

that should provide the sort of SiOH surface functionality present on the SiO<sub>2</sub>. We conclude that attachment of I to n-type Si proceeds as on high surface area SiO<sub>2</sub>. Models of the oxide/hydroxides of Pt, Au, and Ge have not been studied by solid-state NMR, but we believe that the electrochemical data are consistent with a mode of reaction as illustrated in eq 2. The reason for the relatively low coverage of I on high surface area SiO<sub>2</sub> vs. the smooth surface is not clear. It is possible that not all surface SiOH's are accessible to the derivatization agent.

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**Registry No.** I, 72380-68-8; Au, 7440-57-5; Pt, 7440-06-4; Ge, 7440-56-4; Si, 7440-21-3; SiO<sub>2</sub>, 7631-86-9.

Contribution from the Institute of Inorganic Chemistry, University of Fribourg, Pérolles, CH-1700 Fribourg, Switzerland

## Formation of Ternary Copper(II) Complexes at the Surface of Silica Gel As Studied by ESR Spectroscopy

ALEX VON ZELEWSKY\* and JEAN-MARIE BEMTGEN

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ESR spectroscopy is applied in the investigation of the adsorption behavior of Cu(II) complexes and Cu(II) ions on silica gel. With this method, results of pH titration measurements,<sup>1,2</sup> which indicate the formation of ternary surface complexes involving some ligands and chelating SiO<sup>-</sup> groups, are confirmed. N-chelating ligands with conjugated  $\pi$  systems enhance the adsorption by formation of ternary surface complexes (bpy, phen, terpy), whereas aliphatic amine ligands (en) attenuate adsorption, as compared to Cu<sup>2+</sup> ions. Unsaturated ligands having N/O mixed chelates (pic) form less stable ternary surface complexes, as compared to N chelates. Saturated ligands (gly) show, again, attenuation of adsorption. Fully coordinated cationic complexes are adsorbed on the negatively charged surface of silica gel at pH values above ca. 5.5 by Coulombic forces. Neutral or anionic complexes are not at all adsorbed at high pH values. Some complexes (Cu(bpy)<sub>2</sub><sup>2+</sup>, Cu(phen)<sub>2</sub><sup>2+</sup>, and Cu(pic)<sub>2</sub>) adsorb even in quite acidic solution (pH range of 1-4). This is interpreted as being due to the formation of ternary chelates with surface SiOH groups.

### Introduction

The investigation of adsorption equilibria between oxide surfaces and solutes in liquid solutions is a subject of interest in various fields of chemistry. In particular, equilibria involving transition-metal complexes have been studied in recent years in regard to natural water systems. The work of Stumm et al.<sup>3-6</sup> and Schindler et al.<sup>1,7-11</sup> has shown that a description of the adsorption of metal ions on oxide surfaces has to take into account the complex formation between the ions and the ionized surface. The coordinate binding model<sup>7-9,12</sup> gives an adequate description of the adsorption phenomena. A striking manifestation of surface complex formation has been found by Schindler et al.<sup>1</sup> They found a strongly enhanced or diminished adsorption for Cu(II) depending on ligands bound to Cu<sup>2+</sup> in solution. The enhancement of, e.g., the adsorption of Cu(bpy)<sub>2</sub><sup>2+</sup>, as compared to the aquated Cu<sup>2+</sup> ion, is analogous to the stabilization of ternary complexes in solution.<sup>13,14</sup>

Hitherto, the metal complex adsorption equilibria were investigated by titration methods.<sup>1</sup> No direct structural information is available from these measurements.

In the present paper, ESR spectroscopy is applied as a tool in determining adsorption equilibria, which can yield structural information on adsorbed species. In principle, ESR spectroscopy can also easily distinguish between freely tumbling complexes in solution and immobilized adsorbed species. In fluid solution with a rotational correlation time of the order of  $\tau_c = 10^{-10}$  s, the anisotropic contributions to the  $g$  and hyperfine coupling constants are virtually averaged. In the adsorbed state, the anisotropic interactions contribute fully to the spectra. The line shapes expected are the same as in other immobilized nonoriented systems such as, e.g., polycrystalline samples and frozen solutions. These line shapes are well understood,<sup>15</sup> and the spectra can be accordingly analyzed.

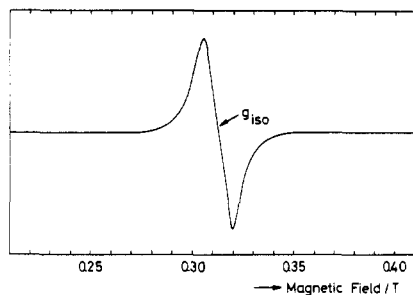
This ESR method can be applied to adsorption processes in all such cases where a transition-metal ion yields resolved spectra at temperatures at which the liquid phase is in a fluid state. Only then can the distinction between mobile and immobilized species be made. Cu<sup>2+</sup> as a  $d^9, S = 1/2$  system fulfills this requirement as it yields resolved ESR spectra at room temperature and even above. Since this ion has been investigated by titration methods in the past, a comparison between results obtained in completely independent ways is possible.

### Experimental Section

**Reagents.** The following aqueous solutions (in twice distilled water) with a constant ionic strength (NaNO<sub>3</sub> = 0.1 M) and a defined metal:ligand ratio were prepared (if not otherwise indicated, the total

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**Figure 1.** ESR spectrum of an aqueous solution of  $\text{Cu}^{2+}(\text{aq})$  in a solution of  $\text{Cu}(\text{NO}_3)_2$ . The spectrum is independent of pH in acidic solutions ( $\text{pH} < 6$ ) and  $g_{\text{iso}} = 2.225$ .

metal concentration  $[\text{Cu}^{2+}]_{\text{tot}} = 10^{-3}$  M,  $\text{Cu}^{2+}$  as  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , p.a., Fluka);  $\text{Cu}^{2+}:\text{bpy} = 1:1, 1:2, 1:6$  (bpy = 2,2'-bipyridine, p.a., Fluka);  $\text{Cu}^{2+}:\text{phen} = 1:1, 1:2, 1:6$  (phen = 1,10-phenanthroline, p.a., Fluka);  $\text{Cu}^{2+}:\text{en} = 1:1, 1:2, 1:6$  (en = 1,2-ethylenediamine, p.a., Fluka);  $\text{Cu}^{2+}:\text{terpy} = 1:1, 1:2$  (terpy = 2,2',6',2''-terpyridine, p.a., Fluka);  $\text{Cu}^{2+}:\text{EDTA} = 1:1$  (EDTA = ethylenediaminetetraacetate, p.a., Siegfried);  $\text{Cu}^{2+}:\text{IDA} = 1:1.1$  (IDA = iminodiacetate, p.a., Fluka);  $\text{Cu}^{2+}:\text{NTA} = 1:1, 1:2$  (NTA = nitrilotriacetate, p.a., Fluka);  $\text{Cu}^{2+}:\text{pic} = 1:1, 1:2$  (pic =  $\alpha$ -picolinate, purum, Fluka, two times recrystallized from  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ );  $\text{Cu}^{2+}:\text{gly} = 1:1, 1:5$  (gly = glycinate, p.a., Fluka);  $\text{Cu}^{2+}:\text{cyclam} = 1:1$  (cyclam = 1,4,8,11-tetraazatetradecane, synthesized according to the literature<sup>16</sup>);  $\text{Cu}^{2+}:\text{DOHDO-pn} = 1:1$  (DOHDO-pn = 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime, the synthesis will be published later).<sup>17</sup>

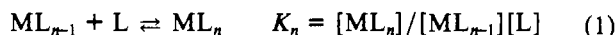
To 25 mL of each solution was added 1 g of silica gel ("Aerosil 300", Degussa, Frankfurt), and the pH ( $0 \leq \text{pH} \leq 7$ ) was adjusted by addition of  $\text{HNO}_3$  or  $\text{NaOH}$ . The resulting suspensions were saturated with  $\text{N}_2$  and equilibrated by stirring overnight.

The solutions were centrifuged ( $\sim 2500\text{g}$ ). This operation compressed the gel to ca. 40% of the total volume of solution. The resulting gel was transferred with syringes into flat quartz cells (0.25 mm thick), and the ESR spectra were measured at room temperature on a Varian E9 X-band spectrometer. For spectra at low temperature (77 K), the gel was transferred into Teflon tubes ( $\phi_{\text{ext}} = 4$  mm,  $\phi_{\text{int}} = 2.5$  mm).

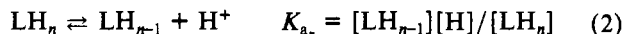
The spectra of the corresponding clear solutions at room temperature were measured in the same flat cells; for the spectra at liquid- $\text{N}_2$  temperature, 5% glycerol was added to the aqueous solutions in order to form a glassy matrix.

## Results and Discussion

The concentrations of the various species in solution in the absence of silica gel were calculated with well-established methods. The composition of the solutions as a function of pH was calculated with the program CHEL<sup>18</sup> with use of the stability constants  $K_n$



and  $\text{p}K$  values of the ligands.

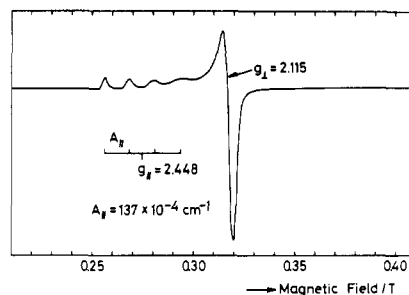


The evaluation of the relative amounts of adsorbed (immobilized) and "free" (mobile) complexes were carried out with the amplitudes of such ESR lines which showed the minimum degree of overlap. The calibration could, in most cases, be made internally since at a suitable pH, only one species was present. The accuracy of this procedure is inherently not very high because some overlap always occurs. All determinations were made with more than one line and several independent measurements. The error estimates are indicated as vertical bars in the concentration profiles of the figures.

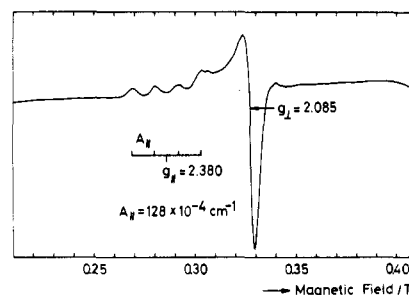
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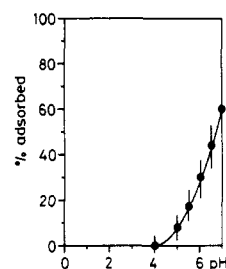
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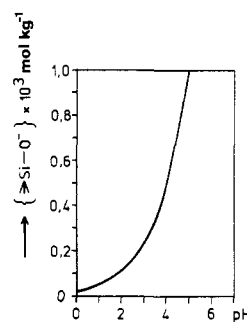
**Figure 2.** ESR spectrum of the same solution as in Figure 1 at 77 K in the glassy state. 5% glycerol was added.



**Figure 3.** ESR spectrum of adsorbed  $\text{Cu}^{2+}(\text{aq})$ :  $[\text{Cu}^{2+}] = 10^{-3}$  M, pH 7, aqueous solution with  $40 \text{ g L}^{-1}$  of Aerosil.

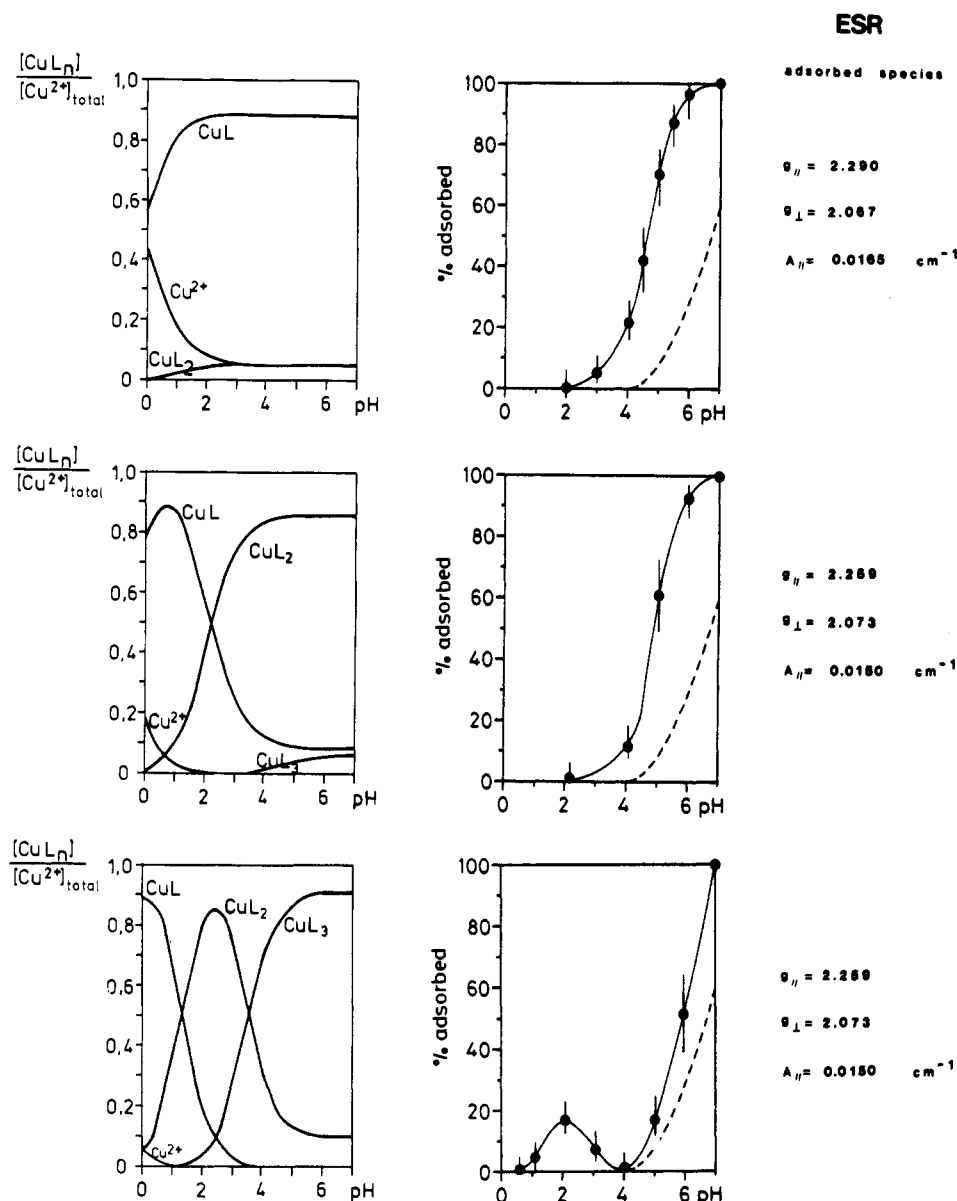


**Figure 4.** Adsorbed  $\text{Cu}^{2+}$  as a function of the pH:  $[\text{Cu}^{2+}] = 10^{-3}$  M,  $40 \text{ g L}^{-1}$  of Aerosil.



**Figure 5.** Concentration of surface  $\equiv\text{SiO}^-$  groups. Values are given in  $\text{mol L}^{-1}$  for an aqueous solution containing  $40 \text{ g L}^{-1}$  of Aerosil.<sup>1</sup>

**Adsorption of Uncomplexed  $\text{Cu}^{2+}(\text{aq})$ .** Figure 1 shows the ESR spectrum of an acidic solution of  $\text{Cu}^{2+}(\text{aq})$  at 300 K. The same solution yields the spectrum of Figure 2 upon cooling to 77 K if crystallization is prevented by addition of 5% glycerol. The striking difference is due to the immobilization which takes place in the transition from the fluid solution to the glassy state. A spectrum of immobilized  $\text{Cu}^{2+}$  is also observed (Figure 3) with the sample which contains silica gel even at room temperature. The paramagnetic ion has thus become *immobilized by adsorption*. The parameters of the spectra ( $g$  and  $A$  values) are, however, different from those measured in the aqueous solution, indicating a species which is structurally different from the simple hydrated  $\text{Cu}^{2+}$  ion. Thus, complex formation at the surface has taken place. The

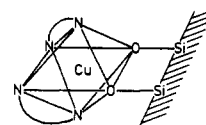


**Figure 6.** Percentage of adsorbed copper complexes in solutions containing bpy as a ligand at different pH values and calculated mole fractions of Cu<sup>2+</sup> and of the complexes in solution ( $\log K_1 = 8.00$ ,  $\log K_2 = 5.60$ ,  $\log K_3 = 3.48$ ,  $pK_a = 4.49$ ,  $[\text{Cu}^{2+}]_0 = 10^{-3} \text{ M}$ ;  $[\text{bpy}] = 10^{-3} \text{ M}$  (top),  $2 \times 10^{-3} \text{ M}$  (middle),  $3 \times 10^{-3} \text{ M}$  (bottom));  $T = 298 \text{ K}$ . The dashed lines are the corresponding curves for uncomplexed Cu<sup>2+</sup>(aq).

pH dependence corroborates this view in that the adsorption follows the deprotonation curve of the  $\equiv\text{SiOH}$  groups which function as surface ligands. The adsorption curve as estimated from the ESR spectra is given in Figure 4. It parallels the surface concentration of  $\equiv\text{SiO}^-$ , which has been calculated according to Bourg et al.<sup>1</sup>, yielding the values shown in Figure 5.

**Adsorption of Complexed Cu<sup>2+</sup> Species.** The investigation of the adsorption of complexed Cu<sup>2+</sup> essentially follows the same line as that described for the aqua ion. The results are discussed as follows:

**bpy.** Adsorption diagrams, solution composition, and ESR parameters are given in Figure 6 for three ratios of Cu<sup>2+</sup>:ligand concentrations. In the 1:1 case, mainly CuL is present over the whole pH range. Its adsorption is considerably enhanced compared to Cu<sup>2+</sup>(aq) and the ESR parameters correspond to a ternary surface complex  $\text{Cu}(\text{bpy})(\equiv\text{SiO}^-)_x$ . At a ratio of 1:2 a species with significantly different ESR parameters occurs which can be assigned to  $\text{Cu}(\text{bpy})_2(\equiv\text{SiO}^-)_x$ . It is a well-known fact that the  $g$  anisotropy decreases with an increasing number of N-donor atoms in the coordination sphere.<sup>19,20</sup> The parameters are also in agreement with the



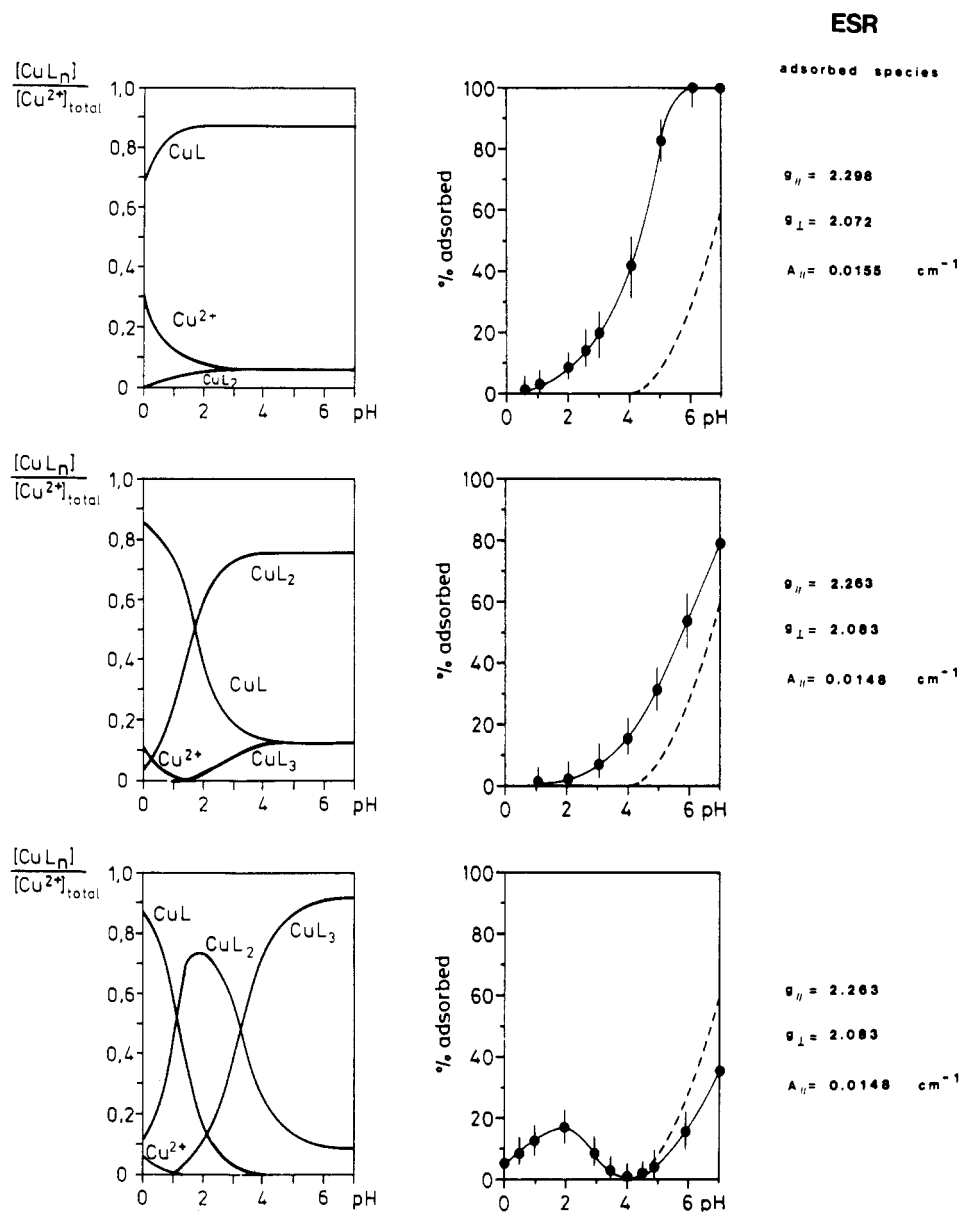
**Figure 7.** Proposed structure of the ternary surface complex  $\text{cis-Cu}(\text{bpy})_2(\equiv\text{SiO}^-)_2$ .

assumption of a cis configuration which is known to exist in the complex  $\text{Cu}(\text{bpy})_2(\text{H}_2\text{O})_2^{2+}$ .<sup>19</sup> We therefore propose the structure shown in Figure 7 for the adsorbed complex.

An interesting phenomenon is observed for a ratio of 1:6. A species which has ESR parameters similar to those of  $\text{Cu}(\text{bpy})_2(\equiv\text{SiO}^-)_2$  complex adsorbs at low pH values. A small adsorption maximum is reached at about pH 2. We interpret this species as a  $\text{Cu}(\text{bpy})_2^{2+}$  complex bound to surface  $\equiv\text{SiOH}$  groups. Indeed, a high concentration of the complex  $\text{Cu}(\text{bpy})_2^{2+}$  exists in this solution at pH  $\sim 2$ , where the surface groups are still almost completely protonated (Figure 6).

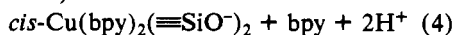
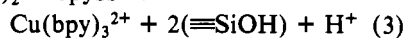
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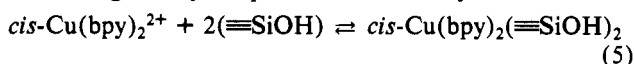


**Figure 8.** Percentage of Cu adsorbed in solutions containing phen as a ligand at different pH values and calculated mole fractions of  $\text{Cu}^{2+}$  and of the complexes in solution ( $\log K_1 = 8.82$ ,  $\log K_2 = 6.57$ ,  $\log K_3 = 5.02$ ,  $\text{p}K_a = 4.96$ ,  $[\text{Cu}^{2+}]_0 = 10^{-3} \text{ M}$ ;  $[\text{phen}] = 10^{-3} \text{ M}$  (top),  $2 \times 10^{-3} \text{ M}$  (middle),  $3 \times 10^{-3} \text{ M}$  (bottom)). The dashed lines are the corresponding curves for uncomplexed  $\text{Cu}^{2+}(\text{aq})$ .

Increasing the pH value decreases the amount of  $\text{CuL}_2^{2+}$  in solution, and  $\text{CuL}_3^{2+}$  is formed which can adsorb at higher pH values only by losing one ligand. This is represented by eq 3 and 4. The adsorption of  $\text{CuL}_2^{2+}$  at the "acidic" surface

$$\text{cis-Cu}(\text{bpy})_2(\equiv\text{SiOH})_2 + \text{bpyH}^+ \rightleftharpoons$$


does not involve protons (eq 5) and, consequently, it cannot be investigated by the pH methods used by Schindler et al.<sup>1</sup>



An excess of bpy does not easily displace  $\text{Cu}(\text{bpy})_2^{2+}$  from the surface, which means that equilibrium 6 lies on the left

$$\text{Cu}(\text{bpy})_2(\equiv\text{SiO}^-)_2 + \text{bpy} \rightleftharpoons \text{Cu}(\text{bpy})_3^{2+} + 2(\equiv\text{SiO}^-) \quad (6)$$

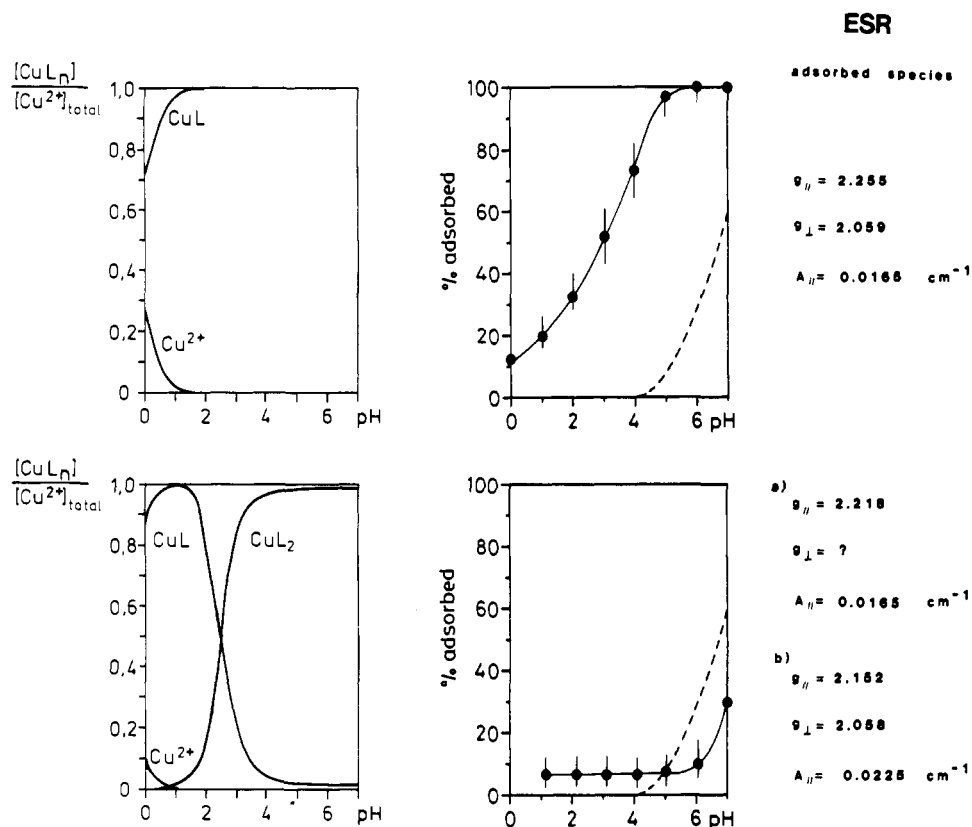
This indicates again the special stability of the adsorbed ternary complex. The stability of the surface complex decreases as follows:  $[\text{Cu}(\text{bpy})_2^{2+}] \gtrsim [\text{Cu}(\text{bpy})_2^{2+}] \gg [\text{Cu}^{2+}(\text{aq})]$ .

**phen.** (*o*-Phenanthroline)copper(II) complexes behave in a similar manner to the analogous bipyridine complexes. The formation of ternary surface complexes is even slightly enhanced compared with bpy. This can be easily seen upon comparison of the diagrams of the adsorption behavior of the phen complexes in Figure 8 with those of the bpy complexes (Figure 6). The structure of the adsorbed phen complexes must also be similar, as indicated by the ESR parameters.

Because the stability constants of the phen complexes are slightly higher, adsorption of the phen complexes at low pH values on  $\equiv\text{SiOH}$  groups (first maximum) already occurs at a metal:ligand ratio of 1:3. Here again, the stability of the surface complexes decreases as follows:  $[\text{Cu}(\text{phen})^{2+}] > [\text{Cu}(\text{phen})_2^{2+}] \gg [\text{Cu}^{2+}(\text{aq})]$ .

**terpy.** A considerable increase in the stability of ternary surface complexes is observed for the terpy complexes (Figure 9).

The ESR measurements show very clearly the change in the adsorption mechanism going from the 1:1 to the 1:2 complex.  $\text{Cu}(\text{terpy})^{2+}$  is strongly adsorbed by coordination to  $\equiv\text{SiO}^-$  groups on the silica gel surface, whereas  $\text{Cu}(\text{terpy})_2^{2+}$  (the existence of which is evidenced by the very large  $A_{\parallel}$



**Figure 9.** Percentage of Cu adsorbed in solutions containing terpy as a ligand at different pH values and calculated mole fractions of Cu<sup>2+</sup> and of the complexes in solution ( $\log K_1 = 12.29$ ,  $\log K_2 = 6.82$ ,  $pK_a^1 = 4.38$ ,  $pK_a^2 = 3.64$ ,  $[\text{Cu}^{2+}]_0 = 10^{-3} \text{ M}$ ;  $[\text{terpy}] = 10^{-3} \text{ M}$  (top),  $2 \times 10^{-3} \text{ M}$  (bottom)). The dashed lines are the corresponding curves for uncomplexed Cu<sup>2+</sup>(aq).

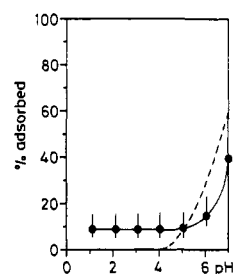
splitting, typical for a CuN<sub>4</sub> chromophore) is adsorbed by a much weaker electrostatic interaction between the positively charged complex and the negatively charged silicate surface at pH  $\geq 2$ .

In solutions with a metal to ligand ratio equal to 1:2 and a high proton concentration ( $0 \leq \text{pH} \leq 1.5$ ), a different species is immobilized on the surface, the ESR parameters of which are typical for Cu(terpy)<sub>2</sub><sup>2+</sup>. Contrary to the case of the 1:1 solution, this species has no  $\equiv\text{SiO}^-$  groups in the first coordination sphere (the  $g_{\parallel}$  values are significantly smaller). This is in agreement with the calculated concentrations of terpy complexes in homogeneous solutions. A graphic representation of the different complex concentrations, as a function of pH, is shown in Figure 9.

These data can be explained by the following model: in solution with a low pH value ( $0 < \text{pH} < 2$ ), Cu(terpy)<sub>2</sub><sup>2+</sup> is immobilized on the surface by the formation of bonds to  $\equiv\text{SiOH}$  groups (probably again the two  $\equiv\text{SiOH}$  are in cis configuration). At higher pH, the concentration of Cu(terpy)<sub>2</sub><sup>2+</sup>, as well as the concentration of the deprotonated surface hydroxy groups, increases and Cu(terpy)<sub>2</sub><sup>2+</sup> will be bound electrostatically.

So that the adsorption behavior of terpy complexes could be explained, three different mechanisms must be taken into account. One of them (Cu(terpy)<sub>2</sub><sup>2+</sup>, solution 1:1) corresponds to the model of Schindler et al., but the two others do not form coordinate bonds to the deprotonated silicate surface. As this is a requirement for the measurement of adsorption by potentiometric methods, the adsorption of Cu(terpy)<sub>2</sub><sup>2+</sup> should not be detected when the latter method is used. The series of stability of the adsorbed complex is in this case  $[\text{Cu}(\text{terpy})_2^{2+}] \gg [\text{Cu}^{2+}(\text{aq})] [\text{Cu}(\text{terpy})_2^{2+}]$ .

**cyclam.** 1,4,8,11-Tetraazatetradecane (cyclam, a tetradentate, macrocyclic ligand) forms stable, square-planar copper complexes for which coordination of other ligands in the axial

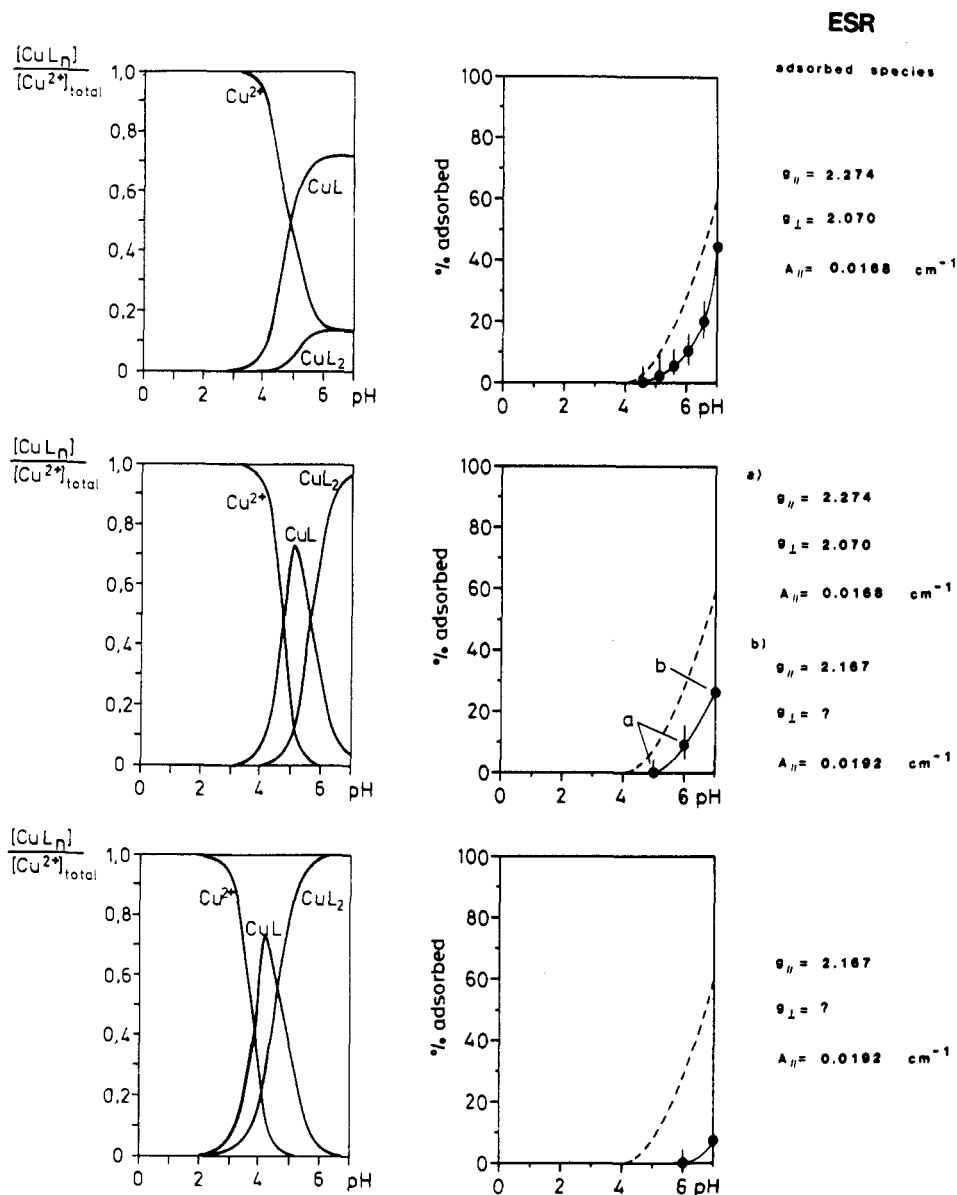


**Figure 10.** Percentage of Cu adsorbed in solutions containing cyclam as a ligand at different pH values:  $[\text{Cu}^{2+}]_0 = 10^{-3} \text{ M}$ ,  $[\text{cyclam}] = 10^{-3} \text{ M}$ ;  $T = 298 \text{ K}$ . The dashed line is the corresponding curve for uncomplexed Cu<sup>2+</sup>(aq).

position is unlikely. Therefore, we can expect this complex to have behavior similar to Cu(terpy)<sub>2</sub><sup>2+</sup>, i.e., not to bind coordinatively to  $\equiv\text{SiO}^-$  groups but to be immobilized by Coulomb forces on the negative surface. The data of Figure 10 agree with this model, and, once again, the adsorption should not be detectable by potentiometric titrations.

**en.** Both en and bpy are bidentate N-donor ligands forming five-membered chelate rings. Sigel<sup>13</sup> has shown that bpy (and also phen) behaves very differently in ternary complexes. The stability of the latter is strongly enhanced in the case of bpy compared to en. This difference is also clearly seen in the adsorption behaviour of complexes with en (Figure 11) and bpy as ligands. In agreement with Schindler et al.,<sup>10</sup> we find a strongly reduced adsorption strength of Cu(en)<sub>2</sub><sup>2+</sup> compared to Cu(bpy)<sub>2</sub><sup>2+</sup>. The former is considerably more weakly adsorbed than Cu<sup>2+</sup>(aq).

The spectrum of the gel solution Cu<sup>2+</sup>:en 1:2 at pH 6 shows the presence of two adsorbed species, where the concentration of both is about the same. This corresponds approximately to the composition calculated for a clear solution. The ESR



**Figure 11.** Percentage of Cu adsorbed in solutions containing en as a ligand at different pH values and calculated mole fractions of  $\text{Cu}^{2+}$  and of the complexes in solution ( $\log K_1 = 10.72$ ,  $\log K_2 = 9.31$ ,  $\text{p}K_a^1 = 10.03$ ,  $\text{p}K_a^2 = 7.22$ ,  $[\text{Cu}^{2+}]_0 = 10^{-3} \text{ M}$ ;  $[\text{en}] = 10^{-3} \text{ M}$  (top),  $2 \times 10^{-3} \text{ M}$  (middle),  $6 \times 10^{-3} \text{ M}$  (bottom)). The dashed lines are the corresponding curves for uncomplexed  $\text{Cu}^{2+}(\text{aq})$ .

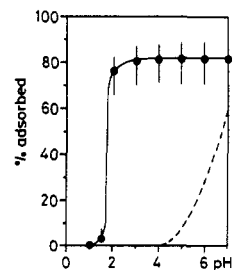
spectrum of the second species can be assigned to  $\text{Cu}(\text{en})_2^{2+}$ .

**DOHDO-pn.** The adsorption behavior of complexes with this ligand is completely different compared to the other compounds investigated (Figure 12).

The adsorption of the complex occurs parallel to the formation of the complex and is independent of the concentration of the  $\equiv\text{SiO}^-$  surface groups (as the stability constants of the complex are not known, the formation had to be controlled spectroscopically by ESR). The ESR parameters are typical for a  $\text{CuN}_4$  chromophore. Therefore, a metal to  $\equiv\text{SiO}^-$  bond can be excluded. An electrostatic interaction can also be excluded as the adsorption is independent of the charge of the surface.

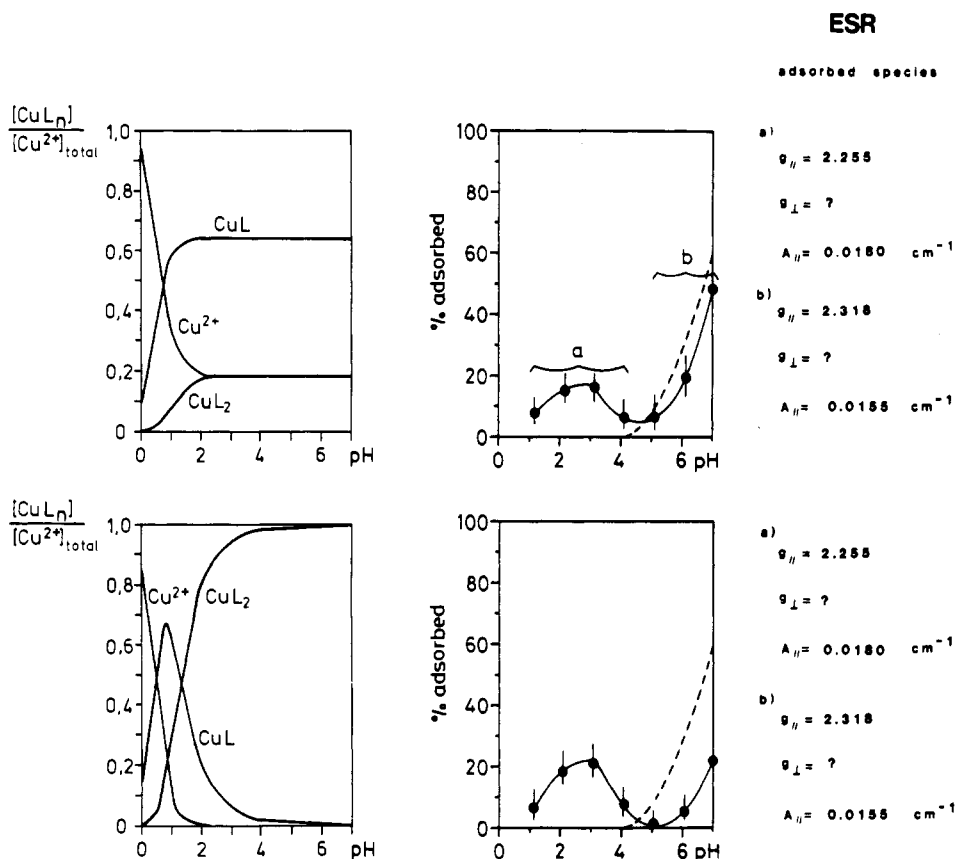
The complex is adsorbed at the surface independently whether the latter is protonated or not. This could be accomplished by hydrogen bonds between the oxime oxygens and the surface or/and by apical coordination of  $\equiv\text{SiOH}$  and/or  $\equiv\text{SiO}^-$  groups.

**pic.** The main difference between pic and the other bidentate ligands bpy, phen, and en is its negative charge. The 1:1 complex  $\text{Cu}(\text{pic})^+$  has only one positive charge and  $\text{Cu}(\text{pic})_2$  is uncharged. The adsorption behavior is shown in



**Figure 12.** Percentage of Cu adsorbed in solutions containing DOHDO-pn as a ligand at different pH values:  $[\text{Cu}^{2+}]_0 = 10^{-3} \text{ M}$ ,  $[\text{DOHDO-pn}] = 10^{-3} \text{ M}$ . The dashed line is the corresponding curve for uncomplexed  $\text{Cu}^{2+}(\text{aq})$ .

Figure 13. It can consistently be interpreted by assuming an adsorption via hydrogen bonds of  $\text{Cu}(\text{pic})_2$  at the "acidic" surface of silica gel. At higher pH values  $\text{Cu}(\text{pic})^+$  adsorbs weakly onto the deprotonated silica gel surface.  $\text{Cu}(\text{pic})_2$  does not adsorb at all at higher pH values because the surface cannot form hydrogen bonds and  $\text{Cu}(\text{pic})_2$  is probably trans configured.



**Figure 13.** Percentage of Cu adsorbed in solutions containing pic as a ligand at different pH values and calculated mole fractions of Cu<sup>2+</sup> and of the complexes in solution ( $\log K_1 = 8.70$ ,  $\log K_2 = 7.60$ ,  $pK_a^1 = 5.20$ ,  $pK_a^2 = 1.60$ ,  $[\text{Cu}^{2+}]_0 = 10^{-3} \text{ M}$ ;  $[\text{pic}] = 10^{-3} \text{ M}$  (top),  $2 \times 10^{-3} \text{ M}$  (bottom)). The dashed lines are the corresponding curves for uncomplexed Cu<sup>2+</sup>(aq).

**Table I.** Percentage of the Adsorbed Amount of Cu(II) in Various Complexes with Respect to the Total Amount of Cu(II) Present ( $[\text{Cu}^{II}]_{\text{total}} = 10^{-3} \text{ M}$ , Silica Gel = 40 g L<sup>-1</sup>)

	pH		
	4	5	6
Cu <sup>2+</sup>	0	7	30
Cu(en) <sup>2+</sup>	0	1	10
Cu(bpy) <sup>2+</sup>	20	70	95
Cu(bpy) <sub>2</sub> <sup>2+</sup>	10	60	90
Cu(phen) <sup>2+</sup>	35	80	100
Cu(phen) <sub>2</sub> <sup>2+</sup>	15	30	50
Cu(pic) <sup>+</sup>	5	5	15
Cu(terpy) <sup>2+</sup>	70	100	100

**Complete inhibition** of adsorption was found for the ligands GLY, IDA, NTA, and EDTA. In all these cases, only ESR spectra of mobile Cu complexes were observed. This shows that neutral or negatively charged species cannot generally adsorb onto the silica gel surface. The only exception is Cu(pic)<sub>2</sub>, which is weakly adsorbed. Here again the  $\pi$ -electron system enhances the stability of the ternary surface complex, as is the case for ternary complexes in solution.

### Conclusions

ESR spectroscopy is shown to be a suitable method for the investigation of the adsorption behavior of Cu(II) complexes. It allows an easy and direct distinction of mobile and adsorbed species, but the results are generally less accurate than those of the pH method. Some indications of the structure of the adsorbed species can be made. The method is complementary

to the pH titration procedure of Schindler et al. Table I gives approximate figures for the percentage of adsorption for different complexes. The observed adsorption can be explained by four different modes: through a coordinate bond formation between Cu<sup>2+</sup>(aq) of CuL and surface  $\equiv\text{SiO}^-$  groups as, e.g., Cu(bpy)<sup>2+</sup>, Cu(bpy)<sub>2</sub><sup>2+</sup>, etc.. (this mode of adsorption can also be detected by pH titrations); through the formation of coordinate bonds between  $\equiv\text{SiOH}$  groups and *cis*-CuL<sub>2</sub><sup>n+</sup> complexes at low pH; through the formation of hydrogen bonds between  $\equiv\text{SiOH}$  and suitable groups in the ligand of CuL complexes as, e.g., in Cu(DOHDO-pn)<sup>+</sup>; through a purely electrostatic interaction (formation of a "surface ion pair") between  $\equiv\text{SiO}^-$  groups and CuL<sub>x</sub><sup>2+</sup> species. The complexes are immobilized by incorporation into the Gouy-Chapman layer. This is, e.g., the case for Cu(cyclam)<sup>2+</sup> and Cu(terpy)<sub>2</sub><sup>2+</sup>.

The method could be refined and used as a quantitative measure of adsorption if more accurate intensity determinations by digital integration were applied.

Adsorption of complexes of other metals which cannot be detected by ESR spectroscopy could be studied by using the copper complexes as competing species.

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**Registry No.** Cu, 7440-50-8; bpy, 366-18-7; phen, 66-71-7; en, 107-15-3; terpy, 1148-79-4; EDTA, 60-00-4; IDA, 142-73-4; NTA, 139-13-9; pic, 98-98-6; gly, 56-40-6; cyclam, 295-37-4; DOHDO-pn, 7223-54-3; SiO<sub>2</sub>, 7631-86-9.