Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen). Bis zum 10. des Monats bei der Redaktion eingehende Manuskripte können günstigenfalls am 15. des folgenden Monats veröffentlicht werden.

Phosphor-Betaine als Wittig-Zwischenstufen: Es gibt sie doch!*

Herrn Professor Dres. mult. *G. Wittig* anlässlich seines 80. Geburtstages (16. Juni 1977) mit vielen guten Wünschen gewidmet.

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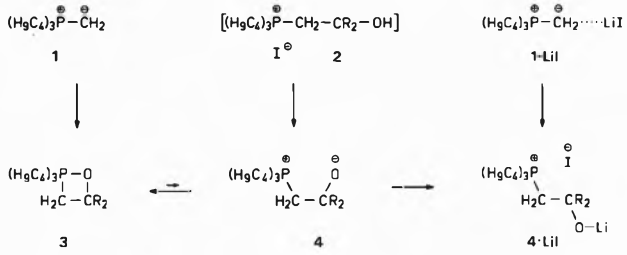
Summary

Trialkyl(aryl)phonio-alkylids can combine with carbonyl compounds to afford zwitterionic "phosphorus betaïnes" as detectable intermediates of the Wittig reaction, provided however that the negative charge residing at the oxygen atom is substantially reduced by binding to a lithium cation or by resonance delocalization into an adjacent carbonyl group.

Bei der Metallierung von Tributyl-methyl-phosphonium-jodid mit *s*-Butyllithium in Tetrahydrofuran entsteht ein mittels Phosphorresonanz ($\delta = +29$ [1]) identifizierbares Ylid, das vermutlich mit Lithiumjodid assoziiert ist (**1**·**LiI**). Nach Zugabe von Benzophenon bei -30 °C verschiebt sich das Signal geringfügig ins tiefere Feld ($\delta = +34$ [1]) und spricht somit für das Auftreten eines ringoffenen Adduktes («Phosphor-Betain»), das wohl in Form eines LiI-Assoziates (**4**·**LiI**) vorliegt. Bei Raumtemperatur zerfällt die Zwischenstufe binnen einiger Stunden zu Tributylphosphinoxid ($\delta = +45$ [1]) und 1,1-Diphenyl-äthylen [2]. Die gleichen Zwischen- und Endprodukte werden beobachtet, wenn man das Tributyl-(2-hydroxy-2,2-diphenyl-äthyl)-phosphonium-jodid (**2**, Fp. 90–92 °C) mit Butyllithium behandelt oder das Oxaphosphetan **3** ($\delta = -68$ [1]; aus «salzfreiem» Tributylphosphonio-methylid [3] und Benzophenon oder aus **2**, Trimethylsilylmethylkalium und Benzophenon gewonnen) mit einer Lösung von Lithiumjodid in Tetrahydrofuran versetzt.



Damit gelang es erstmals, ringoffene Ylid/Carbonyl-Addukte spektroskopisch aufzuspüren. Gestützt auf ähnliche Ergebnisse mit anderen Carbonyl-Komponenten (Formaldehyd, Pivalaldehyd), wagen wir zu verallgemeinern: Die fassbaren, obschon thermolabilen Zwischenstufen besitzen gewöhnlich Betain-Struktur, sofern assoziationsfähige Lithium-Salze zugegen sind. Die von Tri*phenyl*phosphonio-Yliden abgeleiteten Addukte sollten hier keine Ausnahme bilden, da ja die stationären Reste am Phosphor (Butyl, Phenyl etc.) das reaktive Verhalten zwar graduell, aber nicht grundsätzlich ändern. Lediglich ihrer Schwerlöslichkeit wegen haben sie sich bislang der Beobachtung entzogen. Ferner sind betain-artige Strukturen bereits nachgewiesen [4] für die Zwischenprodukte der *Horner*-Variante, die von metallierten Phosphinoxiden («PO-Yliden») ausgeht. Sobald jedoch eine *Wittig*-Reaktion ohne Mitwirkung eines Metalls abgewickelt wird, markieren regelmässig Oxaphosphetane [5] den «Zwischenhalt»***.

Welche Rolle spielt nun das Lithium-Salz? Wir veranschlagen für die Ringöffnung des Oxaphosphetans (**3**) zum «salzfreien» Betain (**4**) einen Aufwand im Bereich von 10 kcal/mol [6]. Dieser Verlust kann mehr als aufgewogen werden durch die Vereinigung eines Lithium-Kations mit dem Oxid-Ion in **4** zu einem Derivat **4**·**LiI** mit der Bindungsbeziehung eines Lithiumalkoholat-Kontaktpaares [7]. Die Rückreaktion, also die Dissoziation von **4**·**LiI** zu **4**, ist energetisch sehr ungünstig und läuft entsprechend langsam ab. Oxaphosphetan **3** und Betain-Abkömmling **4**·**LiI**, bei $-30°$ gemischt, vermögen sich nicht ineinander umzuwandeln und zeigen deshalb nebeneinander die ihnen eigenen Phosphorresonanz-Signale. Die Dissoziation **4**·**LiI** zu **4** ist ferner unerlässlich, wenn man die *Wittig*-Reaktion bis zu Ende führen will. Dazu sind bei **4**·**LiI** (R = Phenyl) lange Reaktionszeiten bei 25 °C nötig, in anderen Fällen (R = Alkyl) ausserdem hohe Temperaturen; es sei denn, man lockt durch Kalium-*t*-butanolat-Zusatz [8] das Lithium vom Betain-Sauerstoff weg. Oxaphosphetane **3** (R = H, Alkyl, Aryl), vom Salz befreit oder in salzfreiem Medium erzeugt, zerfallen bereits um 0° rasch zu Tributylphosphinoxid und Alken [9].

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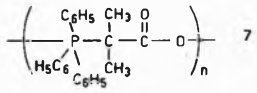
*** Sterische Einflüsse können Abweichungen von der Norm bedingen: das Addukt aus Tri*phenyl*phosphoniomethylid und Pivalaldehyd liegt in Tetrahydrofuran hauptsächlich in der Oxaphosphetan-Ringstruktur vor, selbst wenn ein grosser Überschuss an Lithiumjodid zugegen ist.

Addukt	Y	$\delta_{^{31}P}$ [ppm]
a	$C(C_6H_5)_2$	- 39
b	$NC(CH_3)_3$	- 40
c	O	-



Müssen wir umgekehrt nun folgern, Ylid/Carbonyl-Addukte bevorzugten immer und überall die Oxaphosphetan-Form, solange kein Lithium-Salz im Spiel ist? Wir haben Triphenylphosphonio-isopropylid an Diphenylketen [10], *t*-Butyl-isocyanat und Carbondioxid angelagert und die Struktur dieser Produkte untersucht. Die Möglichkeit zur mesomeren Ladungsausbreitung sollte einen Anreiz bieten zur Einstellung der zwitterionischen Form (Phosphonio-enolat, -amidat bzw.-carboxylat **6**). In Wirklichkeit beobachtet man jedoch in den ersten beiden Fällen Signale ($\delta = -39$ bzw. -40 ppm), die den Oxaphosphetanen **5a** und **5b** zuzuordnen sind [12]. Das Carbondioxid-Addukt ist hingegen unlöslich. Eine cyclisch-oligomere oder polymere Struktur **7** muss demnach in Betracht gezogen werden. Laut Infrarotspektrum ($\tilde{\nu}_{-COO^{\ominus}}$ 1630 und 1320 cm^{-1}; Nujol) dürfte es sich jedoch tatsächlich um das Phosphonio-carboxylat **6c** handeln.

Die in der Titelzeile getroffene Aussage lässt sich jetzt genauer formulieren: Phosphor-Betaine können durchaus aus Trialkyl- oder Triphenylphosphonio-alkyliden und Carbonyl-Verbindungen als beobachtbare Zwischenstufen entstehen, aber nur dann, wenn die negative Ladung am Sauerstoff durch Kombination mit einem Lithium-Kation oder durch wirkungsvolle Delokalisation beansprucht und somit stabilisiert wird.

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5 *E. Vedejs* und *K. A. J. Snoble:* J. Amer. Chem. Soc. *95* (1973) 5778 sowie unveröffentlichte Ergebnisse; siehe auch [4].

6 Beim Übergang von **3** nach **4** wird der PO-Abstand von ungefähr 1,6 Å (*R. D. Spratley, W. C. Hamilton* und *J. Ladell:* J. Amer. Chem. Soc. *89* [1967] 2272 und dortige Zitate) auf ungefähr 2,9 Å (*gauche*-Konformation) geweitet. Die dann noch verbleibende elektrostatische Anziehung bewerten wir grob mit 30 kcal/mol; die PO-Bindungsstärke in einem Alkoxyphosphoran schätzen wir auf 60 kcal/mol; die Ringspannungsenergie von **3** vermuten wir in der Nähe von 20 kcal/mol.

7 Eine genaue Betrachtung hätte zu berücksichtigen:
a) Das Lithiumjodid ist in Tetrahydrofuran nur teilweise, nicht vollständig in solvens-getrennte Ionenpaare übergeführt oder zu freien Ionen dissoziert;
b) Die Solvathüllen eines Lithiumalkoholat-Kontaktpaares und eines Lithium-Ions sind verschieden (vermutlich 3 bzw. 4 Tetrahydrofuran-Molekeln in der innersten Koordinationssphäre;
c) Lithiumalkoholate können sich zu Aggregaten zusammenschliessen (*V. A. Bessonov, P. P. Alikhanov, E. N. Guryanova, A. P. Simonov, I. O. Shapiro, E. A. Yakovleva* und *A. I. Schatenstein:* Zhur. Obshch. Khim. *37* [1967] 109; *V. Halaška, L. Lochmann* und *D. Lím:* Coll. Czech. Chem. Commun. *33* [1968] 3245).

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11 *M. Schlosser, T. Kadibelban* und *G. Steinhoff:* Justus Liebigs Ann. Chem. *743* (1971) 25.

12 Freilich liegt die Absorption bei deutlich tieferem Feld als jene von typischen Oxaphosphetanen ($\delta = -50$ bis -60 ppm). Wir deuten dieses abweichende Verhalten mit zunehmender Polarisierung und Schwächung der P—O-Bindung.

Complexes with macrocyclic ligands, VIII [1]. Stability of the Cu(II) complexes with 1,4,7-triazacyclodecane and 1,5,9-triazacyclododecane*

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Abstract

The potentiometric and spectrophotometric study of the complexation of the title compounds (L) with Cu(II) has shown that CuL^{2+}, CuL_2^{2+} and $(CuLOH)_2^{2+}$ are the species present in solution. Their stability constants at 25 °C and I = 0.5 and their spectral properties are given in Table 1 and 2, respectively. The results of both techniques indicate that all three amino groups of the ligand are involved in bonding, which is possible only if facial co-ordination in octahedral geometry occurs.

Often classical techniques cannot be used to measure the stability of macrocyclic complexes because of the slow reaction with which the equilibrium is attained [2]. However, the stochiometry and stability of transition metal ions with such ligands have been determined by special techniques, for example through competition with cyanide [3] or from their rate of formation and dissociation [4, 5]. From these equilibrium and calorimetric studies the "macrocyclic effect" was postulated [3, 6]. It was therefore interesting to investigate other ligands with smaller ring size such as the cyclic triamines 1,4,7-triazacyclodecane ([10]aneN$_3$) and 1,5,9-triazacyclododecane ([12]aneN$_3$). These react with Cu^{2+} fairly rapidly, probably because they are not able to surround the metal ion like the tetraazamacrocycles. The publication of two papers related to the co-ordination ability of cyclic triamines [7, 8] induced us to present our own results, which on one side supplement previous observations, but on the other side also include several important differencies.

Experimental part

The cyclic triamines [10]aneN$_3$ and [12]aneN$_3$ were synthesized by a combination of the methods described by [9, 10] and were characterized by their melting points, NMR spectra and analysis: [10]aneN$_3$. 3HBr, mp 240–241 (242–243 [10]); NMR (D_2O) 2.08 (p), 3.16 (s), 3.37 (t); $C_7H_{20}N_3Br_3$ found C 21.81, H 5.33, N 10.86%, calc. C 21.78, H 5.22, N 10.89%. [12]aneN$_3$. 3HBr, mp 266–267 (267.5–268.5[10]); NMR (D_2O) 2.25 (p), 3.40 (t); $C_9H_{24}N_3Br_3$ found C 25.88, H 5.98, N 9.88, calc. C 26.11, H 5.84, N 10.15%.

The equilibria were followed by titrating solutions of 5.10^{-4} to 3.10^{-3} M ligand and 0, 0.18, 0.45 and 0.9 equivalent Cu^{2+} with standard sodium hydroxide (Titrisol Merck) at 25 ± 0.1 °C and I = 0.5 (KNO_3) under nitrogen. pH values were measured with a Metrohm Compensator E388 and a Metrohm glass electrode standardized against Metrohm buffers of pH 4.00 and 7.00.

From the titration curves of the two ligands it was apparent that the p$K_{H,1}$ values were too high to be determined potentiometrically. Extraction experiments with $CHCl_3$ and NMR shift measurements were therefore undertaken in order to determine p$K_{H,1}$. The partition coefficient of [10]aneN$_3$ and [12]aneN$_3$ between water and $CHCl_3$ was found to be linearly dependent on the pH up to 12 at I = 0.5, which indicates that p$K_{H,1}$ > 12. For the NMR measurements in 10^{-3} to 5 M NaOH dioxane was used as an internal standard. The shift of the α-CH_2 methylene groups was followed from pH 11 up to 5 M NaOH without control of the ionic strength. The pH meter readings between 11 and 13 were corrected for the alkali error according to the indication of the manufacturer.

Assuming that the shifts at pH 11 and in 5 M NaOH correspond to those of the monoprotonated (δ_{HL}) and deprotonated (δ_L) species respectively, the p$K_{H,1}$ was calculated from the shifts at intermediate pH values with (1). For [10]aneN$_3$ values of 12.8

$$pK_{H,1} = pH + \log[(\delta_L - \delta)/(\delta - \delta_{HL})] \quad (1)$$

(from pH = 12.44) and 12.7 (from pH = 12.85), whereas for [12]aneN$_3$ 13.1 (from pH = 12.66) and 13.0 (from pH = 12.97) were obtained. The spectrophotometric titrations of the Cu^{2+} complexes were recorded on a Cary 118 spectrophotometer, in the cell compartement of which a 1 cm cuvette equiped with a magnetic stirrer, a pH microelectrode Metrohm X and an Agla micrometer syringe were introduced [11]. The ligand concentration was 1.0 – $1.25.10^{-3}$ M with 0.45 or 0.9 equivalent of Cu^{2+}.

Results and discussion

The pH titrations of the two ligands show that the protonation of the cyclic triamines takes place stepwise (Fig. 1). The acid dissociation constants calculated from the potentiometric and NMR measurements are given in Table 1. The p$K_{H,1}$ values of the two cyclic amines are higher than one would expect. However, inspection of structural models indicates that the monoprotonated species can adopt a conformation which allows the interaction of all three nitrogen lone pairs with the proton at once. Through internal hydrogen bonds the proton is therefore more strongly bound than in an open chain triamine. Our p$K_{H,1}$ values contrast with that measured potentiometrically for the analogue amine [9]aneN$_3$ [8]. The authors probably did not realize that the p$K_{H,1}$ was too high to be determined by a pH titration.

In the presence of one equivalent of Cu^{2+} up to four protons are released upon complexation (Fig. 1), indi-

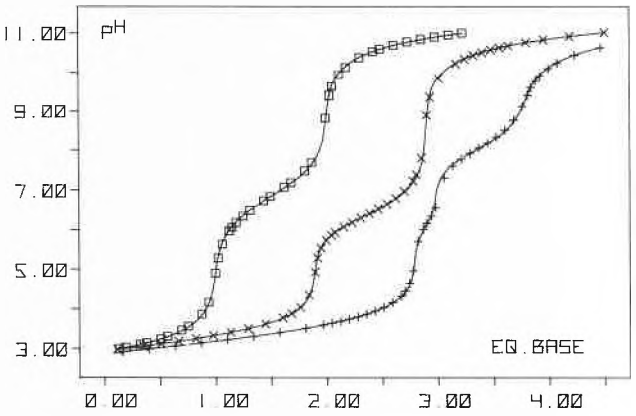

Fig. 1: Titration curves of 10^{-3} M [10]aneN$_3$ in the presence of 0 (□), 0.45 (×) and 0.9 (+) equivalent Cu^{2+}. — calculated curves with the constants given in Table 1.

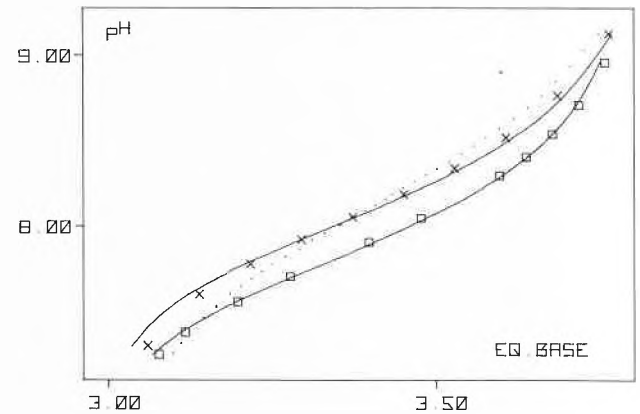

Fig. 2. Titration curves of 10^{-3} M (×) and $3.4 \cdot 10^{-3}$ M (□) [10]aneN$_3$ with 0.9 equivalent Cu^{2+} between 3 and 4 equivalent base. — calculated curves with the constants of Table 1, taking into account the dimeric species $(CuLOH)_2^{2+}$; ... calculated curve with $CuLOH^+$ for 10^{-3} M [10]aneN$_3$.

* Received April 23, 1977

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cating that besides CuL^{2+} a hydrolyzed species is formed. In addition it was evident from titrations with excess of ligand that CuL_2^{2+} also exists in solution. In a first attempt CuL^{2+}, CuL_2^{2+} and $CuLOH^+$ were used to calculate the titration curves. For this a new version of the program Variat [12] based on Marquardt's non-linear curve fitting procedure [13] was used. For both ligands the fit was excellent, except for the region where $CuLOH^+$ was present. There the calculated curve was steeper than the experimental one and the apparent hydrolysis constant was concentration dependent (Fig. 2). Both observations point at the presence of a dimeric species $(CuLOH)_2^{2+}$. Introduction of this complex instead of $CuLOH^+$ into our calculation gives a satisfactory fit of all titration curves (Fig. 1 and 2). The computed constants K_1 (2), K_2 (3) and K_3 (4), also given

$$K_1 = [Cu^{2+}] \cdot [L] / [CuL^{2+}] \quad (2)$$
$$K_2 = [CuL^{2+}] \cdot [L] / [CuL_2^{2+}] \quad (3)$$
$$K_3 = [CuL^{2+}]^2 \cdot [OH^-]^2 / [(CuLOH)_2^{2+}] \quad (4)$$

in Table 1, are weighted mean values with standard deviations obtained from different curves.

Table 1: pK_H values and stability constants of [10]aneN$_3$ and [12]aneN$_3$ with Cu^{2+} at 25 °C and I = 0.5 (KNO_3).

	[10]aneN$_3$	[12]aneN$_3$
$pK_{H,1}$	12.75	13.15
$pK_{H,2}$	6.86 ± 0.02	7.97 ± 0.03
pK_1	16.14 ± 0.09	13.16 ± 0.02
pK_2	10.26 ± 0.03	7.68 ± 0.04
pK_3	14.52 ± 0.09	13.23 ± 0.08

With the stability constants of Table 1 the spectra of each species were calculated from the spectrophotometric titrations by using the computer program Spana [11]. The absorption maxima and molar absorptivities of CuL^{2+}, CuL_2^{2+} and $(CuLOH)_2^{2+}$ are presented in Table 2.

Table 2: Absorption maxima and molar absorptivities of the Cu^{2+} complexes with [10]aneN$_3$ and [12]aneN$_3$

	[10]aneN$_3$	[12]aneN$_3$
CuL^{2+}	659 nm (66 M^{-1} cm^{-1})	689 nm (138 M^{-1} cm^{-1})
CuL_2^{2+}	622 nm (45 M^{-1} cm^{-1})	662 nm (185 M^{-1} cm^{-1})
$(CuLOH)_2^{2+}$	629 nm (194 M^{-1} cm^{-1})	649 nm (285 M^{-1} cm^{-1})

The results of *Zompa* et al. [7, 8] on the complexation of cyclic triamines with Cu^{2+} significantly differ from ours not only in regard to the values of the equilibrium constants but also in regard to the species chosen to explain the titration curves. The main reason for the discrepancy in pK_1 probably lies in the different values of $pK_{H,1}$ (vide supra). The species used by the authors to explain the titration curves were CuL^{2+} in the case of [10]aneN$_3$ and [12]aneN$_3$ [7] and CuL^{2+} and $CuLOH^+$ in the case of [9]aneN$_3$ [8]. No indication of dimeric hydroxo species or 1:2 complexes was given, although a few crystalline compounds of the latter type were prepared.

The ring size of the ligands here described is too small to completely encompass the metal ion. One can therefore ask whether all three amino groups of the ligand are involved in co-ordination. Is this the case, then facial co-ordination either in octahedral or tetrahedral geometry can occur. The stability constants of the 1:1 complexes with [10]aneN$_3$ and [12]aneN$_3$ are between those of dien (pK_1 = 16.0 [14]) and of en (pK_1 = 10.76 [15]) and are comparable to those found for triamines such as cis,cis-1,3,5-triaminocyclohexane (pK_1 = 10.6 [16]) or 1,2,3-triaminopropane (pK_1 = 11.1 [17]), which are known to bind with facial arrangement of their nitrogen atoms. The ease with which 1:2 complexes are formed by the cyclic triamines is also indicative for facial co-ordination, since dien only gives a much weaker complex (pK_2 = 5.3 [14]).

The question whether facial arrangement takes place in an octahedral or tetrahedral ligand field can be answered from the spectral properties of the complexes (Table 2). Tetrahedrally coordinated Cu^{2+} generally exhibits one absorption band between 1100 and 1250 nm, whereas tetragonally or trigonally distorted octahedral complexes absorb between 500 and 850 nm [18]. The absorption of the 1:1 complexes at 659 and 689 nm and of the 1:2 complexes at 622 and 662 nm clearly indicate pseudo-octahedral coordination geometry.

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X-ray Induced Photo-electron Spectrometric Evidence for Heavy Metal Adsorption by Molybdenum Disulfide from Aqueous Solution*

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Abstract

The adsorption of Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II) and Pb(II) aquo ions, and of $PdenCl_2$, on the surface of MoS_2 is studied through the photo-electron spectra. If MoS_2 has been immersed in pure or alkaline water, a mono-molecular oxide layer is formed, which seems to attach at least cobalt, nickel and lead.

MoS_2 is a stoichiometric compound with many properties in common with graphite, such as lubrification related to the lamellar structure, and the formation of intercalate molecular adducts. Recent measurements [1] of the adsorption on MoS_2 of metal ions in aqueous solution show a pH dependence very similar to the one found with oxide surfaces [2]. Water adsorption isotherms, and calculated isosteric heats of adsorption, indicate that the surface of the MoS_2 used in our experiments was partially oxidized [3]. In spite of well-known limitations of photo-electron spectra [4, 5] for analytical porposes [6, 7] it looked attractive to study selected samples by this technique.

When our MoS_2 (BDH) is treated by hydrogen at 380 °C and cooled, it has a highly reproducible spectrum given in Table 1. The sulphur signals may be compared with crystalline S_8 [8] I(S2s) = 233.35 eV and I(S2p) = 170.1 & 168.95 eV, 1.3 eV higher than our sulphide. The inner shells of molybdenum show I some 3 eV below solid molybdates [4] and Haber [9] studying various reduced oxides recognized a shift 1.5 and 3.3 eV, respectively, toward lower I values, when monomeric Mo(IV) and another species with short Mo–Mo distances is formed from Mo(VI). We do not here discuss the valence region in detail, though it is interesting to note the lowest I = 7.5 eV corresponding to the two 4d electrons in the non-bonding $(3z^2 - r^2)$ orbital in the trigonal-prismatic chromophore Mo(IV)S_6 whereas a broad feature at 10 eV corresponds to M. O. mainly formed by S 3p in the L. C. A. O. model, and a S 3s signal can be recognized at 19 eV.

The relative atomic concentrations [6] of about one oxygen atom per molybdenum do not look convincing for a high purity of the sample surface. However, there is no doubt that the high I value close to 537.5 eV corresponds to adsorbed water molecules, whereas oxo-anions of elements in high oxidation states have I(O1s) between 536 and 538 eV, and typical oxides [10, 11] of bivalent and trivalent elements 534 to 535 eV. If MoS_2 is treated with distilled water or with a strongly alkaline solution, and dried at 100 °C, typically 10 to 15 percent of the molybdenum seems oxidized (presumably by air oxygen) to a Mo(VI) oxide, and a weak oxygen signal above 538 eV also appears. The relative intensities suggest a "monomolecular layer", but other evidence [1] can be interpreted as a slightly thicker oxide forming "patchwork" on the surface. Other samples, which were dried in vacuo at room temperature, showed a decreased intensity of the Mo(VI) compared with the untreated sample. This suggests a partial re-oxidation of the sample treated with base when it is wet and in contact with oxygen. MoS_2 treated with 10% hydrogen peroxide for 30 minutes develop a ratio 0.35 between Mo(VI) and Mo(IV) intensities, and a sulphate signal a-third as strong as the sulphide signal. For comparison, it may be mentioned that treatment of MoS_2 with bromine does not allow detection of sulphate, but the fixation of two kinds of bromine, about 0.5 and 0.25 per Mo. One may compare with the iodine adsorption [12] on metallic gold.

Treatment of MoS_2 with aqueous solutions of sodium (I), manganese (II) and iron (II) perchlorate has almost the same effect as water alone. As seen from Table 1, cobalt (II) and nickel (II) are adsorbed from nitrate solution to a (at least predominantly) paramagnetic species with characteristic satellites [4]. The strongest $Co2p_{3/2}$ signal has almost the same I as the charge-corrected 787.8 eV for CoF_2 [4] and it is almost excluded that it is not due to the oxide layer whereas sulphur neighbour atoms would provide far lower I. The same is (less extremely) true for Ni(II), but I(Ni $2p_{3/2}$) is still 2.8 eV higher than the charge-corrected value for NiO and 4 eV higher than for diamagnetic sulphur-containing nickel (II) complexes. The situation is rather different for samples of CoS and NiS both showing a sulphate signal $I(S2p_{3/2})$ = 173.4 eV of intensity comparable with a broad sulphide structure around 167 eV. The corresponding $M2p_{3/2}$ show "paramagnetic" satellites and occur at 786.5 and 860.9 eV after correction for a surface charge $(C_{st} - C'_{st})$ = 1.6 and 1.9 eV, respectively.

The behaviour with copper (II) nitrate or perchlorate is rather complicated. The typical spectrum in Table 1 develops after careful washing with ethanol and seems

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Table 1: Photo-electron spectra of the samples with ionization energies I relative to vacuo (obtained by adding C_{st} to the I^* recorded by the instrument). Values connected with "&" correspond to two j-values of the same nl-shell; values separated by a comma refer to non-equivalent atoms of the same element. Shoulders are given in parentheses and satellites indicated by (sat.)

Chemical composition Semi-quantitative analysis	C_{st}	I(Mnl) values in eV
MoS_2 treated with H_2 at 380 °C 1Mo: 0.8 O: 2S	4.6	Mo3p: 418.2 & 400.8; Mo3d: 238.0 & 234.9 Mo4p: (45) & 42.3; S2s: 232.1; S2p(168.8) & 167.6; O1s: 537.6
MoS_2 treated with distilled water (0.12+1) Mo: (0.4+0.6)O: 2S	4.8	Mo3p: 422, 418.2 & (404), 400.9; Mo3d: 241.2, 238.0 & 234.8; S2s = 232.1; S2p (168.9) & 167.7; O1s: 538.3, 536.4
MoS_2 treated with 3 M NaOH (0.15+1)Mo: (0.3+0.9) O: 2S	4.8	Mo3p: 418.1 & 404, 400.6; Mo3d: 240.7, 237.8 & 234.7; S2s: 231.9; S2p: (168.7) & 167.5; O1s: (539), 537.1
MoS_2 with cobalt (II) (0.10+1)Mo: 1.1O: 0.15 Co: 2S	4.6	Mo3p$_{3/2}$: 404, 400.8; Mo3d: 238.0 & 234.8; S2s: 232; S2p (169) & 167.7; O1s: 537.5; Co2p: 808 (sat.) 802.8 & 795 (sat.) 790 (sat.) 787.6
MoS_2 with nickel (II) (0.1+1)Mo: 1.50: (0.3 N?): 0.4Ni: 2S	4.8	Mo3p$_{3/2}$: 400.6; Mo3d: 241, 237.8 & 234.6; S2s: 231.9; S2p: (168.7) & 167.5; O1s: 538.0; N1s: (414?); Ni2p: 886 (sat.) 880.5 & 869 (sat.), 862.9
MoS_2 with copper(II) (0.15+1)Mo: 1.30: (0.3 Cu): 2S	4.7	Mo3p: (425), 422, 418.3 & 404, 400.8; Mo3d: 241, 238.1 & 234.9; S2s: 232.1; S2p: (168.8) & 167.6; O1s: 537.2; Cu2p: 959 & 941, 938.4
MoS_2 with zinc(II) 1Mo: 0.7 O: 0.11 Zn: 2S	4.8	Mo3p: 425, 422.6, 418.2 & (404.4), 400.8; Mo3d: 241, 238.0 & 234.8; S2s: 232.0; S2p: (168.8) & 167.6; O1s: 537.3; Zn2p: 1052 & 1028.0
MoS_2 with silver(I) (0.1+1)Mo; (0.5+0.9)O: 0.22 Ag: 2S	4.7	Mo3p: 418.4 & (404), 401.0; Mo3d: 241.3, 238.0 & 234.9; S2s: 232.2; S2p: (168.8) & 167.6; O1s: (538.2), 536.5; Ag3d: 379.8 & 373.8
MoS_2 with cadmium(II) (< 0.1 + 1)Mo: 1O: 0.06 Cd: 2S	4.6	Mo3p$_{3/2}$: 400.8; Mo3d: 241, 238.1 & 235.0; S2s: 232.0; S2p: (168.8) & 167.7; O1s: 537.3; Cd3d$_{5/2}$: 411.2
MoS_2 with lead(II) (< 0.1+1)Mo: (1.3+0.6) O: (0.16+0.05 Pb: 2S	4.5	Mo3p$_{3/2}$: 400.8; Mo3d: 238.1 & 235.0; S2s: 232.2; S2p: (168.9) & 167.7; O1s: 538.5, 537; Pb4f: 150.7 (149.4) & 145.8 (144.5)

to contain two kinds of copper atoms, perhaps Cu(I) as the major and Cu(II) (with smeared-out satellites) as a smaller constituent. Before washing, a spectrum with clearcut satellites (I = 949.2, 946.3, 940.8 and 937.8 eV in the Cu2p$_{3/2}$ region) is sometimes observed reminescent of Cu(II) hydroxide. The behaviour of precipitated CuS is also irreproducible. From the crystal structure of covellite, one would expect a-third Cu(II) and two-thirds Cu(I), but many samples seem to contain only Cu(I). Zinc(II) is adsorbed on MoS_2 but here, the chemical shifts are so weak [4] that it is difficult to distinguish between oxide and sulphide coordination. We reacted MoS_2 with a dilute solution of the ethylenediamine palladium(II) complex PdenCl$_2$. Only if buffered by potassium phatalate at pH = 5 [13] adsorption took place (0.9 O : 0.2 N : 0.07 Pd) with I(Pd3d) = 348.8 eV and 343.8 eV (typical for [4] amine complexes) and I(N1s) close to 404 eV, suggesting replacement of the two chloride ligands with the surface sulphur atoms. There is a trace of Pd with lower I, conceivably the metallic element. Silver(I) and cadmium(II) on MoS_2 also seem to be bound to sulphur atoms, though again the range of chemical shifts is not too significant. The situation is more unexpected in lead (II). The sample given in Table 1 contains a smaller component (in parentheses) which can be almost anything, and a major component having higher I values than any lead-containing sample. The highest I'(Pb4f$_{1/2}$) known [4] is 144.7 eV for Pb(NO$_3$)$_2$. There is little doubt that this component is bound to the superficial oxide layer. It was sometimes difficult to avoid interferences (*e.g.* with an Auger signal of nickel, and with Cd3d$_{5/2}$ and Pd4d$_{5/2}$ signals) with Mo3p$_{1/2}$ but this signal has an odd structure above 425 eV which may be due to an unrecognized Auger signal, or to the Gelius effect [14, 15].

Though the conclusions of these measurements are not all clear-cut, it is conspicuous that surface chemistry can be highly different from the ideas based on homogeneous solution chemistry. Molybdenum(IV) sulphide seems to be reluctant to oxidize to sulphate (unlike most metal sulphides [4, 16]) but carries a monomolecular oxide layer able to from a kind of strongly bound molybdates, with bivalent cobalt, nickel and lead. The interatomic relaxation effect [5, 13] may be smaller for surface atoms, increasing their I values.

Experimental

The preparation of Mn(II), Fe(II), Cu(II), Cd(II) and Pb(II) perchlorate solutions is described elsewhere [1, 17]. 100 ml of such a 0.1 M solution (or of Co(II), Ni(II), Cu(II), Zn(II), Ag(I) or Pb(II) nitrate from *p.a.* chemicals) was each time equilibrated with 3 g of MoS_2 (British Drug Houses) at the maximum pH

still compatible with the hydroxide not percipitating. Then, the solution was filtered through a millipore filter (pore size 300 nm) and the remnant sulphide washed three times with 20 ml ethanol and finally dried in vacuo at room temperature.

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