

## THE ORIENTATION AND INTERACTION OF ETHYLENEDIAMINE COPPER (II) WITH MONTMORILLONITE

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**Abstract**—The  $d(001)$  spacings for a series of montmorillonite samples containing increasing amounts of  $\text{Cu}(\text{en})_3^{2+}$  were recorded after exposure to 50% humidity, 10% humidity, and air that had been saturated with ethylene glycol. It was found that  $\text{Cu}(\text{en})_3^{2+}$  is too large to fit between the montmorillonite particles and that in those samples with large amounts of ethylenediamine Cu(II) added, the clay platelets are associated with stronger interactions than those with small amounts of Cu(II) complex added.

Infrared spectroscopy and electron spin resonance analysis indicate that the absorbed copper (II) complex is the square planar *bis* ethylenediamine Cu(II) and that the complex ion is oriented so that the  $d_{z^2}$  orbital is perpendicular to the clay surface. The montmorillonite particles may act as ligands and coordinate with  $\text{Cu}(\text{en})_2^{2+}$  ions.

### INTRODUCTION

Recently there has been an interest in the study of coordination compounds sorbed to clay minerals, (Theng, 1974; Clementz, 1973; McBride, 1974; McBride, 1975; Rupert, 1973; and Thielmann, 1975). Thielmann examined the feasibility of using complexes of various *tris* ethylenediamine metal ions with montmorillonite as gas chromatography columns for the separation of light hydrocarbons. *Tris* ethylenediamine copper(II) montmorillonite was one of the complexes that was examined. Because of its rather extraordinary properties, such as the ability to form stable gels with relatively small amounts of montmorillonite, further examination was of interest.

This paper deals with results obtained from X-ray powder diffraction, Fourier synthesis and transform calculations, infrared spectroscopy, and electron spin resonance analysis of the *tris* ethylenediamine copper(II) montmorillonite system.

### EXPERIMENTAL TECHNIQUES

A dispersion of  $\text{Na}^+$  montmorillonite containing 4.6% clay by weight was prepared from spray-dried 100%  $\text{Na}^+$  exchanged Wyoming Bentonite. From this suspension and a 0.1 N solution of  $\text{Cu}(\text{en})_3\text{SO}_4$ , samples containing 0, 10, 20, 40, 50, 75, 100, and 120 mequiv.  $\text{Cu}(\text{en})_3^{2+}/100$  g of clay were prepared by pipetting various amounts of the complex ion into a known volume of the clay dispersion. The total volume of each sample was adjusted to 250 ml and the clay was transferred to polyethylene bottles. Each dispersion was then dispersed with an ultrasonic cell disrupter. The per cent clay by weight of each sample was 1%.

A 1% dispersion of 100% exchanged Cu(II) mont-

morillonite was prepared by the addition of an excess amount of Cu(II) chloride solution. The clay was washed by successive centrifugation until addition of ammonia to the wash water did not produce a blue solution. Ammonia was added to 25 ml of the Cu(II) montmorillonite, and the excess was removed by successive washings. Another sample was prepared first by reacting a solution of Cu(II) chloride with ammonia then the solution was reacted with  $\text{Na}^+$  montmorillonite and the clay was washed until a negative AgCl test was obtained.

Dispersions containing 0, 10, 20, 50, 75, 100, and 120 mequiv. of  $\text{Cu}(\text{en})_3^{2+}$  added/100 g of clay were used in the X-ray experiments. Three samples were taken from each dispersion and dried on petrographic microscope slides.

A series of experiments was carried out in which the samples were placed in a desiccator for 48 hr at room temperature and X-rayed. Three desiccators were used in the following order; saturated calcium nitrate, which has a relative humidity of 51%; dried calcium chloride, 10% relative humidity; and ethylene glycol.

The 100 mequiv.  $\text{Cu}(\text{en})_3^{2+}/100$  g of montmorillonite samples were left in the ethylene glycol desiccator for 30 days. The samples were X-rayed and compared to X-ray patterns of Cu(II) montmorillonite and the two Cu(II) ammonia clay complexes, each of which were exposed to ethylene glycol for 48 hr.

The infrared analysis utilized samples containing 0, 40, and 100 mequiv.  $\text{Cu}(\text{en})_3^{2+}/100$  g of clay. Oriented films of these clays were made by drying portions of the clays on petrographic microscope slides. Slivers were peeled from the slides and placed in supports which held them firmly in place. Spectra were then recorded of these samples for comparison purposes.

The orientation studies were carried out on samples of 40 mequiv.  $\text{Cu}(\text{en})_3^{2+}/100$  g of clay which were washed by centrifugation until a negative  $\text{AgCl}$  test was obtained. This clay was used rather than the 100 mequiv.  $\text{Cu}(\text{en})_3^{2+}/100$  g of clay sample because the 100 mequiv.  $\text{Cu}(\text{en})_3^{2+}/100$  g of clay flocculated to such an extent that the films made from it did not make uniformly thick samples.

The samples containing 40 mequiv.  $\text{Cu}(\text{en})_3^{2+}/100$  g of clay were heated at  $108^\circ\text{C}$  for 8 hr and cooled in a desiccator containing calcium chloride. Two infrared spectra were then recorded in which the angles of orientation between the clay film and the infrared beam were  $90$  and  $40^\circ$ .

A 1% dispersion of montmorillonite, which was 100% exchanged with  $\text{Cu}(\text{en})_3^{2+}$  and then washed to remove any ions that were not adsorbed, was prepared as a self-supporting film. This was then mounted on a flat fused silica orientation device for electron spin resonance.

Spectra were recorded with the film oriented perpendicular and parallel to the flux of the magnetic field.

## DISCUSSION

### General observations

Addition of  $\text{Cu}(\text{en})_3\text{SO}_4$  solution to  $\text{Na}^+$  montmorillonite causes immediate flocculation of the clay. Even in dispersions containing small amounts, 0.1% clay by weight, aggregates form readily. The aggregates will break apart when the dispersions are agitated with an ultrasonic cell disrupter, but after treatment they reform. The addition of  $\text{Cu}(\text{en})_3^{2+}$  also causes the color of montmorillonite to change from tan for  $\text{Na}^+$  montmorillonite, to pink for montmorillonite with  $\text{Cu}(\text{en})_3^{2+}$  added.

$\text{Na}^+$  montmorillonite has a pH of about 7. Addition of 100 mequiv.  $\text{Cu}(\text{en})_3^{2+}/100$  g of clay causes the pH of montmorillonite to change to about thirteen. This change in pH is due to the dissociation of  $\text{Cu}(\text{en})_3^{2+}$  to  $\text{Cu}(\text{en})_2^{2+}$  in water solution (Huheey, 1972). Thus, the ion in solution is  $\text{Cu}(\text{en})_2^{2+}$  rather than  $\text{Cu}(\text{en})_3^{2+}$ .

### X-ray powder diffraction analysis

The thickness of  $\text{Cu}(\text{en})_3^{2+}$  is about  $6 \text{ \AA}$ , as measured by Fisher-Hirschfelder-Taylor Metal-Coordination models, and the thickness of a clay platelet is  $9.6 \text{ \AA}$  (Grim, 1968). The  $d(001)$  spacing of a montmorillonite sample is the sum of the theoretical thickness of the clay particle and the thickness of any material lying between the clay platelets. Thus, the calculated  $d(001)$  spacing of a sample of montmorillonite with 100 mequiv. of  $\text{Cu}(\text{en})_3^{2+}$  added/100 g of clay is about  $15.6 \text{ \AA}$ , while the observed  $d(001)$  spacing is only  $12.6 \text{ \AA}$ . Therefore the  $\text{Cu}(\text{en})_3^{2+}$  ion is  $3 \text{ \AA}$  too thick to fit in the observed space and cannot be the adsorbed ion. Cloos reported that  $d(001)$  spacing for  $\text{Cu}(\text{en})_2^{2+}$  montmorillonite is  $12.6 \text{ \AA}$  and that the thickness of  $\text{Cu}(\text{en})_2^{2+}$  is about  $3 \text{ \AA}$  (Theng, 1974). The

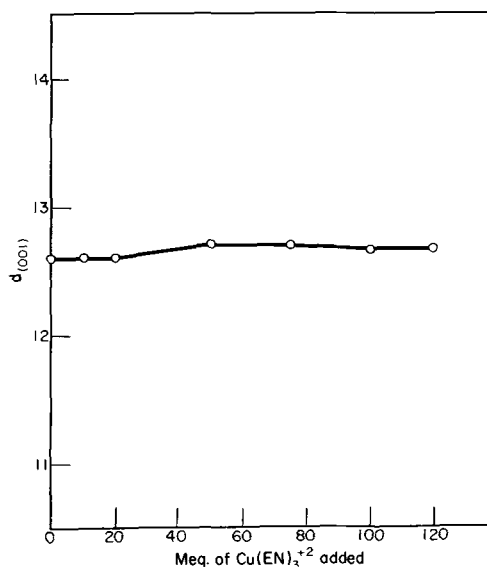


Figure 1. Plot of  $d(001)$  spacing vs the amount of ethylenediamine  $\text{Cu}(\text{II})$  added for samples at 51% humidity.

thickness of  $\text{Cu}(\text{en})_2^{2+}$ , obtained from Fisher models, is about  $4 \text{ \AA}$ . The calculated  $d(001)$  spacing for  $\text{Cu}(\text{en})_2^{2+}$  montmorillonite can then be either  $12.6 \text{ \AA}$  if the thickness of  $\text{Cu}(\text{en})_2^{2+}$  is considered to be  $3 \text{ \AA}$ , or  $13.6 \text{ \AA}$  if a thickness of  $4 \text{ \AA}$  is used. If the thickness of  $\text{Cu}(\text{en})_2^{2+}$  is slightly greater than  $3 \text{ \AA}$ ,  $\text{Cu}(\text{en})_2^{2+}$  could still yield a  $d(001)$  spacing of  $12.6 \text{ \AA}$  if the complex is able to key into hexagonal holes in the surface of the clay or if the bonding between the metal complex and the clay causes a shortening of the bond distances.

Figure 1 is a plot of  $d(001)$  vs the amount of ethylenediamine  $\text{Cu}(\text{II})$  that was added to the clay. This plot pertains to clay at 50% humidity. As the ethylenediamine  $\text{Cu}(\text{II})$  is added there seems to be little change in the  $d(001)$  spacing.

Figure 2 is a plot of Warren's constant, which is a measure of uniform stacking in clay (Brown, 1961) vs the amount of ethylenediamine  $\text{Cu}(\text{II})$  added. The

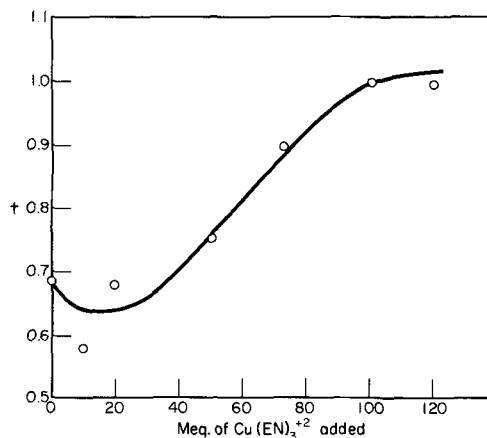


Figure 2. Plot of Warren's constant,  $t$  vs the amount of ethylenediamine  $\text{Cu}(\text{II})$  added for samples at 51% humidity.

plot indicates an increase in uniform stacking when more than 40 mequiv. ethylenediamine Cu(II) is added/100 g of clay.

In Figure 3, which is a plot of  $d(001)$  spacing vs mequiv. of ethylenediamine Cu(II) added/100 g of clay for samples desiccated over calcium chloride, the  $d(001)$  spacing increases from 9.8 Å for 100% Na<sup>+</sup> montmorillonite to a value of 12.6 Å when 75 mequiv. ethylenediamine Cu(II) are added/100 g clay. The 9.8 Å basal spacing of the Na<sup>+</sup> clay indicates that good desiccation was obtained.

From a comparison of Figure 3 with Figure 4, which is a plot of a  $d(001)$  spacing vs mequiv. ethylenediamine Cu(II) added/100 g of clay for samples that were exposed to ethylene glycol, one can see that the  $d(001)$  spacing of Na<sup>+</sup> montmorillonite samples expanded from 9.8 Å for the fully desiccated clay to 16.8 Å for the ethylene glycol saturated clay. The clays with ethylenediamine Cu(II) added expanded less than the 16.8 Å  $d(001)$  spacing obtained for the Na<sup>+</sup> montmorillonite.

For example, the  $d(001)$  spacing of the 40 mequiv. ethylenediamine Cu(II)/100 g of clay samples expanded from 12 Å to 16.5 Å, and the  $d(001)$  spacings of the 120 mequiv. ethylenediamine Cu(II)/100 g of clay samples expanded from 12.6 Å to 13.4 Å. Thus, samples, with a small amount of ethylenediamine Cu(II) added, will adsorb ethylene glycol more readily than montmorillonite samples containing greater amounts of ethylenediamine Cu(II).

The clay samples were taken from the desiccator containing calcium chloride and placed directly in the desiccator containing ethylene glycol. Thus, they were dehydrated at the time they were placed in contact with the ethylene glycol. The samples with small amounts of ethylenediamine Cu(II) present were collapsed as shown by the  $d(001)$  spacings less than 12 Å (Figure 3) while those with greater than 75 mequiv. ethylenediamine Cu(II)/100 g of montmorillonite were still expanded as evidenced by  $d(001)$  spacings of

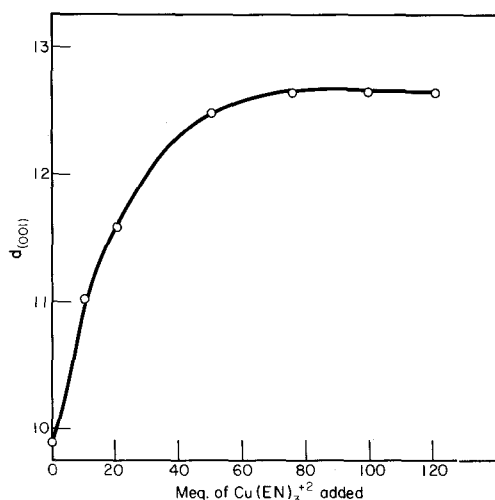


Figure 3. Plot of  $d(001)$  spacing vs the amount of ethylenediamine Cu(II) added for samples at 10% humidity.

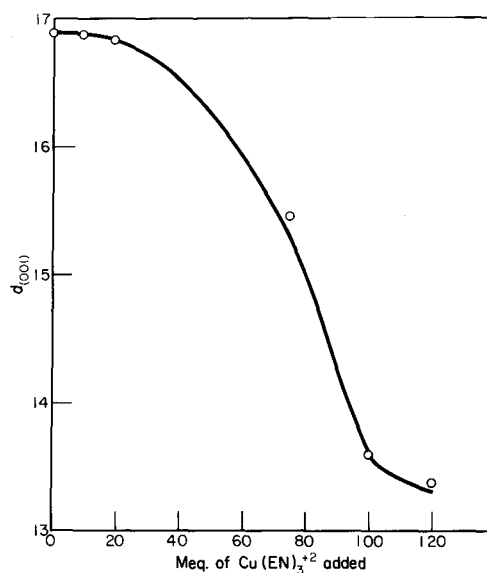


Figure 4. Plot of  $d(001)$  spacing vs amount of ethylenediamine Cu(II) added for samples exposed to ethylene glycol vapour for 48 hr at room temperature.

12.6 Å. Therefore, the ethylene glycol should be able to enter the expanded clay more readily than the collapsed or partially collapsed clay. Furthermore, Thielmann has shown, by adsorption of nitrogen gas on dehydrated clays, that ethylenediamine Cu(II) montmorillonite has a specific surface area of 246 m<sup>2</sup>/g, while the specific surface area of Na<sup>+</sup> montmorillonite is only 39 m<sup>2</sup>/g (Thielmann, 1974). Thus, the ethylenediamine Cu(II) montmorillonite has more available surface area for adsorption of ethylene glycol than Na<sup>+</sup> montmorillonite. One possible reason for the lack of expansion would be that the particles of the ethylenediamine Cu(II) clay are held together more tightly than those of the Na<sup>+</sup> clay. Also it was observed that after 30 days, the clay containing 100 mequiv. ethylenediamine Cu(II)/100 g of clay expanded appreciably to produce a broad peak at  $d(001)$  of 16 Å with a shoulder occurring at about 13 Å. Five peaks that correspond to (001) reflections were observed for the expanded clay.

X-ray powder diffraction patterns were obtained for samples of Cu(II) + ammonia added to montmorillonite, Cu(II) montmorillonite + ammonia, and 100 mequiv. ethylenediamine Cu(II) added/100 g of montmorillonite, after they were exposed to ethylene glycol for 48 hr while the ethylenediamine Cu(II) montmorillonite was exposed for 30 days. The Cu(II) montmorillonite sample readily expanded to 17.6 Å. The thickness of ethylene glycol is about 4 Å, and a double layer of glycol is about 8 Å thick. Taking the theoretical thickness of one clay plate to be 9.6 Å, the calculated  $d(001)$  spacing is 17.6 Å. Thus, when Cu(II) montmorillonite is exposed to ethylene glycol, it adsorbs a double layer of the glycol. The Cu(II) + ammonia montmorillonite complex expanded to a  $d(001)$  spacing of about 17.6 Å with a shoulder at 13 Å, and the Cu(II) montmorillonite with ammonia

added produced a diffraction pattern with two peaks that can be attributed to two different stacking arrangements, the first with a  $d$ -spacing of about 17 Å and a second of 13 Å.

The 100 mequiv. ethylenediamine Cu(II) montmorillonite sample also expanded to a  $d(001)$  spacing of 16 Å with a shoulder at 13 Å. As indicated above, the observed expansion required 30 days compared to 48 hr for the other Cu(II) montmorillonite samples that were examined.

The appearance of the shoulders on the  $d(001)$  peaks is an indication that there are areas where the  $d(001)$  spacing is about 13 Å and expanded areas whose basal spacings are 16 Å.

Fourier synthesis and Fourier transform calculations were done for  $\text{Cu}(\text{en})_3^{2+}$  montmorillonite before and after it was expanded with ethylene glycol, and plots of the Fourier transform functions are shown in Figures 5 and 6. In order to calculate the Fourier functions, it was necessary to calculate structure factor curves for montmorillonite considering no ethylene glycol and a double layer of ethylene glycol associated with clay.

The structure factor calculations consider the copper complex to be *bis* ethylenediamine Cu(II).

In the Fourier synthesis function of the ethylenediamine Cu(II) clay before it was exposed to ethylene glycol, three peaks are observed. The first two are clay peaks due to the aluminate and silicate layers, respectively. The third peak occurs at 0.5. This peak is due to material lying between the clay particles and indicates that the copper complex lies directly between the montmorillonite particles. The Fourier transform function in Figure 5 gives an indication of what basal spacings are combined to yield the observed  $d(001)$  spacing. The occurrence of the 13 Å peak and its 26 Å multiple is an indication that the stacking of the clay particles is very regular.

The Fourier synthesis function for 100 mequiv. ethylenediamine Cu(II)/100 g of clay after it was

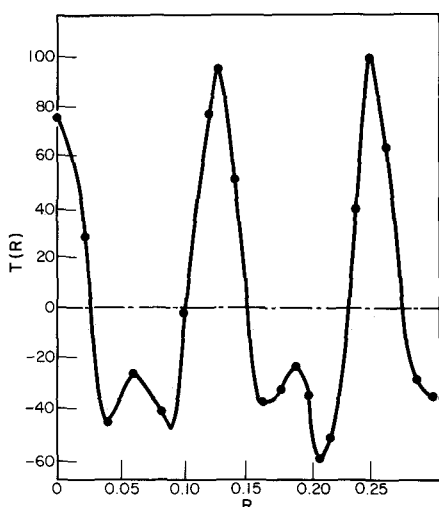


Figure 5. Fourier transform of 100 mequiv. ethylenediamine Cu(II) added/100 g of clay.

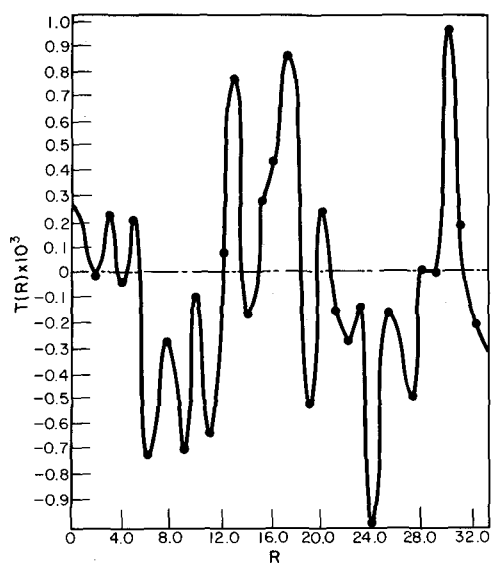


Figure 6. Fourier transform of 100 mequiv. ethylenediamine Cu(II) added/100 g of clay after exposure to ethylene glycol vapour for 30 days at room temperature.

exposed to ethylene glycol for 30 days shows peaks corresponding to the alumina and the silica layers of the montmorillonite particle along with a third peak which is due to ethylene glycol. Since the function is symmetric, this Fourier synthesis describes a clay system with two layers of ethylene glycol between the particles. The Fourier transform of the same montmorillonite, Figure 6, yields three peaks of significance occurring at 13 Å, 17 Å and 30 Å. The other peaks seen in the plot are satellite peaks and are products of the cosine series involved in the function. The plot indicates that there is a significant amount of 13 Å clay in the sample along with some 17 Å material which can be attributed to a double layer of ethylene glycol between the clay particles. The 30 Å peak is a combination of the 13 Å and 17 Å peaks. The presence of 13 Å material may be due to particles that are so strongly attracted to one another that the ethylene glycol cannot separate them.

#### Infrared analysis

Figure 7 is the infrared spectrum obtained for a sample of 40 mequiv. ethylenediamine Cu(II)/100 g of clay. In this spectrum, the two peaks at 3260 and 3340  $\text{cm}^{-1}$  superimposed on the water peak can be attributed to  $-\text{NH}_2$  symmetric and asymmetric stretching, respectively. The peaks at 2925 and 2959  $\text{cm}^{-1}$  are  $-\text{CH}_2$  symmetric and asymmetric stretching frequencies. The remaining peaks at 1600, 1480, 1420 and 1300  $\text{cm}^{-1}$  are due to scissoring, wagging, and twisting modes of  $-\text{NH}_2$  and  $-\text{CH}_2$ . These assignments are made on the basis of work done by Cloos on  $\text{Cu}(\text{en})_2^{2+}$  montmorillonite (Theng, 1974). These absorption bands are also very similar to those of  $\{\text{Cu}(\text{en})_2 \text{PtCl}_4\}$  (Theng, 1974).

The  $-\text{NH}_2$  groups in  $\text{Cu}(\text{en})_3^{2+}$  possess a  $C_s$  symmetry since they have one reflection plane, the plane

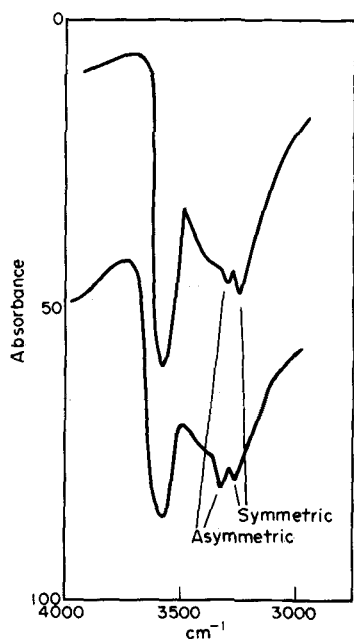


Figure 7. Infrared spectra of the  $-\text{NH}_2$  stretching region of 40 mequiv. ethylenediamine Cu(II) added/100 g of clay montmorillonite for two orientations:  $90^\circ$ , top; and  $40^\circ$ , bottom.

containing copper, carbon and nitrogen. The asymmetric stretching frequency is an  $A''$  interaction and should be polarized along the  $z$  axis which would be the Cu-N bond (Cotton, 1971).

Experimentally, as the angle of incidence between the infrared beam and the clay film is decreased (Figure 7) the  $-\text{NH}_2$  asymmetric stretching mode becomes more intense than the symmetric stretching frequency. This data suggests that decreasing the angle of incidence the clay film and the infrared beam is analogous to orienting the Cu-N bonds parallel to the infrared beam. For such an increase to occur, all of the Cu-N bonds must be coplanar and probably lie in a plane parallel to the clay surface. Thus, the complex ion is planar. The only planar Cu(II) ethylenediamine complex is the *bis* ethylenediamine Cu(II) which is square planar.

An increase in the intensity of the asymmetric  $-\text{NH}_2$  stretching frequency upon decreasing the angle between the incident infrared beam and the clay film was reported by Cloos. He also reported that his Cu(II) ethylenediamine complex ion was *bis* ethylenediamine Cu(II) which he concluded was oriented with the plane of the ion parallel to the clay surface.

#### Electron spin resonance analysis

An electron spin resonance spectrum was obtained for a sample of DPPH which has a  $g$  value of 2.0030 which is very close to the  $g$  value of a free spinning electron (Wertz, 1972). This sample was used to calibrate the magnetic field of the electron spin resonance unit. A film of 100% exchanged ethylenediamine Cu(II) montmorillonite was oriented perpendicular and parallel with respect to the magnetic field (Figure

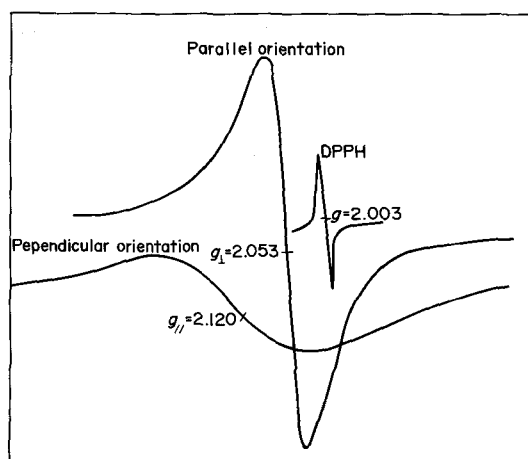


Figure 8. Electron spin resonance spectra of a DPPH standard. 100% exchanged ethylenediamine Cu(II) montmorillonite oriented parallel top, and perpendicular, bottom, to the flux of the magnetic field.

8). The sample was found to be anisotropic and the two  $g$  values obtained for parallel and perpendicular orientation were 2.053 and 2.120.

This data is similar to that reported by Clementz and Mortland who studied hydrated Cu(II) montmorillonite. They concluded that at a low degree of hydration the Cu(II) species is  $\text{Cu}(\text{OH}_2)_4^{2+}$  which is a square planar complex which is oriented with the plane containing the nitrogens lying parallel to the silicate surface. The  $d_{z^2}$  orbital is pointed toward the clay surface and is coordinated with the silicate oxygens (Clementz, 1973).

On the basis of X-ray powder diffraction and infrared analysis of montmorillonite with ethylenediamine Cu(II) added, the complex is considered to be  $\text{Cu}(\text{en})_2^{2+}$ . The copper atom in this ion has a site symmetry of  $D_{4h}$  and can be considered axially symmetric.

For tetragonally distorted  $d^9$  complexes with axial symmetry,  $g_{\parallel}$  is greater than  $g_{\perp}$ . This requires the ion to be oriented with its  $z$  axis, the  $d_{z^2}$  orbital, perpendicular to the clay surface (Wertz, 1972).

#### CONCLUSIONS

X-ray powder diffraction analysis indicates that the complex ion that is adsorbed from solution by montmorillonite *cannot* be *tris* ethylenediamine copper(II). This is consistent with the solution chemistry of *tris* ethylenediamine copper(II) since, according to Huheey, *tris* ethylenediamine copper(II) is very labile in water and dissociates to *bis* ethylenediamine copper(II) (Huheey, 1972).

Infrared analysis indicates that the complex ion is *bis* ethylenediamine copper(II) with the plane of the ion containing the four nitrogens lying parallel to the clay surface.

Electron spin resonance data suggests that the  $d_{z^2}$  orbital of the ion points toward the clay surface.

Adsorption of ethylene glycol and the  $d(001)$  spacing of  $\text{Cu}(\text{en})_2^{2+}$  montmorillonite indicates that  $\text{Cu}(\text{en})_2^{2+}$  bonds the clay particles together more

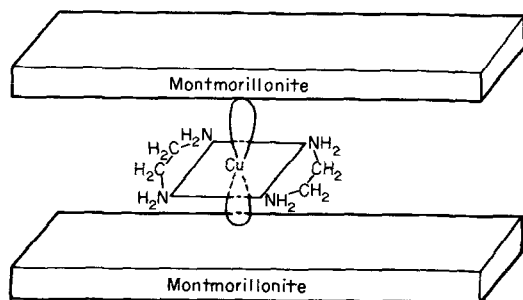


Figure 9. Proposed orientation of  $\text{Cu(en)}_2^{2+}$  between two montmorillonite particles.

tightly than would be expected from simple electrostatic interactions. The bond between the complex ion and the clay surface may be a partially covalent interaction with surface oxygens. The oxygens would coordinate with the  $d_{z^2}$  orbital of  $\text{Cu(en)}_2^{2+}$  (Figure 9).

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