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.

The Co-ordination Number of Aquairidium (III)*

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Abstract

Crystalline iridium(III) perchlorate hydrate has been prepared and used to determine the co-ordination number of aquairidium (III). Its X-ray powder patterns were recorded and turned out to be almost identical with that of $Rh(OH_2)_6(ClO_4)_3$. With an ^{18}O-tracer technique the co-ordination number of aquairidium (III) was found to be 6.0 ± 0.2. Thereby the octahedral geometry of $Ir(OH_2)_6^{3+}$, previously inferred from the u. v.-visible spectrum, is strongly supported.

In a previous paper [1] describing the preparation of aquairidium(III), it was concluded from its u. v.-visible spectrum that the water molecules adopt an octahedral configuration around the central Ir(III). In order to determine the co-ordination number directly, an ^{18}O-tracer technique based on the inertness of the $5d^6$ Ir(III) centre was employed. ^{18}O-labelled aquairidium (III) perchlorate was prepared and dissolved in water of normal isotopic composition. Complete exchange between ligand and solvent water was effected by heating with concentrated $HClO_4$. Water was sampled from the reactant mixture and its ^{18}O-content determined by mass spectrometry. From the experimentally observed parameters, as mol fractions of ^{18}O in the starting material and in the reaction products after having attained exchange equilibrium, and the analytical composition of the system, the coordination number of Ir(III) was evaluated.

Preparation of aquairidium(III) perchlorate

$(NH_4)_2IrCl_6$ (1 g; Fluka puriss.) was dissolved in ^{18}O-labelled NaOH (4% ^{18}O; 0.1 mol dm^{-3}; 600 cm^3). Under these conditions $[IrCl_6]^{2-}$ is reduced spontaneously to $[IrCl_6]^{3-}$ [2]. The solution was kept at 35–40°C for 3–4 h. Complete substitution of Cl^- by OH^- was indicated by a gradual colour change from green to light yellow. Immediately after the first tinge of blue had appeared, 10 cm^3 of reactant solution were set aside for later determination of the $H_2{}^{18}O$-content (solution A). Ascorbic acid (200 mg) was added to the remaining solution and after cooling to 5°C the pH was brought to ca. 8 with 0.1 mol dm^{-3} $HClO_4$. A light yellow precipitate consisting of iridium(III) hydroxide hydrate was formed. The solid product was thoroughly washed with water and dissolved in $HClO_4$ (1 mol dm^{-3}; 4 cm^3). After dilution with H_2O (100 cm^3) the resulting solution was chromatographed on a cation-exchange column (Dowex 50 W × 8, mesh 50/100) to separate mono- and polynuclear Ir(III) cations.
The intermediate fraction of the eluate with 2 mol dm^{-3} $HClO_4$ contained aquairidium(III) ion showing the typical pronounced absorption bands at 265 and 310 nm [1]. When this solution was evaporated under vaccum at room temperature aquairidium perchlorate crystallized out in form of needles 1–2 mm in length. The extremely hygroscopic substance was transferred rapidly to a filtering crucible and sucked until most of the adherent mother liquor was removed. The still wet crystals were mounted on glass carriers and X-rayed immediately to avoid untimely dissolution, which usually started after ca. ½ h.

X-ray powder pattern of aquairidium(III) perchlorate

Powder patterns with Cu-K_α radiation were recorded for the crystals obtained as described above. The data can be indexed on the basis of a face centered cubic structure with a unit cell of 1.115 ± 0.002 nm. Almost identical patterns have been observed with $Rh(OH_2)_6(ClO_4)_3$ [3], suggesting that aquairidium(III)

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** Correspondence should be addressed to Prof. Dr. H. Gamsjäger perchlorate has the same structure and formula. For comparison the principal lines of the two substances are given in Table 1.

Table 1: Principal X-ray diffraction lines for $Ir(OH_2)_6(ClO_4)_3$ and $Rh(OH_2)_6(ClO_4)_3$ respectively

h k l	*d*/nm (calc.) Ir	*d*/nm (calc.) Rh	*d*/nm (obs.) Ir	*d*/nm (obs.) Rh	I/I_1 Ir	I/I_1 Rh
1 1 1	0.644	0.644	0.645	0.646	28	24
2 0 0	0.558	0.558	0.557	0.560	29	21
2 2 0	0.394	0.395	0.393	0.394	100	100
3 1 1	0.336	0.336	0.335	0.336	14	10
4 0 0	0.279	0.279	0.279	0.279	59	36
3 3 1	0.256	–	0.257	–	11	–
4 2 0	0.249	0.250	0.249	0.249	19	9
4 2 2	0.228	0.228	0.228	0.228	16	16
511, 3 3 3	0.215	0.215	0.214	0.215	24	24
4 4 0	0.197	0.198	0.197	0.197	10	10
5 3 1	0.188	0.189	0.188	0.189	12	10
600, 4 4 2	0.186	0.186	0.186	0.186	12	10
6 2 0	0.176	0.176	0.176	0.176	17	14
6 2 2	0.168	–	0.168	–	5	–
711, 5 5 1	–	0.156	–	0.156	–	9
4 4 4	0.161	–	0.162	–	8	–
6 4 2	0.149	0.149	0.149	0.149	9	14
882, 6 6 0	–	0.132	–	0.131	–	3

Direct determination of the co-ordination number

Labelled $Ir(OH_2)_6(ClO_4)_3$ (ca. 100 mg) was dissolved in $HClO_4$ (2 cm³; 50%) and kept overnight on a steam bath at 90–100 °C. Eventually, the light yellow solution became dark violet (solution B) and exchange equilibrium was attained. It should be noted that even under these conditions ClO_4^- does not participate in the exchange reaction. A similar solution with $Ir(OH_2)_6(ClO_4)_3$ of normal isotopic composition was prepared and used as blank (solution C).

Solution B was carefully analyzed. The Ir content was determined according to the method of *Zinser* and *Page* [4]. The total ClO_4^--concentration was analyzed by a cation exchange technique and the analytical excess of acid was titrated potentiometrically using a Gran type procedure [5]. The amount of H_2O present was then calculated from the difference.

For mass spectrometric analysis the water of solutions A, B and C, was completely removed by vaccuum distillation using an apparatus described by *Baertschi* et al. [6]. The destillate water was equilibrated with carbon dioxide which was isotopically analyzed in a double collector mass spectrometer.

The co-ordination number *N* was calculated from equation (1)

$$N = \frac{(x_b - x_c) \cdot W}{(x_a - x_c) \cdot M} \qquad (1)$$

where x_a, x_b, x_c are mol fractions of $H_2{}^{18}O$ in solutions *A*, *B* and *C* respectively, W/mmol g^{-1} is the amount of water per mass of solution*B* and M/mmol g^{-1} is the amount of iridium per mass of solutions *B*.

In four experiments the following values for *N* were found: 6.0, 6.1, 5.7, 6.2. This leads to a co-ordination number of

$$N = 6.0 \pm 0.2$$

It should be emphasized that during the preparation and purification of $Ir(OH_2)_6^{3+}$ apparently no exchange between ligand and solvent water occurred. This indicates a high degree of inertness comparable to that of $Rh(OH_2)_6^{3+}$ [7].

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Stabile Zink-Komplexe von 3-Amino-2H-azirinen *

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Abstract

3-Dimethylamino-2,2-dimethyl-2H-azirine (**4a**), which is known to react easily with Brönsted acids and electrophiles, forms a stable complex **5a** with $ZnBr_2$. In contrast to all other reactions of **4a**, the three-membered ring in this complex is preserved. The spectral data are discussed in comparison with the recently reported Pd(II)-complexes of 2H-azirines.

2H-Azirine haben als Synthone für Heterocyclen in den letzten Jahren eine grosse Bedeutung erlangt (vgl. [1–5]). Gut untersucht sind vor allem thermische und photochemische Reaktionen, während Reaktionen in Gegenwart von Metallkomplexen oder Metallsalzen erst in neuerer Zeit beschrieben worden sind [6–9].

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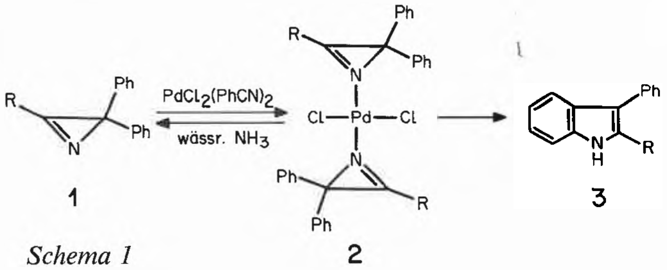
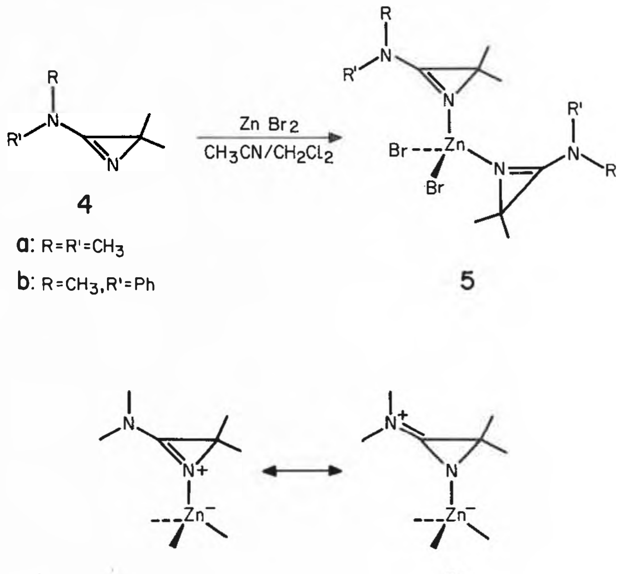
Dabei sind in erster Linie Dimerisierungsprodukte der 2H-Azirine oder intramolekulare Ringschlussreaktionen beobachtet worden. Vor kurzem berichtete z.B. eine japanische Arbeitsgruppe [8] über die Palladium(II)-katalysierte Umwandlung von 2,2-Diphenyl-2H-azirinen (**1**) in Indole (**3**, Schema 1). Diese Isomerisierung, die für R = CH_3 in Decalin rein thermisch bei 170 °C mit einer Halbwertszeit von 53 Min. verläuft, weist in Benzol bei 30 °C in Gegenwart von 0,05 Moläquiv. Dichlor-bis-benzonitril-palladium(II) eine Halbwertszeit von 360 Min. auf [8]. Als Zwischenprodukte konnten Palladium(II)-Komplexe isoliert werden, denen die Struktur **2** zugeschrieben wurde. Bei der Behandlung dieser Komplexe **2** mit wässerigem Ammoniak werden die entsprechenden 2H-Azirine wieder freigesetzt. Kürzlich ist nun von *Hassner* et al. [10] die Synthese und Struktur einer Reihe dieser Palladium(II)-Komplexe publiziert worden. Die Struktur des Dichlor-bis[3-(4-tolyl)-2H-azirin]palladiums – die vier Liganden um das planare Palladium weisen trans-Konfiguration auf – ist durch eine Röntgen-Kristallstrukturanalyse gesichert [10].



Schema 1

Im Rahmen unserer Untersuchungen zur Reaktivität von 3-Dialkylamino-2H-azirinen (**4**; für Reaktionen mit Brönstedsäuren siehe [11], mit Elektrophilen siehe [12]) interessierte uns auch das Reaktionsverhalten von **4** in Gegenwart von Lewissäuren. Die Umsetzung von 3-Dimethylamino-2,2-dimethyl-2H-azirin (**4a**) mit 0,5 Moläquiv. Zinkbromid in einem 1:1-Gemisch von Acetonitril/Methylenchlorid bei Raumtemperatur lieferte nach Abdampfen des Lösungsmittels und Umkristallisation aus Aceton/Äther einen farblosen Festkörper vom Smp. 92,5–94,5 °C. Aufgrund der Elementaranalyse (C, H, N; ± 0,3 %) handelt es sich dabei um einen 2:1-Komplex des 2H-Azirins **4a** und Zinkbromid. Im IR-Spektrum ($CHCl_3$) weist der Komplex bei 1804 cm^{-1} eine intensive ν(C=N)-Bande auf, die im KBr-Spektrum als Doppelbande bei 1826 und 1801 cm^{-1} erscheint. Weitere charakteristische Banden treten in $CHCl_3$ bei 1438, 1417, 1378, 1329, 1126, 1068, 1002 und 887 cm^{-1} auf. Im ^{1}H-NMR-Spektrum ($CDCl_3$) absorbieren die C-Methylgruppen als Singulett bei 1,52 ppm und die $(CH_3)_2N$-Gruppen als zwei Singulette bei 3,30 und 3,15 ppm; das protonenentkoppelte ^{13}C-NMR-Spektrum ($CDCl_3$) weist Signale bei 163,6 (C(3)), 43,8 (C(2)), 39,8 und 38,3 ($(CH_3)_2N$) und 24,0 ppm ($(CH_3)_2C$) auf[*].

Diese Daten stimmen sehr gut mit den Werten überein, die von *Hassner* et al. für den Palladium(II)-Komplex des 3-Amino-2H-azirins **4a** publiziert wurden [10]. Am deutlichsten sind die Unterschiede zum freien Liganden **4a** im IR-Spektrum[*]: Die (C=N)-Bande ist im Komplex um 34 cm^{-1} nach höheren Wellenzahlen verschoben, wie es für komplexierte Imine bekannt ist (vgl. die in [10] zitierte Literatur). Die Lage der C=N-Bande bei 1804 cm^{-1} zeigt auch, dass die Dreiringstruktur erhalten geblieben ist, da für entsprechende ungespannte Amidiniumsalze ν(C=N) im Bereich von 1720–1630 cm^{-1} auftritt [13] (vgl. auch [14]). Die Nichtäquivalenz der Methylprotonen der $(CH_3)_2N$-Gruppen im ^{1}H-NMR-Spektrum weist auf eine erschwerte Rotation um die C(3),N-Bindung, d.h. einen wesentlichen Beitrag der mesomeren Grenzstruktur *B* (Schema 2) hin. Erstaunlich gering sind die Differenzen der chemischen Verschiebungen in den ^{13}C-NMR-Spektren des 2H-Azirins **4a** und des Komplexes **5a**; auch dies steht in guter Übereinstimmung mit den Palladium(II)-Komplexen von 3-Aryl-2H-azirinen [10].



Schema 2

Ein zu **5a** analoger Komplex **5b** (Smp. 149,8–151,7 °C) wurde bei der Umsetzung von 3-(N-Methylanilino)-2,2-dimethyl-2H-azirin (**4b**) [15] und Zinkbromid erhalten (Ausbeute 90 %).

Wie schon seit langem bekannt ist, bilden Zinkhalogenide mit Aminen Komplexe des Typs $ZnX_2(Amin)_2$ (vgl. z.B. [16]). Ihr tetraedrischer Bau ist seither durch Röntgen-Kristallstrukturanalysen mehrfach bewiesen worden, so z.B. für die Zinkchlorid-Komplexe von

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[*] Das 2H-Azirin **4a** weist die folgenden spektralen Daten auf: IR ($CHCl_3$): 1768 (C=N), 1451, 1432, 1410, 1372, 1326, 1240, 1203, 1115, 1065, 996 und 878; ^{1}H-NMR ($CDCl_3$): 2,95 (s, $(CH_3)_2N$), 1,31 (s, $(CH_3)_2C$); ^{13}C-NMR ($CDCl_3$): 167,7 (C(3)), 39,7 (C(2)), 37,5 (breit, $(CH_3)_2N$), 25,0 ($(CH_3)_2C$).

1,10-Phenanthrolinen [17], Pyridinen [18], Imidazolen [19], 4-Methylanilin [20] usw. Wie anhand der Komplexe $ZnX_2(Pyridin)_2$ (X = Cl [18a], X = N_3 [21] oder X = NO_3 [22]) oder ZnX_2 (γ-Picolin)$_2$ (X = Cl [18b] oder X = Br [23]) gezeigt wurde, ist die Struktur von $ZnX_2(Amin)_2$-Komplexen von der Art der Liganden weitgehend unabhängig. Aufgrund dieser Daten nehmen wir an, dass die hier beschriebenen $ZnBr_2(Azirin)_2$-Komplexe ebenfalls eine tetraedrische Struktur besitzen (Schema 2). Dass die Komplexbildung mit dem Zink über das sp^2-hybridisierte Ringstickstoffatom der 3-Amino-2H-azirine **4** erfolgt, wird durch das ^1H-NMR-Spektrum von **5a** (nicht identische N-Methylgruppen), die Analogie zu Imidazol-Komplexen, die über N(3) koordiniert sind [19] [24], und die Analogie zum Palladium(II)-Komplex von **4a** [10] nahegelegt*.

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* Über Reaktionen mit den beschriebenen Komplexen soll in einer folgenden Arbeit berichtet werden.

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Ternary Surface Complexes
1. Complex Formation in the System Silica-Cu(II)-Ethylenediamine*

Preliminary Communication

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Abstract

Studies on the adsorption of Cu(II) from aqueous solutions containing ethylenediamine (en) at the silica-water interface reveal the formation of the ternary surface complexes ($\geqslant$Si—O)Cu(en)$^+$ (I) and ($\geqslant$Si—O)$_2$Cu(en)^0 (II). Compairing the experimentally obtained stability constants with statistical predictions indicates that the formation of (I) is slightly favored whereas the formation of (II) is slightly hindered.

The adsorption of metal ions from aqueous solutions at oxide-water interfaces can be described in terms of surface complex formation with deprotonated surface OH groups as ligands [1, 2]. *Schindler* et al. [1] recently reported the stability constants (see Table 1) of Cu(II)-silica surface complexes:

$$\geqslant \mathrm{Si{-}OH} + \mathrm{Cu^{2+}} \rightleftarrows (\geqslant \mathrm{Si{-}O})\mathrm{Cu^{+}} + \mathrm{H^{+}} \qquad (1)$$

$$^{*}K_1^{s}(\mathrm{Cu}) = \{(\geqslant \mathrm{Si{-}O})\mathrm{Cu^{+}}\}[\mathrm{H^{+}}]/\{\geqslant \mathrm{Si{-}OH}\}[\mathrm{Cu^{2+}}] \qquad (1a)$$

$$2\geqslant \mathrm{Si{-}OH} + \mathrm{Cu^{2+}} \rightleftarrows (\geqslant \mathrm{Si{-}O})_2\mathrm{Cu^{0}} + 2\,\mathrm{H^{+}} \qquad (2)$$

$$^{*}\beta_2^{s}(\mathrm{Cu}) = \{(\geqslant \mathrm{Si{-}O})_2\mathrm{Cu^{0}}\}[\mathrm{H^{+}}]^2/\{\geqslant \mathrm{Si{-}OH}\}^2[\mathrm{Cu^{2+}}] \qquad (2a)$$

[ ]: Concentrations of species in the aqueous phase (mole/dm^3),
{ }: Concentrations of surface species (mole/kg of the solid oxide).

Within the scope of this model it was assumed that

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only the "free" $Cu(II)^{2+}$ ions participate in the surface reaction.

In this communication evidence of the existence of the ternary surface complexes $(>Si-O)Cu(en)^+$ and $(>Si-O)_2Cu(en)^0$ is presented. The e. s. r. studies by *Takimoto* and *Miura* [3] of Cu(II) complexes adsorbed at alumina and silica surfaces already indicate the possibility of the presence of ternary surface complexes. However their experiments were performed on dehydrated gels and their results are therefore not necessarily applicable to aquatic systems. Our evidence is based on a study of the adsorption of Cu(II) from aqueous solutions containing ethylenediamine (en) at the silica-water interface.

Experimental

(a) Survey: Samples of 2.5 g of silica were immersed in 50 ml of solutions of the composition $[Cu(II)]_{total} = 1.57 \times 10^{-4} M$, $[en]_{total} = [Cu(II)]_{total}$, $[H^+] = H_i\ M$, $[Na^+] = (1\text{-}2\,[Cu(II)]_{total} - H_i)\ M$, $[ClO_4^-] = 1\ M$. The mixtures were then alkalized by addition of variable amounts of solutions of the composition $[OH^-] = C\ M$, $[ClO_4^-] = (1\text{-}C)\ M$, $[Na^+] = 1\ M$. The mixtures were agitated for 90 min. at 25 ± 0.05 °C, after which $[H^+]$ was calculated from emf measurements. The supernatant liquid was decanted after centrifugation and the total amount of Cu(II) adsorbed was obtained from atomic absorption spectrophotometric analysis of the total Cu(II) left in solution. The method of standard additions was used to eliminate possible interferences due to en. The adsorption of Cu(II) in the absence of en has been described previously [1].

(b) Auxiliary Constants: The acidity constants of enH_2^{2+} and the stability constants of Cu(II)-en complexes, for the ionic medium used, were determined separately by standard methods (see Table 1). The concentration of surface silanol groups is not only changed by reactions such as (1) and (2), but also by deprotonation. The empirical equation

$$\{>Si-O^-\} = (-\log[H^+])/10.8)^{5.0} \qquad (3)$$

was obtained from potentiometric titration of the silica sample in 1 M $NaClO_4$ (at 25 °C).

(c) Details: Details concerning the silica sample («Aerosil 200» from Degussa), the preparation of the solutions, the evaluation of the amount of reacting surface groups and of $[H^+]$ have been described previously [1]. The adsorption of enH^+ and enH_2^{2+} was found to be negligible with respect to the concentration of surface hydroxyl groups [4].

Results and Discussion

The experimental data (Fig. 1) indicate that the presence of en does not prevent the adsorption of Cu(II) although the percentage of adsorbed Cu(II) at a given log $[H^+]$ value is markedly reduced. If one assumes that only $Cu(II)^{2+}$ is involved in the surface reactions, the maximum percentage of adsorbed Cu(II) should be 50%, the remaining Cu(II) being present as $Cu(en)_2^{2+}$. The fact that Cu(II) becomes quantitatively adsorbed indicates that $Cu(en)^{2+}$ may participate in the surface reaction. Possible equations are:

$$>Si-OH + Cu(en)^{2+} \rightleftarrows (>Si-O)Cu(en)^+ + H^+ \qquad (4)$$

$${}^*K_1^s(Cuen) = \{(>Si-O)Cu(en)^+\}[H^+]/\{>Si-OH\}[Cu(en)^{2+}] \qquad (4a)$$

$$2>Si-OH + Cu(en)^{2+} \rightleftarrows (>Si-O)_2Cu(en)^0 + 2H^+ \qquad (5)$$

$${}^*\beta_2^s(Cuen) = \{(>Si-O)_2Cu(en)^0\}\ [H^+]^2/\{>Si-OH\}^2[Cu(en)^{2+}] \qquad (5a)$$

The percentage of adsorbed Cu(II) is then given by:

$$\%\ \text{adsorbed} = 100\tfrac{A}{V}[\{(>Si-O)Cu^+\} + \{(>Si-O)_2Cu^0\} + \{(>Si-O)Cuen^+\} + \{(>Si-O)_2Cuen^0\}]\ / \ ([Cu]_{total} + \tfrac{A}{V}\{Cu\}_{total}) \qquad (6)$$

where A is the weight of silica [kg] and V the volume of solution [dm^3].

Approximate values for ${}^*K_1^s(Cuen)$ and ${}^*\beta_2^s(Cuen)$ can be derived from statistical considerations as presented by *Sharma* and *Schubert* [5] and *Sigel* [6]:

${}^*K_1^s(Cuen) = S_1\ {}^*K_1^s(Cu)$ and ${}^*\beta_2^s(Cuen) = S_2\ {}^*\beta_2^s(Cu)$

where $S_1 = 2/3$ (or possibly 1/3) and $S_2 = 1/12$ (or possibly 5/12). These values already give a surprisingly good approximation of the experimental data (Figure 1). The best fit is obtained when the statistical factors 2/3 and 1/12 are replaced by 2 and 1/24 respectively (Fig. 1). The stability of $(>Si-O)Cu(en)^+$ is higher than expected from statistics. This enhanced stability is consistent with *Sigel*'s observation [6] on the stability of the ternary complex $(oxalate)Cu(en)^0$. On the other hand, the reduced stability of $(>Si-O)_2Cu(en)^0$ is probably caused by steric restrictions.

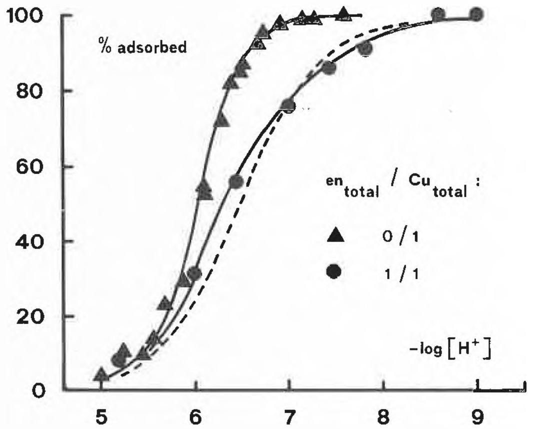

Fig. 1: Adsorption of Cu(II) (1 M $NaClO_4$, 25 °C) at silica as a function of log $[H^+]$. The curves are calculated with the stability constants given in Table 1. (a) $[en]_{total} = 0$, with ${}^*K_1^s(Cu)$ and ${}^*\beta_2^s(Cu)$ from *Schindler* et al. [1], (b) $[en]_{total} = [Cu(II)]_{total}$, with the aforementioned constants modified from statistical considerations ($S_1 = 2/3$ and $S_2 = 1/12$) in the case of the dotted line and for the best empirical fit in the case of the solid line.

The distribution of the various dissolved and adsorbed Cu(II) species can be calculated from the constants given in Table 1 (Fig. 2). Obviously the adsorbed Cu(II) is preponderantly present in the form of ternary surface complexes whereas binary surface complexes are of minor importance. However, this is not necessarily true for other $[en]_{total}$-$[Cu(II)]_{total}$ ratios.

Table 1: Equilibrium Constants (25 °C, 1 *M* $NaClO_4$)

Formation of surface complexes	Auxiliary constants
Binary complexes *	Acidity constants of ethylenediamine (en)
$\log {}^*K_1^s(\mathrm{Cu}) = -\ 5.52 \pm 0.13$	$\log K_{a1} = -\ 7.42 \pm 0.01$
$\log {}^*\beta_2^s(\mathrm{Cu}) = -11.19 \pm 0.02$	$\log K_{a2} = -\ 10.11 \pm 0.01$
Ternary complexes	Stability constants of Cu (II)-en complexes
$\log {}^*K_1^s(\mathrm{Cuen}) = -\ 5.22$	$\log K_1 = 10.745 \pm 0.003$
$\log {}^*\beta_2^s(\mathrm{Cuen}) = -12.57$	$\log \beta_2 = 20.213 \pm 0.002$

* From *Schindler* et al. [1].

Since there exist in nature numerous systems consisting of solid oxides (i.e. clay minerals) and aqueous solutions containing both metal ions and dissolved (organic and inorganic) ligands, ternary surface complexes may be important in soils as well as in natural waters. Further studies on ternary surface complexes are in progress.

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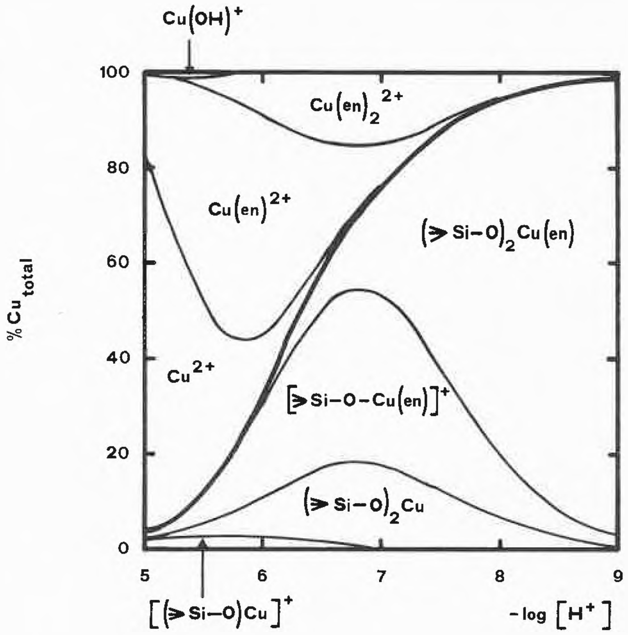

Fig. 2: Distribution of Cu(II) species as a function of log [H⁺]. $[\mathrm{en}]_{\mathrm{total}} = [\mathrm{Cu}]_{\mathrm{total}}$

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