T 8 entwickelt. Angetrieben wird der ULTRA-TURRAX® T 8 durch einen mit Niederspannung (12 V) versorgten Motor. Ein Trafo sorgt für Anschluss an ein 230 V 150/60 Hz Netz.

Zum Arbeiten stehen zwei Dispergierwerkzeuge zur Verfügung, die hohen Materialansprüchen gerecht werden:

- S 8 N - 5 G mit 5 mm Aussendurchmesser für Mengen von 0,1 bis 5 ml.
- S 8 N - 8 G mit 8 mm Aussendurchmesser von 1–50 ml.

Als weiteres Zubehör dient die Dispergierstation T 8.10, geeignet zur Unterbringung, sowie als kompakten Arbeitsplatz für den ULTRA-TURRAX® T 8.

Mit dieser Neuentwicklung können ab sofort wichtige Arbeiten in der Probenvorbereitung wahrgenommen werden, wie z.B.

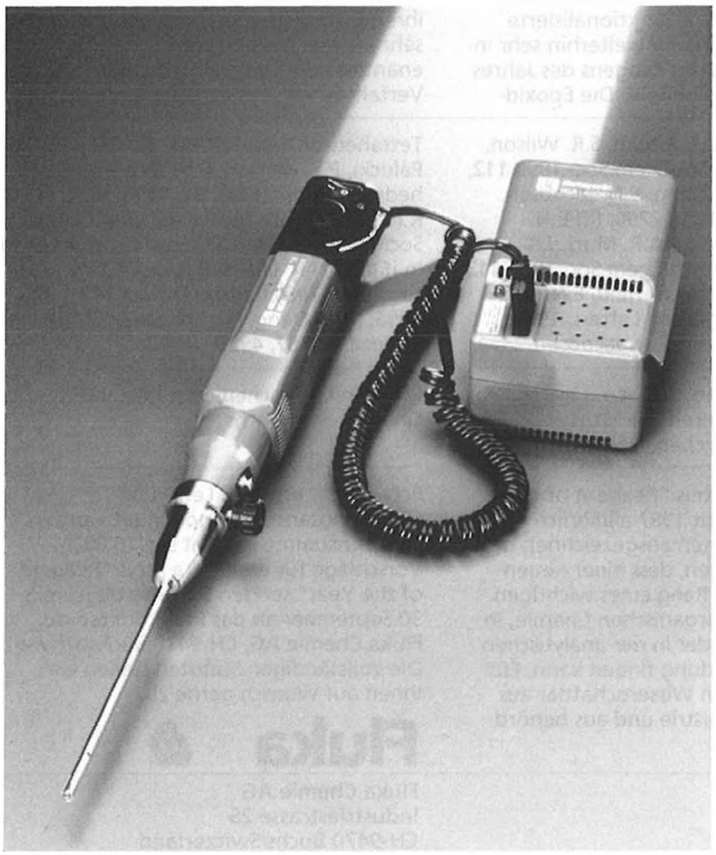
- Homogenisieren von Analysenproben
- Emulgieren von öligen und wässrigen Phasen
- Zerfaserung von pflanzlichen und tierischen Gewebeteilen
- Weitere vielfältige Misch- und Aufschlämmungsarbeiten in kleinen Gefässen, wie Eppendorfröhrchen, Zentrifugengläsern und Küvetten.

Der ULTRA-TURRAX® T 8 zeichnet sich dabei durch folgende Eigenschaften aus: Die Handlichkeit und einfache Montierbarkeit/Zerlegbarkeit des Gerätes gewährt einfaches, übersichtliches und somit rasches Arbeiten. Die Verwendung von hochwertigen, lösemittelbeständigen, auf alle Arten sterilisierbare Materialien eröffnet ein weites Arbeitsfeld. Aus den kurzen Bearbeitungszeiten, oft < 10 s und der hohen Belastbarkeit der Dichtung und des Rotor-Stator-Systems ergibt sich eine lange Lebensdauer.

Weitere Informationen erhalten Sie bei:

• IG Instrumenten-Gesellschaft AG
Räffelstrasse 32
CH–8045 Zürich
Telefon 01 461 33 11
Telefax 01 461 30 01

Leserdienst Nr. 84



Neue Vetretung: Einfachere und schnellere Analysen mit dem neuen Biosensor von FISONS

Bessere Probenhandhabung und einfachere Bedienung machen IAsys von FISONS zur idealen Systemwahl, um biomolekulare Interaktionen in 'real time' zu verfolgen.

Die Ergebnisse einer grossen Anzahl biomolekularer Vorgänge und kinetischer Reaktionen stehen innert wenigen Minuten zur Verfügung und dies ohne Einsatz von gefährlicher radioaktiver Markierung und ohne vorherige, mühsame Reinigungsverfahren oder langweilige Probenvorbereitung. Interaktionen wie Protein-Protein, Protein-DNA, Pharmawirkstoff-Rezeptor, Antikörper-Antigen und sogar Zellen benötigen nur einen Bruchteil der Zeit herkömmlicher Methoden.

Bei IAsys ist der optische Biosensor in einer auswechselbaren Küvette eingebaut. Der Massentransfer wird durch einen Mikro-Rührer garantiert. Somit können Probleme wie verstopfte Leitungen oder unreproduzierbare Flüsse, durch nicht einwandfrei arbeitende Schlauchquetschpumpen, ausgeschlossen werden. Der Wartungsaufwand ist minimal.

Die Möglichkeit der einfachen Entfernung und Wiedereinführung der Messzellen maximiert die Produktivität in der Forschung, speziell wenn mehrere Benutzer dasselbe Gerät für unterschiedliche Projekte einsetzen. Der Bereich der möglichen Anwendungen wird mit dieser neuen und beeindruckenden Technologie enorm erweitert.

Das IAsys Mikro-Küvetten-System macht 'real time' Interaktions-Analysen für viele Labors erschwinglich und eröffnet neue, interessante Perspektiven für die innovative und kreative Forschung.

Seit dem 1. Mai 1994 werden IAsys und die Produkte von FAST (FISONS Applied Sensor Technology) in der Schweiz exklusiv durch die Brechbühler AG vertrieben.

• Brechbühler AG
Steinwiesenstrasse 3
CH–8952 Schlieren/Zürich
Telefon 01 730 48 25
Telefax 01 730 61 41

Leserdienst Nr. 85

MERCK: Neue System-Dimension in der HPLC, eine Weltneuheit wird präsentiert

Durch konsequent kontinuierliche Entwicklungsarbeit ist wiederum Merck in der Lage, eine neue Dimension in der Chromatographie einzuführen – LaChrom. LaChrom steht fortan als Synonym für das perfekte HPLC-System. LaChrom lässt keine Wünsche offen. Die Arbeit im Labor wird wesentlich erleichtert, die Qualität der Analysenergebnisse sowie deren Aussagekraft wird unterstrichen.

LaChrom, die neue Gerätelinie von Merck, garantiert Flexibilität, Datensicherheit, Reproduzierbarkeit im Geräte-System und hält die Kompatibilität zum bisherigen, bewährten LiChro-Graph-System und vorangegangen Modulen offen. Für Geräteanwender von Merck eine vielgeschätzte Selbstverständlichkeit.

Minimale Peak-Dispersion werden durch die neue Konstruktion des LaChrom-Systems gewährleistet. So können die Vorteile der Narrow-Bore-HPLC ohne Umbauten voll genutzt werden. Sicherheit und Vertrauen werden durch den neuen LaChrom Confidence Level

erzielt. Entsprechende Kontrollmethoden für die wichtigsten Geräte- und Chromatographie-Parameter für Einzelmodule, als auch im LaChrom-System sind implementiert und werden automatisch durchgeführt und weltweit erstmalig GLP-gerecht dokumentiert. Die neue Konzeption aller Analysen- und Test-Reports erfüllt die GLP-Grundsätze der eindeutigen, rückverfolgbaren und archivierbaren Dokumentation. LaChrom unterstützt den Anwender bei der Erfüllung der Anforderungen seines Qualitätsmanagement-Systems, beispielsweise durch Erstellung von Logbüchern, übersichtlichem System-Eignungstest, vielfältige Testreports, sowie eine Service Diagnose im Faxformat.

Ebenfalls vollkommen neu konzipiert wurde das ebenfalls hochleistungsfähige Datenkommunikationsnetz D-Line, die interne LaChrom Modul-Kommunikation.

Als Basis für die modular aufgebaute LaChrom Chromatographie-Software wurde das zukunftsorientierte Betriebssystem Windows NT™ ausgewählt, das erstmals sicheres Multitasking für Windows-Anwendungen garantiert. Eine völlig neuartige Hilfe für den Anwender stellt die Multi-Media-HPLC dar. Video- und Audio-gestütztes Arbeiten in der Chromatographie durch Einsatz von Videosequenz, Animationen und Tonpassagen am HPLC-Arbeitsplatz.

LaChrom wird sowohl bei Merck, als auch bei Hitachi, entsprechend der Richtlinien des Qualitätsmanagement-Systems ISO 9001 entwikkelt, produziert, ausgeliefert und gewartet. Test- und Validierungszertifikate dokumentieren die Qualität aller LaChrom Module.

Weitere Informationen erhalten Sie von:

- MERCK
  E. Merck (Schweiz) AG
  Geschäftsbereich MERCK ABS
  Laborsysteme
  Rüchligstrasse 20
  CH–8953 Dietikon
  Telefon 01 745 11 11
  Telefax 01 745 14 20

Leserdienst Nr. 86

Neues Paket zur Validierung von Hard- und Software

Thermo Separation Products (TSP) bietet neu eine Dienstleistung für die Validierung von Hard- und Software an.

Das Paket beinhaltet komplette Testvorschriften und Spezifikationsprüfungen wie sie von offiziellen Stellen wie FDA, IKS gefordert werden.

Die Chromatographiesoftware PC1000 von TSP wird ab sofort mit einem ISO/PMA/ ANSI-konformen Validierungszertifikat ausgeliefert. Dem Benützer wird dadurch erlaubt, jederzeit Informationen über den Lebenszyklus der Software einzuholen, und Unterlagen, welche zur Entwicklung des Produktes erarbeitet wurden, im Fabrikationswerk in Fremont, CA zu inspizieren.

Jedes Hardware-Modul wird neu mit einem kompletten Testprotokoll, Installationsformular und einem Logbuch ausgeliefert. Alle Unterhaltsarbeiten und Spezifikationskontrollen, die während der Lebenszeit des Instrumentes durchgeführt wurden, können auf diese Weise in einer kompakten Form dokumentiert und gesammelt werden.

Für weitere Informationen:

- Thermo Separation Products AG
  Frau M. Egli
  Hegenheimermattweg 6
  CH–4123 Allschwil
  Telefon 061 481 84 00
  Telefax 061 481 37 44

Leserdienst Nr. 87

BASF-Anlage zur Butadienhydrierung in Betrieb

Die BASF hat an ihrem-Standort Antwerpen, Belgien, im Mai 1994 eine Anlage zur selektiven Hydrierung von Butadien in Betrieb genommen. Die zweistufige Hydrierung, die über eine Kapazität von 260000 t C4-Schnitt pro Jahr verfügt, ist Teil des neuen Steamcrakkers der BASF. Kontraktor war die Linde AG, Deutschland.

Das der Hydrieranlage zugrunde liegende Verfahren und der eingesetzte Katalysator sind Eigenentwicklungen der BASF. Einsatzstoff ist der C4-Schnitt des Steamcrakkers, in dem Butadien zu mehr als 40% enthalten ist. Das Butadien wird in den zwei Hydrierstufen mit einer Selektivität von mehr als 96% in 1- und 2-Buten umgewandelt, der Restgehalt an Butadien beträgt weniger als 0,2%. Das im C4-Schnitt enthaltene Isobuten wird durch die Hydrierung nicht verändert.

Das BASF-Hydrierverfahren ist für eine Vielzahl unterschiedlich zusammengesetzter C4-Schnitte geeignet. Durch Prozessvariation lassen sich Butadien-Restgehalte von einigen % bis zu wenigen ppm einstellen. Die BASF wird ihr Hydrierverfahren über anerkannte Kontraktoren lizenzieren.

- BASF (Schweiz) AG
  Appital
  Postfach 99
  CH–8820 Wädenswil/Au
  Telefon 01 781 91 1
  Telefax 01 781 93 88

Leserdienst Nr. 88

Hypermedia in der Spektroskopie

Jetzt macht die Interpretation von Spektren noch mehr Spass: Mit SpecTool ist ein sehr einfach zu bedienendes Werkzeug zur Interpretation von NMR (C und H), IR-, MS- und UV-Spektren erhältlich, das auf über 1300 Seiten ausgewerteter Referenzdaten, heuristischer Regeln, Spektren und Computer-Algorithmen beruht.

Hypermedia heisst die Zauber-Oberfläche, die dem Benutzer erlaubt, gezielt jeweils die Funktion auszuwählen unter der die gerade benötigte Information zu finden ist. SpecTool ist dadurch jedem gedruckten Werk klar überlegen. Es existieren Versionen für McIntosh und MS/Windows, SpecTool ist auch zusammen mit einem Notebook-Computer fertig installiert erhältlich.

- MSP Friedli & Co.
  Bindenhausstrasse 46
  CH–3098 Köniz
  Telefon 031 972 31 52
  Telefax 031 971 46 43

Leserdienst Nr. 89

Neue Generation: FT/IR mit Corner Cube Mirror!

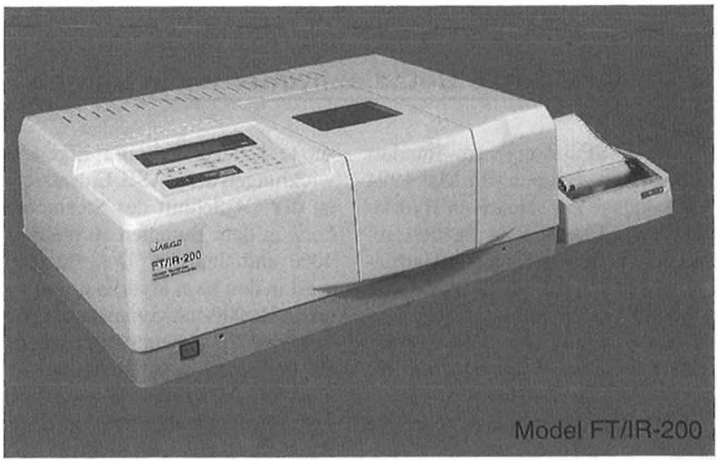
In der neuen FT/IR Spektrometer-Generation wurde der neueste Stand der Technik angewendet um dem Benutzer eine lange Lebensdauer zu gewährleisten. Die leistungsstarke Optik mit moderner Corner Cube Mirror Technologie, macht eine Justierung überflüssig. Die Geräte sind für eine einfache Anpassung an die wechselnden Bedürfnisse konzipiert. Bis zu 4 Detektoren können gleichzeitig eingebaut sein. Die PC-Steuerung des Gerätes und des Zubehörs erfolgt mit modernster Windows-Software. Die Software ist sehr einfach zu bedienen und bietet alle Möglichkeiten für die Akquisition, Manipulation/Berechnung, Konversion, Darstellung und Ausdruck. Eine Spektrenbibliothek ist selbstverständlich auch Teil des Systems. Die Software ermöglicht zusätzlich die Speicherung der Daten im J-Camp oder Spectra Calc Format um die Daten direkt in andere Softwarepakete zu übernehmen.

Die Zubehörpalette ist reichhaltig und umfasst unter anderem ATR, ATR mit variablem Winkel, IR-Polarisationszubehör, beheiztes Diffuse Reflection Zubehör und ein Mikroskop-Zubehör zur Analyse von Proben mit einer Grösse von 10 μ!

Der umfangreiche 16-seitige Prospekt gibt einen umfassenden Überblick über die Gerätefamilie, das Zubehör und die Software.

- OmniLab AG
  Untere Bahnhofstrasse 14
  CH–8932 Mettmenstetten
  Telefon 01 768 22 11
  Telefax 01 768 23 21

Leserdienst Nr. 90



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Mit dem weiterentwickelten Nachbehandlungssystem Seralpur PRO 90 CN bietet Seral ein System, das zur Herstellung von Reinstwasser für besonders kritische Anwendungsfälle wie HPLC, AAS und Ionenchromatografie geeignet ist. Auch für biotechnische und mikrobiologische Prozesse kann mit der zuschaltbaren Ultrafiltrationseinheit Seralpur UF keim- und pyrogenfreies Wasser produziert werden.

Die modulare Konzeption dieses Reinstwasser-Systems macht die anwendungsorientierte Reinstwasser-Gewinnung vor Ort möglich. Die Qualität des erzeugten Reinstwassers entspricht allen internationalen Normen wie ASTM-1, CAP und NCCLS.

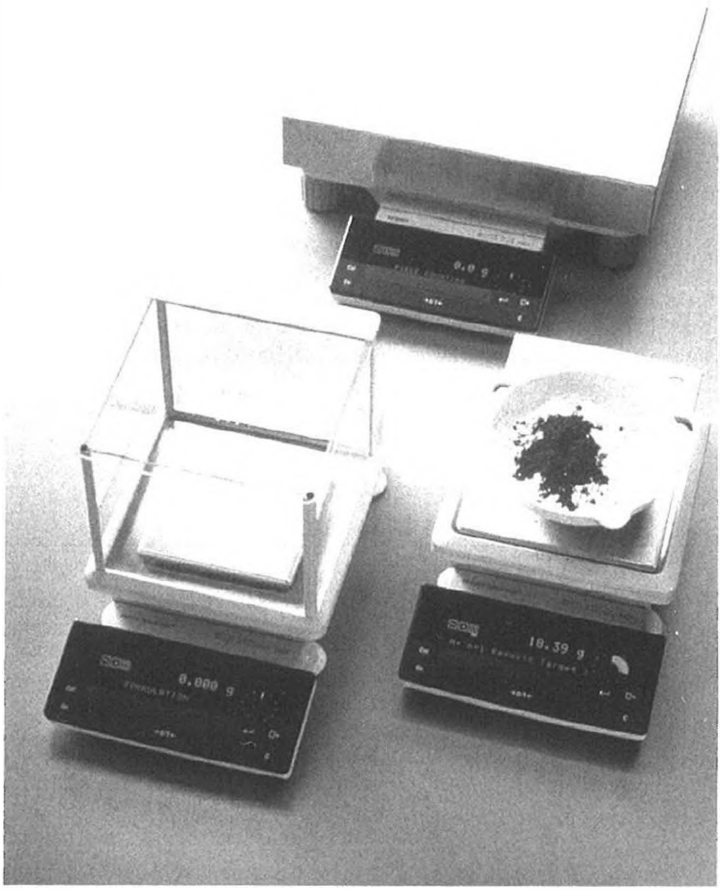
Die Leitfähigkeit beträgt 0,055 µS/cm (18,2 MegOhm x cm) bei 25° C. Die Trenngrenze der Ultrafiltrationseinheit liegt bei 10000 Dalton. Der TOC-Gehalt ist < 20 ppb. Dem Anwender stehen heute zwei Betriebsarten zur Verfügung:

Eine permanente Zirkulation oder ein Intervallbetrieb. Beide garantieren eine optimale Reinstwasserqualität. Der Seralpur PRO 90 CN besteht im wesentlichen aus vier Filterstufen, Zirkulationseinheit, Leitfähigkeitsmessgerät (Messbereich 0–5 µS/cm) und 0,2 µm Membranfilter am Auslauf.
Weitere Informationen erhalten Sie bei:

- IG Instrumenten-Gesellschaft AG
  Räffelstrasse 32
  CH–8045 Zürich
  Telefon 01 461 33 11

Leserdienst Nr. 90

Für höchste Ansprüche:
Die neuen METTLER TOLEDO PR/SR-Waagen



Die neuen PR/SR Präzisionswaagen setzen neue Massstäbe beim professionellen wägen. Präzision, Zuverlässigkeit, Effizienz und einfache, schnelle Bedienung sind auf anspruchsvolle Anwendungen zugeschnitten.

Anforderungen der 'Guten Laborpraxis' (GLP) und anderer moderner QS-Systeme werden kompromisslos erfüllt. Vor allem in den Bereichen Prüfmittelüberwachung und Dokumentation stehen alle notwendigen Eigenschaften und Fä-

higkeiten zur Verfügung. Alle anfallenden Daten, von der Eingangs- bis zur Endkontrolle können sicher erfasst, ausgewertet, dokumentiert und wiederverwendet werden. Grösste Zuverlässigkeit der Resultate garantiert die vollautomatische und selbständige Kalibrierung FACT.

Einfache Bedienung am alphanumerischen Terminal und fest eingebaute, rasch abrufbare Wägeapplikationen machen die PR/SR-Waagen noch komfortabler. Je nach Anwendung kann das Verhältnis der Wägegeschwindigkeit zur Reproduzierbarkeit angepasst werden.

11 PR-Modelle für Höchstlasten von 210 bis 8100 g mit einer Ablesbarkeit zwischen 0,001 und 1 g stehen dem Anwender zur Auswahl. Die Höchstlast der 7 SR-Waagen bewegt sich zwischen 8100 und 32100 g bei einer Ablesbarkeit von 0,1 bzw. 1 g.

- Mettler-Toledo (Schweiz) AG
  Postfach
  CH–8606 Greifensee
  Telefon 01 944 45 45
  Telefax 01 944 45 10

Leserdienst Nr. 91

Umsatzplus bei BOHLIN INSTRUMENTS 10 Jahre BOHLIN INSTRUMENTS

Bohlin Instruments, bekannt als einer der führenden Hersteller hochwertiger Labor-Rheometer, feiert in diesem Jahr sein 10jähriges Firmenjubiläum.

Gegründet als Universitäts-'Ableger' hat sich Bohlin in den vergangenen zehn Jahren zu einer 'Rheologischen Grösse' gemausert, die in der Gerätetechnik immer wieder neue Akzente setzt.

Seit Firmengründung wurde eine durchschnittliche jährliche Umsatzsteigerung von 25% erreicht. Auch für 1993 konnte eine zweistellige Steigerung verbucht werden.

Neben stattlichen Umsatzzahlen schrieb BOHLIN aber auch im Ergebnis weltweit 'schwarze' Zahlen, was bei einer äusserst schwachen Gesamtwirtschaftslage wie sie in 1993 herrschte nicht unbedingt selbstverständlich ist.

Diese Tatsache ermöglicht es Bohlin Instruments auch in Zukunft weiter in den Ausbau und die Optimierung der Firma zu investieren.

Bohlin Instruments möchte sich auf diesem Wege auch bei all seinen Anwendern für ihr entgegengebrachtes Vertrauen bedanken.

- Bohlin Instruments
  Joachim Haag
  Lugwaldstrasse 22
  D–75417 Mühlacker

Leserdienst Nr. 92

The First International Conference on the Scale-Up of Chemical Processes

26–29 September 1994
Grand Hotel and Conference Centre
Brighton, England

Die Veranstaltung wird von Sterling Organics und Scientific Update (England) durchgeführt. Die Thematik des Treffens deckt alle Aspekte des "Scale-up'-Prozesses ab, von den gesetzlichen Vorschriften über die Entwicklung und Implementierung von Reaktionsmodellen bis zur industriellen Produktion. Während der dreitägigen Konferenz werden etliche angesehene und kompetente Fachleute Ihnen ihre Erfahrungen und Ansichten vermitteln.

Die spezifischen Themen sind: "Scale-up'-Theorie, Prozessvalidierung, Theorie der 'Runaway'-Reaktion, die Anwendung von Geräten und Methoden für die Prozesssimulation, die Sicherheit von chemischen Reaktionen, die Modellierung, die Anwendung der Reaktionskalorimetrie in der Prozessentwicklung, und Wärmetransfer.

Gleichzeitig mit der Konferenz findet eine Ausstellung statt, wo Sie sich über die neuesten Entwicklungen auf dem Gebiet der Reaktionsentwicklung im Labor informieren können.

Wenn Sie weitere Auskünfte oder ein Anmeldeformular haben wollen, rufen Sie uns bitte an.

- Scientific Update
  Telefon (+44) 435 87 30 62
  Telefax (+44) 435 87 27 34

Leserdienst Nr. 93

ChemManager Chemie- und Sicherheitsdatenbanken

Die schweizer Firma ASSiST bietet neu eine PC basierte Annex 1 Datenbank mit den von der EG als Gefahrenstoffen klassifizierten Substanzen an (19. und 20. Anpassung an Richtlinie 67/548/EWG).

Die vollständig überarbeitete Version der EG enthält 185 Neueintragungen, 648 Änderungen für Industrieprodukte sowie 1291 Änderungen für Publikumsprodukte. Hersteller und Vertreiber von Gefahrenstoffen haben die Informationen der 19. Anpassung bis zum 1.6.1994 auf die Sicherheitsdatenblätter und Chemikalienetiketten zu übertragen. Stichtag für die 20. Anpassung ist der 1.1.1995.

Im Gegensatz zur Publikation der EG enthält die ChemManager Annex 1 – Datenbank ein Stoffregister sowie Angaben, welche Stoffe geändert und welche Stoffe neu als Gefahrenstoffe klassifiziert sind. Die vollständige Information der EG wird durch Summenformeln, chemische Strukturen sowie Interpretationen in deutsch, englisch und französisch ergänzt.

Neu bietet ASSiST auch eine ELINCS-Datenbank mit den in der EG notifizierten chemischen Stoffen an. Die über 100 000 von der EG als 'Altstoffe' klassifizierten Substanzen können in der EINECS-Datenbank nach CAS-Nr. EINECS-Nr., Summenformel oder IUPAC-Namen effizient aufgefunden werden. Die ChemManager MAK-Liste enthält die Gefahrenklassen und maximalen Arbeitsplatzkonzentrationen für die Schweiz und Deutschland inkl. automatische Interpretation und chemische Strukturen.

Zusätzliche ChemManager Module dienen zur Erstellung von EG-Sicherheitsdatenblättern, Betriebsanweisungen und Chemikalien-Etiketten sowie zur Verwaltung von Chemikalienlagern.

Die Sicherheitsdatenbätter werden nach EG-Normen erstellt und in bis zu 15 Sprachen übersetzt. Dafür sind mehrsprachige Referenzdateien mit Textbausteinen, Stoffdaten, Gefahrenhinweisen, Sicherheitsratschlägen und Gefahrenhinweisen integriert. Entsprechende Chemikalien-Etiketten und Betriebsanweisungen werden automatisch erstellt, basierend auf den Daten im Sicherheitsdatenblatt.

Die ChemManager Lagerverwaltung dient zur effizienten Lagerbewirtschaftung chemischer Stoffe und Abfälle in Labor und Produktion nach ISO 9000 Normen. Der integrierte Etiketten-Generator erstellt Chemikalien-Etiketten für den betriebsinternen Gebrauch mit Angaben zur sicheren Handhabung und zur vorschriftsmässigen Entsorgung.

Die netzwerkfähige Software basiert auf FileMaker Pro und kann auf MS-Windows und Macintosh Systemen eingesetzt werden. ASSiST gewährt dem Benutzer zudem das Recht, Änderungen und Erweiterungen an den einzelnen Modulen selber vorzunehmen.

- ASSiST AG
  Baslerstrasse 21
  CH–4102 Binningen
  Telefon 061 280 75 62
  Telefax 061 421 69 34

Leserdienst Nr. 94

2. Europäisches LIMS-Forum 21./22. September 1994, Messe Basel

Bereits zum zweiten Mal wird das Europäische LIMS Forum von Hewlett-Packard organisiert und durchgeführt. Die Themen des Forums sind:

- Corporate Computing und Informationsmanagement
- Produktionsplanung und Qualitätssicherung
- Qualitätsdaten-Management
- Studienplanung und -verwaltung
- Normen und Richtlinien (GALP, GAMP, ISO, EN)
- Informations-Management-Software: Standardisierung/Harmonisierung
- Posterpräsentationen aus Theorie und Praxis

Besonders angesprochen werden am Europäischen LIMS Forum Abteilungs-, Laborleiter und verantwortliche Personen für EDV-Installationen in Chemie-, Pharmazeutik-, Lebensmittel- und weiteren Produktionsfirmen sowie Behörden mit eigenen analytischen Labors oder Vertragslabors. Speziell richtet sich der Inhalt auch an Verantwortliche für Studienplanung an Hochschulen und in Forschungslaboratorien in den Bereichen Chemie, Pharmazeutik, Nahrungsmittel und Behörden. Unterlagen sind erhältlich bei:

- Hewlett-Packard GmbH
  Analytical Products Group
  Frau Ingrid Bollian
  Hewlett-Packard-Strasse 8
  D–76337 Waldbronn
  Telefax +49 7243 602 155

Leserdienst Nr. 94

CHIMIA 48 (1994) Nr. 7/8 (Juli/August)

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Telefax 042 52 29 48

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Erlenstrasse 27B
CH-4106 Therwil
Telefon 061 721 81 51
Telefax 061 721 88 53

STELLENMARKT

Johannes Kepler Universität Linz

Am Institut für Chemie der Technisch-Naturwissenschaftlichen Fakultät der Universität Linz gelangt die Planstelle eines/r

Ordentlichen Universitätsprofessors/in für Physikalische Chemie

(Nachfolge Janeschitz-Kriegl)

ehestmöglich zur Wiederbesetzung.

Von Bewerber/inne/n wird erwartet, dass sie dieses Fach in Lehre und Forschung vertreten und über einschlägige Forschungserfahrung verfügen. Die Lehrtätigkeit erfolgt im Rahmen der Studienrichtungen 'Technische Chemie', 'Wirtschaftsingenieurwesen – Technische Chemie' und 'Chemie (Lehramt an höheren Schulen)'.
Die gesetzlichen Ernennungserfordernisse sind: Ein in- oder ausländisches facheinschlägiges Doktorat; eine in- oder ausländische facheinschlägige Lehrbefugnis oder eine gleichzuhaltende wissenschaftliche Befähigung und der Nachweis pädagogischer Eignung.
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Bewerbungen unter Beifügung eines Lebenslaufes, einer Darstellung der bisherigen beruflichen Tätigkeit, einer Liste der wissenschaftlichen Veröffentlichungen oder gleichwertiger Arbeiten sind bis 30. Oktober 1994 an den Dekan der Technisch-Naturwissenschaftlichen Fakultät der Universität Linz, A–4040 Linz-Auhof, zu richten.

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CHIMIA-Leserdienst 7/8 – 94

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