

## INFLUENCE OF GLYCINE ON $\text{Cu}^{2+}$ ADSORPTION BY MICROCRYSTALLINE GIBBSITE AND BOEHMITE

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**Abstract**—The adsorption of  $\text{Cu}^{2+}$  on microcrystalline gibbsite and boehmite from aqueous solutions having 2/1 and 5/1 glycine/Cu ratios has been studied using electron spin resonance (ESR). The presence of glycine inhibited metal adsorption on gibbsite above pH 5, apparently by reducing Cu hydrolysis. The preferred adsorbed species on gibbsite and boehmite, based upon the ESR parameters, were probably  $\text{Cu}(\text{gly})^+$  and  $\text{Cu}(\text{gly})_2^0$ , respectively. In both experiments, rigidly-bound ternary complexes formed with  $\text{Cu}^{2+}$  simultaneously bonding to the surface and one or more ligands. A large excess of glycine destabilized the ternary complex and caused the desorption of  $\text{Cu}^{2+}$ . The preferred orientation of the Cu complex on gibbsite suggests that the adsorption occurred at crystal steps and that the glycine molecule hydrogen bonded to hydroxyls of the (001) surface.

**Key Words**—Adsorption, Boehmite, Copper, Electron spin resonance, Gibbsite, Glycine, Hydrolysis.

### INTRODUCTION

It is now well established that metal-complexing ligands in solution can fundamentally alter the ability of metal ions to bond to surfaces. On permanent-charge clays, such as smectites, metal-complexing molecules (e.g., fulvic acids, EDTA, and citric acid) inhibit the adsorption of metals such as  $\text{Cu}^{2+}$  by lowering the free metal ion activity in solution (McBride, 1981). On oxides of Si, Fe, and Al, chelating agents such as EDTA, if present in large excess, generally suppress metal ion adsorption (Elliot and Huang, 1979; Bourg and Schindler, 1979). Conversely, other ligands enhance metal adsorption, presumably by forming stable surface-metal-ligand complexes (Bourg *et al.*, 1979; Davis and Leckie, 1979; Elliot and Huang, 1980). These ligands appear capable of complexing or chelating the metal ion while allowing simultaneous coordination of the metal to the surface. Commonly, this type of ligand forms bidentate chelates (e.g., ethylenediamine, bipyridyl, glycine) with the metal. In any event, the metal/ligand ratio is critical in determining whether metal adsorption at surfaces is enhanced or inhibited, because a large excess of complexing molecules in solution shifts the equilibrium in favor of soluble metal complexes.

In the present study, the effect of the chelating ligand, glycine, on the bonding of  $\text{Cu}^{2+}$  at the surfaces of microcrystalline gibbsite and boehmite was investigated by electron spin resonance (ESR) under conditions of varying pH and Cu/glycine ratios. The spectroscopic analyses were made on moist surfaces to prevent the possible alteration of surface complexes by dehydration. Interpretation of the results was partially based on information from a previous study of the bonding mechanism of  $\text{Cu}^{2+}$  on gibbsite (McBride *et al.*, 1984).

### MATERIALS AND METHODS

The gibbsite and boehmite used in this study have been described elsewhere (McBride *et al.*, 1984; Russell *et al.*, 1974; Blean and McBride, 1985) and have surface areas of 104 and 41  $\text{m}^2/\text{g}$ , respectively. The identification of both materials was confirmed by infrared spectroscopy. Preliminary studies indicated that conventional infrared spectroscopy was not a sufficiently sensitive method to study  $\text{Cu}^{2+}$  and  $\text{Cu}^{2+}$ -glycine adsorption on gibbsite.

$\text{Cu}^{2+}$ -adsorption data with and without glycine present in solution were obtained as follows: 1 ml of gibbsite suspension (26 mg/ml) was added to 5 ml of  $10^{-2}$  M  $\text{CuCl}_2$  and either 10 ml of distilled water or 10 ml of  $10^{-2}$  M glycine. The pH was adjusted to between 3 and 10 using NaOH, and the mixtures were equilibrated for one day. The final pH was then determined, and the supernatants were removed following centrifugation. The gibbsite was washed twice with distilled water and acidified by shaking for 1 hr in 10 ml of 1 M HCl. The acid supernatant was analyzed for Cu by atomic absorption spectrophotometry, and the quantity of adsorbed Cu was obtained from this result. Analysis of acid-washed gibbsites by ESR confirmed that no bound  $\text{Cu}^{2+}$  remained on the surfaces.

The ESR spectra of  $\text{Cu}^{2+}$  adsorbed on gibbsite in the presence of glycine were obtained by immersing thin, self-supporting gibbsite films ( $\sim 2\text{cm}^2$ ) into glycine- $\text{Cu}^{2+}$  solutions prepared by mixing  $10^{-2}$  M glycine and  $10^{-2}$  M  $\text{CuCl}_2$  in either 5/1 or 2/1 mole ratios and adjusting the pH to between 3 and 10 using NaOH. After 1 hr of equilibration, the films were removed from solution and analyzed in the wet condition by ESR using a Varian E-104 (X-band) spectrometer before and after rinsing them in distilled water to remove unbound

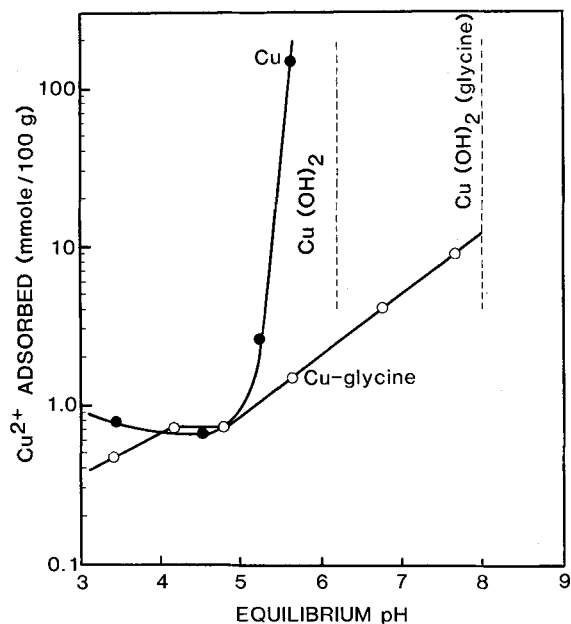


Figure 1. Plot of adsorption of  $\text{Cu}^{2+}$  on microcrystalline gibbsite as a function of pH from aqueous  $\text{Cu}^{2+}$  and  $\text{Cu}^{2+}$ -glycine (glycine/Cu = 2) solutions. Vertical broken lines denote pH at which the  $\text{Cu}^{2+}$  and  $\text{Cu}^{2+}$ -glycine solutions should be saturated with respect to  $\text{Cu}(\text{OH})_2$  precipitation.

$\text{Cu}^{2+}$ . Similar adsorption experiments were conducted using boehmite as the adsorbent.

To test whether pre-adsorbed  $\text{Cu}^{2+}$  could be removed from gibbsite surfaces by the subsequent introduction of excess chelating organic molecules, gibbsite films were equilibrated overnight in a 0.01 M  $\text{CuCl}_2$  solution, removed from solution, and immersed in distilled water to remove excess  $\text{Cu}^{2+}$ . The films were then equilibrated for 1 hr in  $10^{-2}$  M glycine and histidine solutions that had been adjusted to neutral pH. The ESR spectra of the wet unrinsed films were obtained following removal from the solutions.

## RESULTS AND DISCUSSION

The quantity of  $\text{Cu}^{2+}$  adsorbed by gibbsite below pH 5 was about the same for adsorption from a  $\text{Cu}^{2+}$  or from a  $\text{Cu}^{2+}$ -glycine (2/1 mole ratio) solution (Figure 1). Above pH 5, however, the apparent adsorption in the absence of glycine increased sharply as the solution conditions favorable for  $\text{Cu}(\text{OH})_2$  precipitation were approached. The adsorption increased much less steeply with increasing pH in the presence of glycine. The particular  $\text{Cu}^{2+}$ -glycine solution used in this adsorption study reached saturation with respect to  $\text{Cu}(\text{OH})_2$  precipitation at pH 8 (Figure 1), based upon the known stability constants of Cu-hydroxy and Cu-glycine complexes (Baes and Mesmer, 1976; Martell and Smith, 1977). The results in Figure 1 suggest that glycine in-

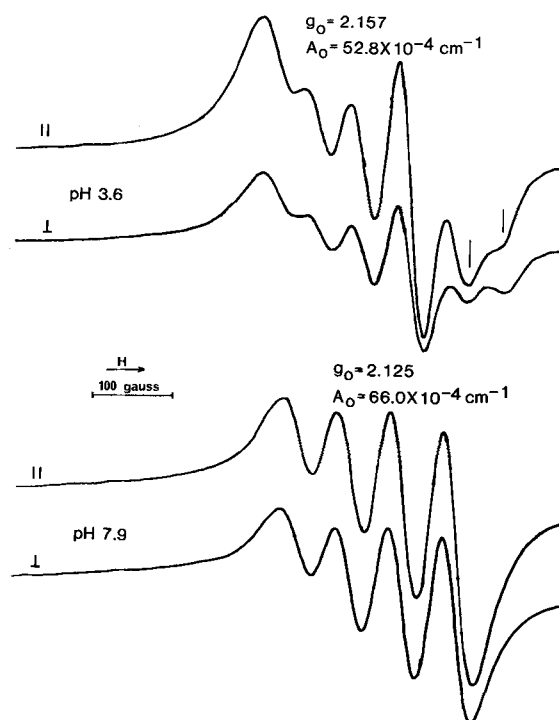


Figure 2. Room-temperature electron spin resonance spectra of oriented gibbsite films that had been equilibrated in  $\text{Cu}^{2+}$ -glycine solutions (glycine/Cu = 2) at pH 3.6 and 7.9. Films were neither rinsed nor dried prior to analysis. || and  $\perp$  refer to parallel and perpendicular orientation of the films relative to the magnetic field.

hibited precipitation or surface nucleation reactions of Cu hydroxide, thereby suppressing sorption at higher pH. Clearly, however, large quantities of  $\text{Cu}^{2+}$  were retained by the gibbsite at pHs well below the threshold of  $\text{Cu}(\text{OH})_2$  precipitation, even with glycine present. Because the density of chemisorption sites on this gibbsite is quite low ( $<1$  mmole/100 g) (McBride *et al.*, 1984), it appears that the surface provided nucleation sites for the adsorption of Cu hydroxide.

The gibbsite films, after immersion in the Cu-glycine solutions, produced ESR spectra which suggest the presence of bound (rigid-limit)  $\text{Cu}^{2+}$  in addition to mobile  $\text{Cu}^{2+}$ -glycine complexes. Figure 2 shows typical spectra at low and high pH for oriented gibbsite films which had been immersed in the solution with a 2/1 mole ratio. The 4-line isotropic signals at low field arose from  $\text{Cu}(\text{glycine})^+$  ( $g_0 = 2.157$ ,  $A_0 = 52.8 \times 10^{-4} \text{ cm}^{-1}$ ) at low pH, and  $\text{Cu}(\text{glycine})_2^0$  ( $g_0 = 2.125$ ,  $A_0 = 66.0 \times 10^{-4} \text{ cm}^{-1}$ ) at high pH in the solution phase (Goodman *et al.*, 1981). These signals were lost when the gibbsite films were rinsed in water. The dependence of the g-values and hyperfine splitting of Cu on pH can be attributed to changes in  $\text{Cu}^{2+}$  speciation in glycine solutions. The predicted speciation of  $\text{Cu}^{2+}$  was cal-

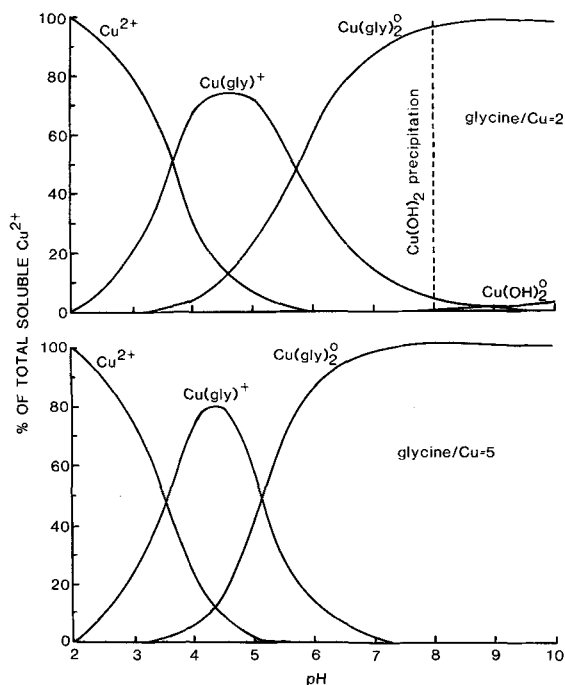


Figure 3. Plots of dependence of Cu speciation in glycine solutions on pH and glycine/Cu ratio.

culated as a function of pH and glycine/Cu ratio using the MICROQL computer program and stability constants from Martell and Smith (1977) and Baes and Mesmer (1976), and is graphed in Figure 3.

The remaining ESR resonances shown in Figure 2 (marked by lines) were not eliminated by rinsing the gibbsite, and are assigned to the resonances of the rigid-limit spectrum of adsorbed  $\text{Cu}^{2+}$ . These resonances were weak below pH 3, but increased in intensity as the adsorption pH was adjusted upward. Above pH 6,

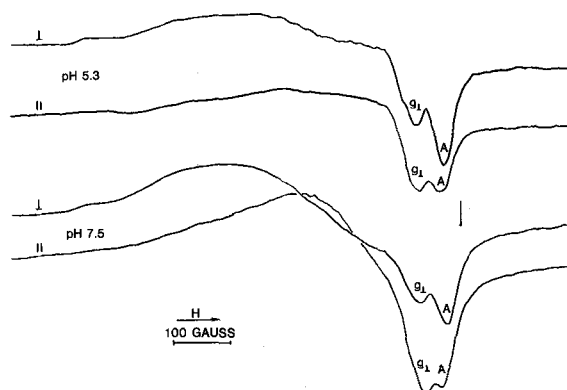


Figure 4. Room-temperature electron spin resonance spectra of oriented, moist gibbsite films that had been equilibrated in  $\text{Cu}^{2+}$ -glycine solutions (glycine/Cu = 2) at pH 5.3 and 7.5, then rinsed in  $\text{H}_2\text{O}$ .  $g_{\perp}$  resonance and extra high-field resonance (A) are labelled; vertical line denotes the free electron ( $g = 2.0023$ ) position.

however, the resonances weakened again. Below pH 6, adsorption from the solution with a glycine/Cu ratio of 2 generated a more intense rigid-limit spectrum than did adsorption from the solution with glycine/Cu = 5, whereas above pH 6, the reverse was true. This effect was probably due to the surface nucleation and precipitation of copper hydroxide or hydroxycarbonate at low glycine/Cu ratios inasmuch as a green precipitate formed in the gibbsite suspensions equilibrated with solutions having a glycine/Cu ratio of 2 and pH > 6.2. In support of this explanation, speciation calculations predicted that  $\text{Cu}(\text{OH})_2$  would precipitate at pH 8 if the glycine/Cu ratio were only 2, whereas precipitation would not occur if the ratio were 5 (Figure 3).

The ESR evidence indicates that the Cu monomer (which generated the rigid-limit spectrum) adsorbed on the gibbsite most effectively at moderate pH. Low

Table 1. Rigid-limit electron spin resonance parameters of  $\text{Cu}^{2+}$  and  $\text{Cu}^{2+}$ -glycine complexes.

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ ( $\text{cm}^{-1}$ )	$A_{\perp}$ ( $\text{cm}^{-1}$ )	
Solution species: <sup>1</sup>					
$\text{Cu}(\text{H}_2\text{O})_6^{2+}$	2.421	2.09	0.0125	ND	
$\text{Cu}(\text{gly})^+$	2.308	ND (2.08) <sup>3</sup>	0.0170	ND	
$\text{Cu}(\text{gly})_2^0$	2.266	2.060 (2.057) <sup>3</sup>	0.0178	0.0016 <sup>4</sup>	
Adsorbed species: <sup>2</sup>					
Boehmite	}	2.251	2.067	0.0176	ND
		2.285	ND	0.0169	ND
Gibbsite		~2.29	2.06 <sup>4</sup>	~0.0172	ND

ND = parameters were not determined because resonances were obscured or unresolved.

<sup>1</sup> Spectra determined at  $-120^\circ\text{C}$  after adding 10% MeOH by volume to aqueous solutions. pH was controlled to generate the species of interest.

<sup>2</sup> Spectra obtained at room temperature on moist samples with 2/1 and 5/1 glycine/Cu ratios and pH values adjusted between 3 and 10.

<sup>3</sup> Values in brackets calculated from measured isotropic  $g$  value ( $g_0$ ) and  $g_{\parallel}$ .

<sup>4</sup> Parameters estimated from computer-simulated spectra used to model the spectral shape in the  $g_{\perp}$  region.

pH inhibited adsorption, probably because of  $H^+$  competition with  $Cu^{2+}$  for surface oxyanion sites. High pH also inhibited monomer adsorption, presumably because  $Cu^{2+}$  coordinated with  $OH^-$  to form polymeric species. Although these polymers may have adsorbed, as suggested by the adsorption data (Figure 1), they did not generate distinctive ESR spectra. The speciation calculations for  $Cu^{2+}$  in glycine solutions (Figure 3) reveal that a pH of 4 to 5 favors the formation of  $Cu(gly)^+$  relative to  $Cu^{2+}$  and  $Cu(gly)_2^0$ . Thus, the maximum adsorption of monomeric Cu in this pH range may have resulted from the preferred adsorption of  $Cu(gly)^+$ .

An attempt was made to identify the ligand environment of surface-bound Cu monomers, based upon the parameters of the rigid-limit spectrum of Cu on water-washed gibbsite (Table 1). Examples of these spectra of Cu bound at two different pH values are shown in Figure 4. The resonance intensities generally increased with increasing pH of adsorption up to about pH 6. Above this pH, a broad resonance at  $g = 2.1$ – $2.2$  appeared (Figure 4), indicating Cu–Cu magnetic dipolar interactions, and suggesting the presence of polymeric hydroxy-Cu species (Martini *et al.*, 1980). The rigid-limit spectrum demonstrates orientation-dependent intensity, with the poorly resolved, low-field ( $g_{\parallel}$ ) resonances appearing most intense and the high-field ( $g_{\perp}$ ) resonance appearing least intense when the gibbsite films were oriented perpendicular to the applied magnetic field. The latter resonance is denoted by the  $\perp$  symbol in Figure 4. The resonance at highest field, denoted by the symbol A, is not a component of the  $g_{\perp}$  signal, but resulted because the  $\parallel$  and  $\perp$  field positions of the  $m_1 = -3/2$  electronic transition are similar for Cu-amine complexes because of their typically low  $g_{\parallel}$  and high  $A_{\parallel}$  values. This additional resonance is present for an orientation of the Cu symmetry axis between the  $\parallel$  and  $\perp$  orientations, appearing as an intense signal at higher field than  $g_{\perp}$  with a dependence of intensity on sample orientation which is different from that of the  $g_{\perp}$  resonance (Figure 4). The existence of this apparently anomalous resonance in the Cu-glycine spectra was verified by generating computer-simulated, rigid-limit Cu ESR spectra (not shown) with parameters equal to those measured experimentally.

The orientation-dependence of the ESR spectra (Figure 4), while quite obvious, was imperfect, suggesting that the symmetry axis (Z) of surface-bonded Cu was not perfectly aligned normal to the (001) plane of the gibbsite crystal. The imperfect alignment cannot be attributed to poor orientation of the (001) faces of crystallites in the gibbsite films, because preliminary ESR investigations of impurities of  $Fe^{3+}$  in these films had shown more perfect orientation-dependence of the  $Fe^{3+}$  signal. The poor resolution of the  $g_{\parallel}$  resonances in the Cu spectra suggests the presence of several bound species

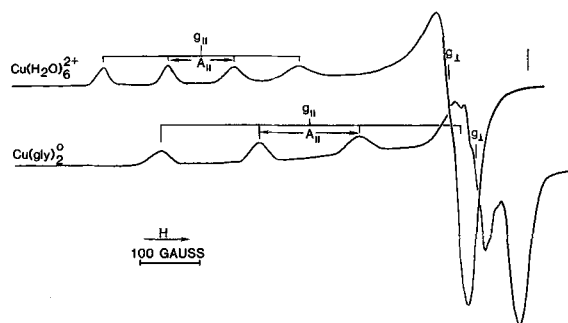
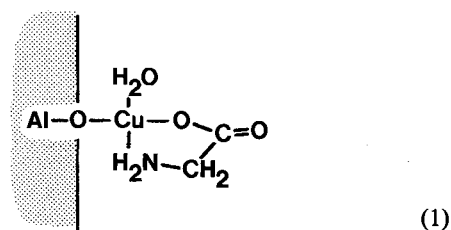


Figure 5. Rigid-limit electron spin resonance spectra of  $Cu(H_2O)_6^{2+}$  and  $Cu(gly)_2^0$  obtained by freezing aqueous  $CuCl_2$  and  $CuCl_2$ -glycine solutions with 10% MeOH at  $-120^\circ C$ . Computer generated rigid-limit spectra using the experimentally determined parameters for  $Cu(gly)_2^0$  had similar features to the displayed spectrum of  $Cu(gly)_2^0$ .

of Cu with slightly different  $A_{\parallel}$  and  $g_{\parallel}$  values, some of which may be oriented differently relative to the surface. The  $g_{\parallel}$  value of Cu adsorbed on gibbsite from Cu-glycine solutions, while difficult to determine with precision because of the broadened  $g_{\parallel}$  resonances, was somewhat lower in value than that of rigid-limit  $Cu(H_2O)_6^{2+}$  (Table 1). In addition, the hyperfine splitting of the adsorbed species was intermediate in value between those of  $Cu(H_2O)_6^{2+}$  and  $Cu(gly)_2^0$ . The rigid-limit spectra of these latter species in solution (Figure 5) have very different  $g$  and  $A$  values, caused by the exchange of the four equatorial  $H_2O$  ligands by two glycine molecules. Complexation of  $Cu^{2+}$  with only one glycine molecule to form  $Cu(gly)^+$  would leave two  $H_2O$  molecules in equatorial positions; therefore, an ESR signal with intermediate parameters would be expected and has been observed (Goodman *et al.*, 1981). In fact, the surface-adsorbed Cu species had ESR parameters fairly similar to those of  $Cu(gly)^+$  (Table 1), suggesting that Cu bonds to surface sites and glycine as shown below:



The quantity of Cu that bonded in this manner was greatly limited on gibbsite because of the few available reactive Al-OH groups, which probably existed only at crystal steps and edges (McBride *et al.*, 1984). Similar adsorption of Cu-glycine solutions on high-surface area boehmite generated much more intense ESR spectra (Figure 6) of Cu bound at the surfaces, probably because the boehmite possessed many more active sur-

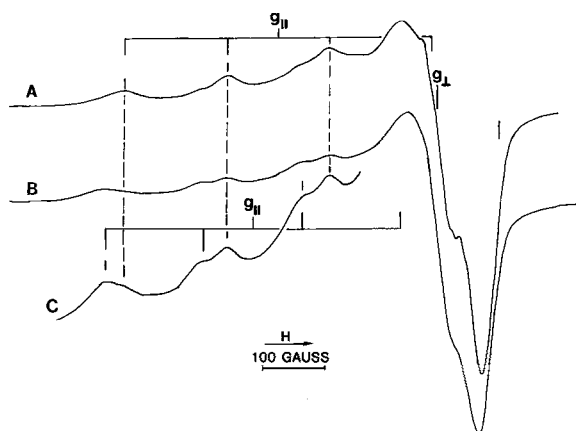
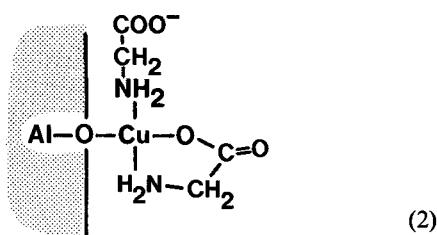


Figure 6. Room-temperature electron spin resonance spectra of moist boehmite powder that had been equilibrated in  $\text{Cu}^{2+}$ -glycine solution (glycine/Cu = 2) at pH 6.2: A. unwashed; B. washed once in water; C. same as B with increased gain.

face- $\text{AlOOH}$  groups per unit of surface area (McBride, 1982). The ESR parameters of the rigidly bonded Cu-glycine complexes on boehmite were determined with greater accuracy than those on gibbsite (Table 1). Two distinct adsorbed species were detected, one with a rather low  $g_{||}$  value (2.25), and one with a  $g_{||}$  value not unlike that of the adsorbed species on gibbsite. The latter species became relatively more prevalent after water-washing the boehmite to remove excess non-adsorbed Cu-glycine (Figure 6B). The former species had a  $g_{||}$  value low enough to indicate that the bound Cu was coordinated to at least two N ligands, possibly in the following manner:



Although the carboxyl group of the second glycine molecule cannot coordinate in an equatorial position, it may take up an axial position. Water washing evidently removed the second glycine as  $\text{H}_2\text{O}$  molecules competed for ligand positions, resulting in a conversion of this complex to the one proposed to form on gibbsite (complex 1). Similar conversion of one Cu-ligand species to another with changing solution conditions has been noted for Cu-ammonia complexes bound to allophane (Clark and McBride, 1984).

The orientation-dependence of the ESR spectra of bound Cu-glycine complexes on gibbsite (Figure 4) is consistent with a scheme of bonding in which  $\text{Cu}(\text{gly})^+$

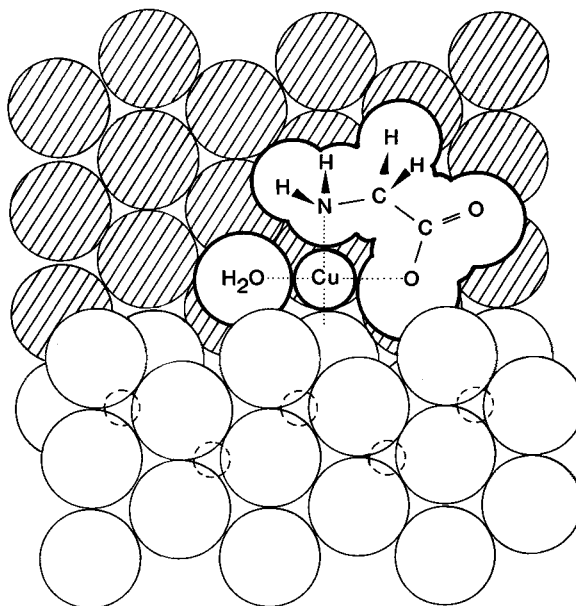


Figure 7. View down the  $c$ -axis of gibbsite of the proposed structure of  $\text{Cu}(\text{glycine})^+$  bound at a crystal step on the (001) surface.

ion coordinated to an exposed OH at a crystal step as depicted in Figure 7. A molecular model of this surface complex indicates that the symmetry axis ( $Z$ ) of  $\text{Cu}^{2+}$  should have been approximately parallel to the  $c$ -axis of the gibbsite crystal, in agreement with the ESR spectra. It is likely that Cu bonded to an OH group that was coordinated to a single Al ion because hydroxyls coordinated to two Al ions are generally non-reactive in metal adsorption processes (McBride *et al.*, 1984). Hydrogen bonding between glycine and the surface hydroxyls may have further stabilized this complex (Elliot and Huang, 1980).

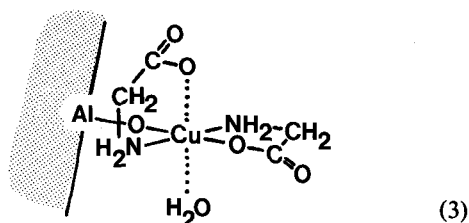
The model in Figure 7 suggests that steric hindrance may have prevented the coordination of two glycine molecules to  $\text{Cu}^{2+}$  adsorbed on the gibbsite. The coordination of two glycine molecules to Cu bound on boehmite may be permitted by a different site geometry. Other studies of  $\text{Cu}^{2+}$ -amino acid adsorption by Al oxides have provided indirect evidence that the  $\text{CuL}^+$  rather than the  $\text{CuL}_2^0$  ( $L$  = ligand) species was adsorbed (Elliot and Huang, 1980). In these studies, the stoichiometry of the reaction was also affected by the nature of the ligand. The adsorption of  $\text{Cu}^{2+}$ -nitriilotriacetic acid (NTA) on  $\gamma\text{-Al}_2\text{O}_3$  appeared to occur as the  $\text{CuL}^-$  species (Elliot and Huang, 1979). Because one  $\text{NTA}^-$  molecule can occupy three equatorial ligand positions of  $\text{Cu}^{2+}$ , leaving the remaining equatorial position to coordinate with a surface OH, a second  $\text{NTA}^-$  molecule could not chelate with  $\text{Cu}^{2+}$  unless the  $\text{Cu}^{2+}$  had desorbed from the surface. Also, the weaker adsorption of higher molecular weight Cu-amino acid

complexes noted by Elliot and Huang (1980) may be related to the steric constraints associated with simultaneous bonding of the metal to the surface and a bulky ligand.

The ratio of complexing ligand to metal in solution is critical to whether adsorption of the metal is enhanced or suppressed relative to adsorption in the absence of ligand (Elliot and Huang, 1979). In the present study,  $\text{Cu}^{2+}$  preadsorbed on gibbsite was readily desorbed by excess glycine or histidine, as shown by the loss in the ESR signal of adsorbed  $\text{Cu}^{2+}$  following equilibration in  $10^{-2}$  M solutions of the amino acids. A large excess of the chelating ligand apparently favored the formation of  $\text{CuL}_2$  species in solution as the amino acids competed with surface hydroxyls for coordination positions on  $\text{Cu}^{2+}$ .

### CONCLUSIONS

In the presence of glycine,  $\text{Cu}^{2+}$  adsorbed on gibbsite and boehmite to form a ternary complex in which the metal coordinated simultaneously with a surface hydroxyl and at least one glycine molecule. With gibbsite, adsorption of the  $\text{Cu}(\text{gly})^+$  species was favored, with a tendency toward orientation of the Cu Z-axis normal to the (001) surface. Under the same solution conditions, boehmite preferentially adsorbed  $\text{Cu}(\text{gly})_2^0$ . A square planar stereochemical configuration of  $\text{Cu}(\text{gly})_2^0$  on boehmite was unlikely because at least one equatorial ligand position probably coordinated to the surface (McBride, 1982). A more plausible description places two amine groups and one carboxyl in equatorial positions, with the second carboxyl occupying an axial (weak ligand) position as shown below:



The second glycine molecule was readily removed by water washing, lending credence to the hypothesis that this glycine was not chelated at equatorial ligand positions of  $\text{Cu}^{2+}$ .

A large excess of the chelating ligand (glycine) in solution caused the desorption of chemisorbed  $\text{Cu}^{2+}$ , although glycine/ $\text{Cu}^{2+}$  molar ratios as high as 5 did not prevent the formation of the ternary surface-metal-

ligand complex. The presence of glycine in solution reduced Cu adsorption on microcrystalline gibbsite above pH 5, evidently by inhibiting  $\text{Cu}^{2+}$  hydrolysis.

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