SILYLATION OF SILICA GEL AND LAYERED SILICATES

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ABSTRACT

SILYLATION OF SILICA GEL AND
LAYERED SILICATES

By

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Coupling agents are ambifunctional silanes containing organic functionality attached to a silane via a hydrocarbon linkage. Their dual reactivity allows the inorganic silanol to react with silanols of a silaceous surface while the organic group is free to perform its designated function. Monolayers of γ-aminopropylsilanes are prepared by washing a treated silica surface containing multilayers of coupling agent with H_2O. Metal cations react with the functionalized surface and result in immobilized metals on the silica surface.

Immobilized Cu (II) on silica gel whose surface was treated with a monolayer of an aminofunctional silane was characterized by esr. Comparison of esr parameters of immobilized Cu (II) to those obtained with ethylenediamine (en) complexes of Cu (II) in a methanol glass showed copper (II) in different environments depending on the particular coupling agent employed. Cu (II) immobilized on silica that had been functionalized with

γ-aminopropylsilyl was complexed by two nitrogen atoms. However, when copper (II) was immobilized on silica which had been treated with N-(β-amino-ethyl)-γ-aminopropylsily the central metal ion was chelated with four nitrogen atoms. Washing the latter complex with boiling water gave both Cu^{+2} (en) and Cu^{+2} $(en)_2$ on the surface. Comparison of esr spectra at 300°K and 77°K showed little change occurred, and spectra at both temperatures showed Cu (II) on amino functional silica gel with distinct $g_{||}$ and $g_{\perp}$ components. This indicates the copper was not free to tumble or translate along the surface. This was not observed when Cu (II) was adsorbed on nonfunctional silica gel.

Quaternary ammonium forms of layered silicates (montmorillonite and hectorite) were treated with N-(β-amino-ethyl)-γ-aminopropyltrimethoxysilane (Z-6020) and the copper complexes were characterized by esr. Analysis of Cu (II) on silylated Bu_4N+ saturated hectorite showed copper in an environment similar to that obtained on silica gel with four nitrogen atoms around the copper atom. Analysis of oriented films of the silylated clay/Cu (II) complexes by scanning electron microprobe showed silylation occurred on the edge of the layered silicate crystal.

SILYLATION OF SILICA GEL AND LAYERED SILICATES

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A THESIS

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DEDICATION

To my family

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I wish to thank Dow Corning Corporation, my many friends and coworkers, and Dr. Thomas J. Pinnavaia for their help and support during the course of this work.

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I. INTRODUCTION

Coupling agents are ambifunctional silanes usually of the formula $RSi(OMe)_3$, where R is an organic radical attached to silicon by a hydrolytically stable silicon-carbon bond. Reactive groups such as $-NH_2$, $-NHCH_2CH_2NH_2$, -SH, $-CH\overset{O}{\diagdown}CH_2$ or Cl are usually part of the organic radical. Hydrolysis of the coupling agent gives a silane triol which can condense to oligomers that contain both silanol and organic reactivity as shown below.

$$RSi(OMe)_3 + H_2O \rightarrow HO(R\overset{|}{\underset{|}{Si}}O)_xH + MeOH$$

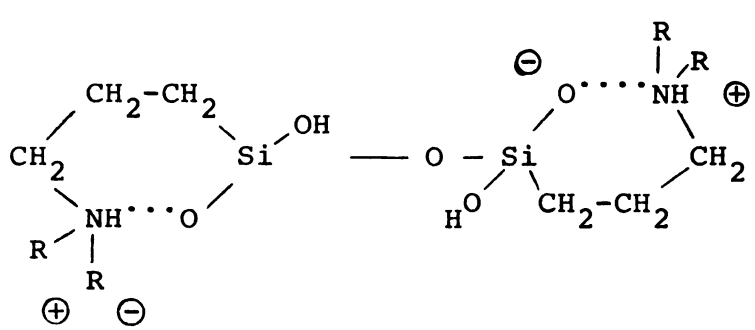
Because of this dual reactivity, coupling agents have been used to increase adhesion between inorganic oxides and plastics, immobilize metals on silica gel, and numerous other applications.[1]

The oligomers formed from coupling agents readily adsorb on oxide surfaces from aqueous solution. Deposits of the coupling agents vary in thickness depending on the solution concentration during application, on the conditions which are employed to deposit the coupling agent, and the nature of the oxide surface. Water desorption studies of ^{14}C labeled γ-aminopropyltriethoxysilane from glass

surface indicate three types of layers are present.[2] The first type consisted of 270 monolayers obtained from the initial deposition. This thick surface coating could be reduced to 10 monolayers after 3-4 hrs of washing at room temperature. Additional washing at 100°C showed the adsorbed silane on the surface as a monolayer.[2]

Adsorption of coupling agents in general on E-glass gave increased thickness as a function of solution concentration, however, a monolayer formed on silica gel regardless of the solution concentration of coupling agent.[3] These data suggest monolayers of coupling agents form on silica gel whereas multilayers are deposited on E-glass.

Stability of $RSi(OH)_3$ in aqueous solution is relatively independent of the substituent group on silicon except when the group is substituted at the γ-position. These latter silanes form more stable solutions, especially when an amine is three carbon atoms removed from silicon. This unique stability has been attributed to cyclicization of the dimer in aqueous solution as shown below.[1]



Silica gels and clays have been used as supports for heterogeneous catalysts and adsorbents for a variety of metals.[4-9] Catalytic activity of metals is greatly determined by its chemical environment, whether the metal ion is in homogeneous solution or immobilized on a solid support. Hectorite and montmorillonite are layered silicates which have exchangeable metal cations in the interlayer. Copper exchange forms of these clays and copper on silica gel have been characterized by electron spin resonance (esr),[5,7] which has provided fundamental information about the chemical environment of the cation. Treatment of silica gel or porous glass beads with aminofunctional coupling agent followed by complexation with a metal ion has been described as a method of concentrating cations and preparing catalysts.[8,9]

The purpose of the present study was to characterize immobilized copper cations and gain information about its chemical environment and the nature of the silylation reaction. Copper which was immobilized on silica and clays by N-(β-amino-ethyl)-γ-aminopropyltrimethoxysilane (Z-6020) and γ-aminopropyltriethoxysilane (A-1100) was characterized by electron spin resonance spectroscopy and electron microprobe analysis.

II. DISCUSSION OF RESULTS

A. Copper Amine Complexes in Methanol

A solution of 3 X 10^{-3} M methanolic $CuCl_2 \cdot 2H_2O$ and its complexes of ethylene diamine (en) or N-(β-amino-ethyl)-γ-aminopropyltrimethoxysilane (Z6020) at various molar ratios were analyzed by esr to obtain g values and coupling constants. These data are summarized in Table 1. Copper at these dilutions should not interact with the magnetic dipoles of electronic and nuclear spins of neighboring copper atoms. Since the esr spectra were obtained in a methanol glass at 77°K, exchange interaction with neighboring unpaired electrons and tumbling should be minimal. These factors should minimize line broadening.

In each case the $g_{||}$ component is resolved into four components which is characteristic of tetragonal Cu (II) with a nuclear spin of 3/2. However, hyperfine splitting of the $g_{\perp}$ component or super hyperfine splitting by N is not observed.

As can be seen in Figure 1, at a molar ratio of 0.5 en/Cu (II) at least two $g_{||}$ components are observed. These are attributed to uncomplexed copper ($g_{||}$ = 2.40, A = 0.0112 cm^{-1}) and copper complexed by one en molecule

Table 1.--Esr parameters at 77°K for Cu^{+2} complexes of amines in methanol glass.

		$H_o^{\parallel}$ GAUSS	$g_{\parallel}$	$A \times 10^4$ cm^{-1}	$H_o^{\perp}$ GAUSS	$g_{\perp}$	$\Delta H_{\perp}$ GAUSS	g_{ave}
	mol/mol							
A.	en/Cu (II)							
	1. 0.5	2905	2.27	159	3200	2.06	130	2.13
		2750	2.40	112	3170	2.08	60	2.19
	2. 1.0	2915	2.26	164	3210	2.05	85	2.12
	3. 2.0	3015	2.19	187	3240	2.03	155	2.08
	4. 4.0	3010	2.19	187	3245	2.03	160	2.08
	5. 10.0	3010	2.19	187	3245	2.03	160	2.08
	mol/mol							
B.	Z6020/Cu (II)							
	6. 0.5	2750	2.40	112	3160	2.09	50	2.19
		2960	2.23	159	3210	2.05	130	2.11
	7. 1.0	2960	2.23	156	3250	2.06	120	2.12
	8. 2.0	3008	2.19	184	3240	2.03	155	2.08
C.	Cu (II) Blank							
	9. MeOH soln.	2755	2.39	112	3160	2.09	50	2.18
		2784	2.37	111	3145	2.10	30	2.19

en = $NH_2CH_2CH_2NH_2$ Z6020 = $(MeO)_3 Si CH_2CH_2CH_2NHCH_2CH_2NH_2$

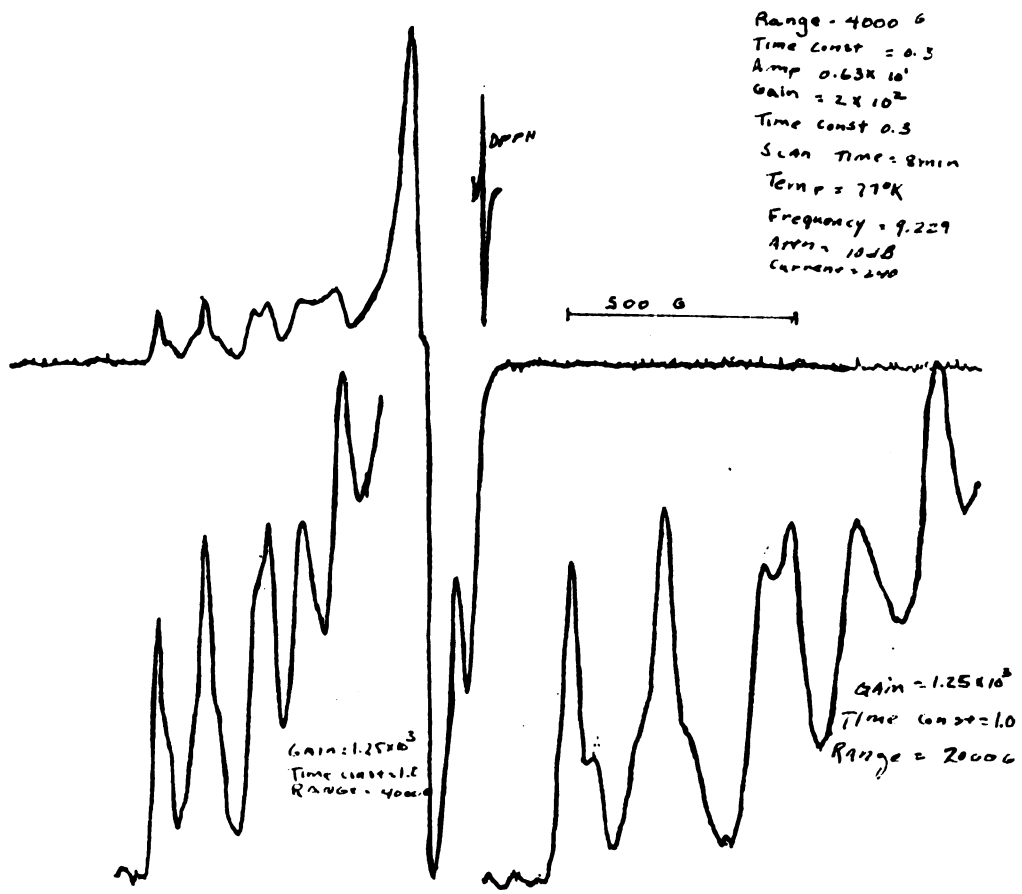


Fig. 1.--Esr spectrum at 77°K for a 0.5:1.0 molar ratio of $H_2NCH_2CH_2NH_2$ and $CuCl_2 \cdot 2H_2O$ in a methanol glass.

($g_{||}$ = 2.27 and A = 0.0159 cm^{-1}). Stability constants for the following equilibria are large.

$$Cu^{+2} + en \rightleftharpoons Cu^{+2} \cdot en \qquad K_1 \simeq 10^{11}$$

$$Cu^{+2} \cdot en + en \rightleftharpoons Cu^{+2} \cdot 2en \qquad K_2 \simeq 10^{9}$$

Since $K_1 >> K_2$, the complexation takes place in a stepwise fashion. The assignment of the $g_{||}$ component = 2.27 to a 1:1 Cu^{+2}:en complex is verified by the presence of a single $g_{||}$ resonance (2.26) at a ligand to Cu^{+2} ratio of 1.0. At en:$Cu^{+2} \geq$ 2:1 a single $g_{||}$ value of 2.19 and A = 0.0187 cm^{-1} is observed. This resonance is characteristic of the Cu $(en)_2^{+2}$ complex as shown in Figures 2-5.

Analysis of N-(β-amino-ethyl)-γ-aminopropyltrimethyoxysilane copper (II) complexes by esr in a methanol glass gave $g_{||}$ and A values that were almost identical with those observed for the en Cu^{+2} complex as shown in Figures 6-9.

The value for the 1:1 complex are $g_{||}$ = 2.23, A = 0.156 cm^{-1}. The 2:1 complex gave $g_{||}$ = 2.19, A = 0.0184 cm^{-1}. These results show that both the coupling agent and en behave in a similar manner in forming Cu^{+2} amine complexes. A slight difference was noticed at a molar ratio of 1.0 in $g_{||}$, A, and $\Delta H_{\perp}$. This might indicate a slight difference in the 1:1 complex, however the evidence strongly suggests the complex is primarily Cu^{II}.

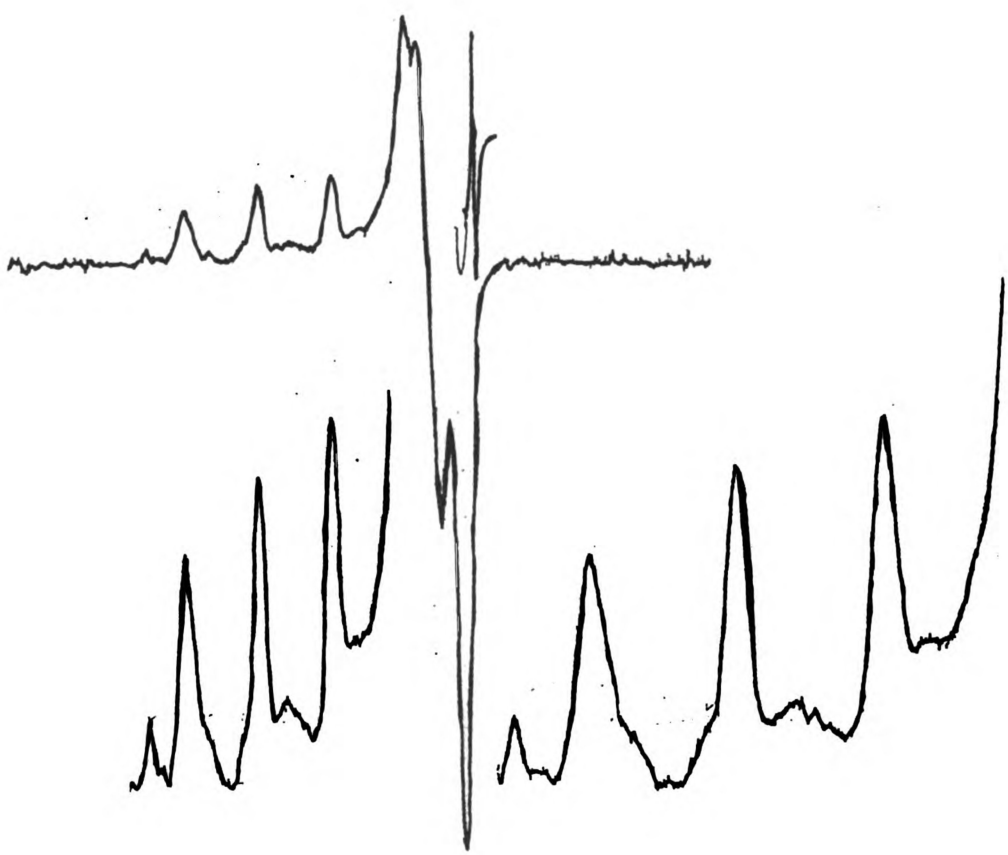


Fig. 2.--Esr spectrum at 77°K for a 1.0:1.0 molar ratio of $H_2NCH_2CH_2NH_2$ and $CuCl_2 \cdot 2H_2O$ in a methanol glass.

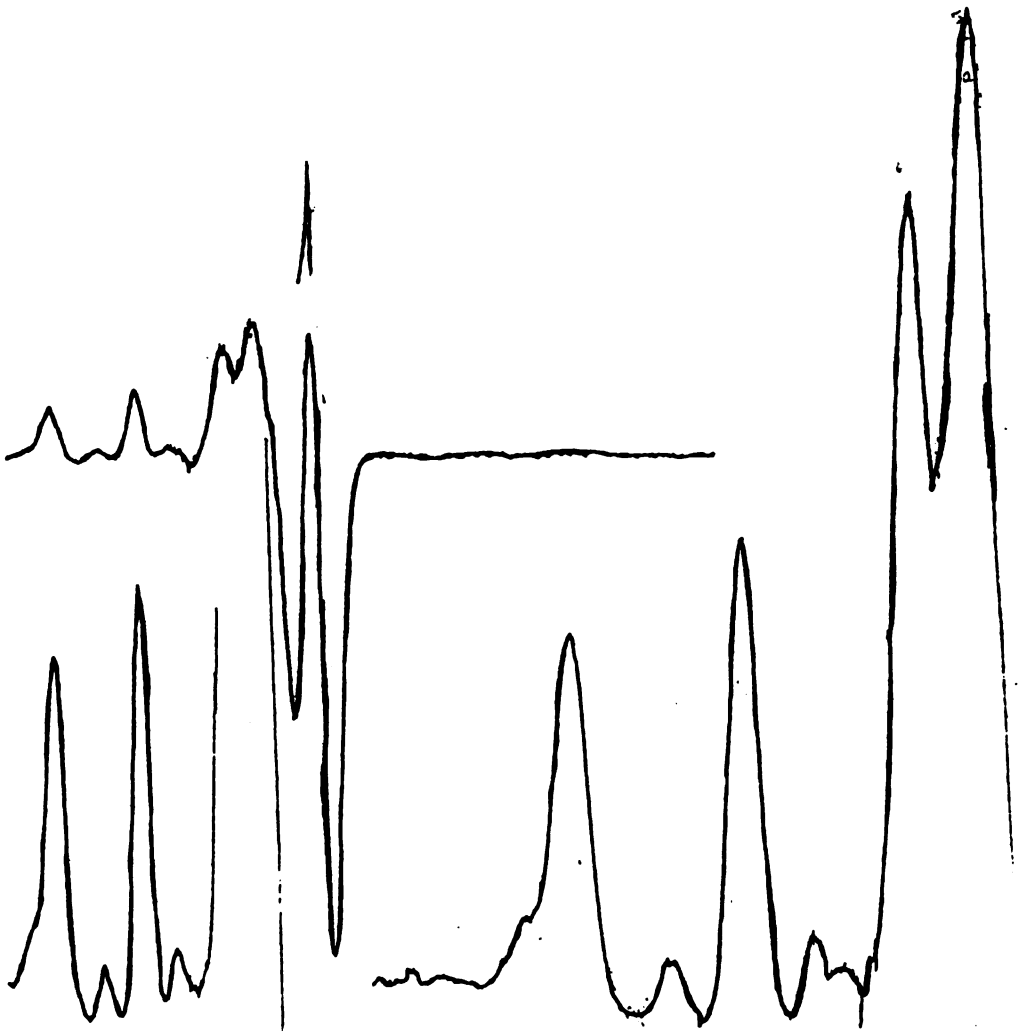


Fig. 3.--Esr spectrum at 77°K for a 2.0:1.0 molar ratio of $H_2NCH_2CH_2NH_2$ and $CuCl_2 \cdot 2H_2O$ in a methanol glass.

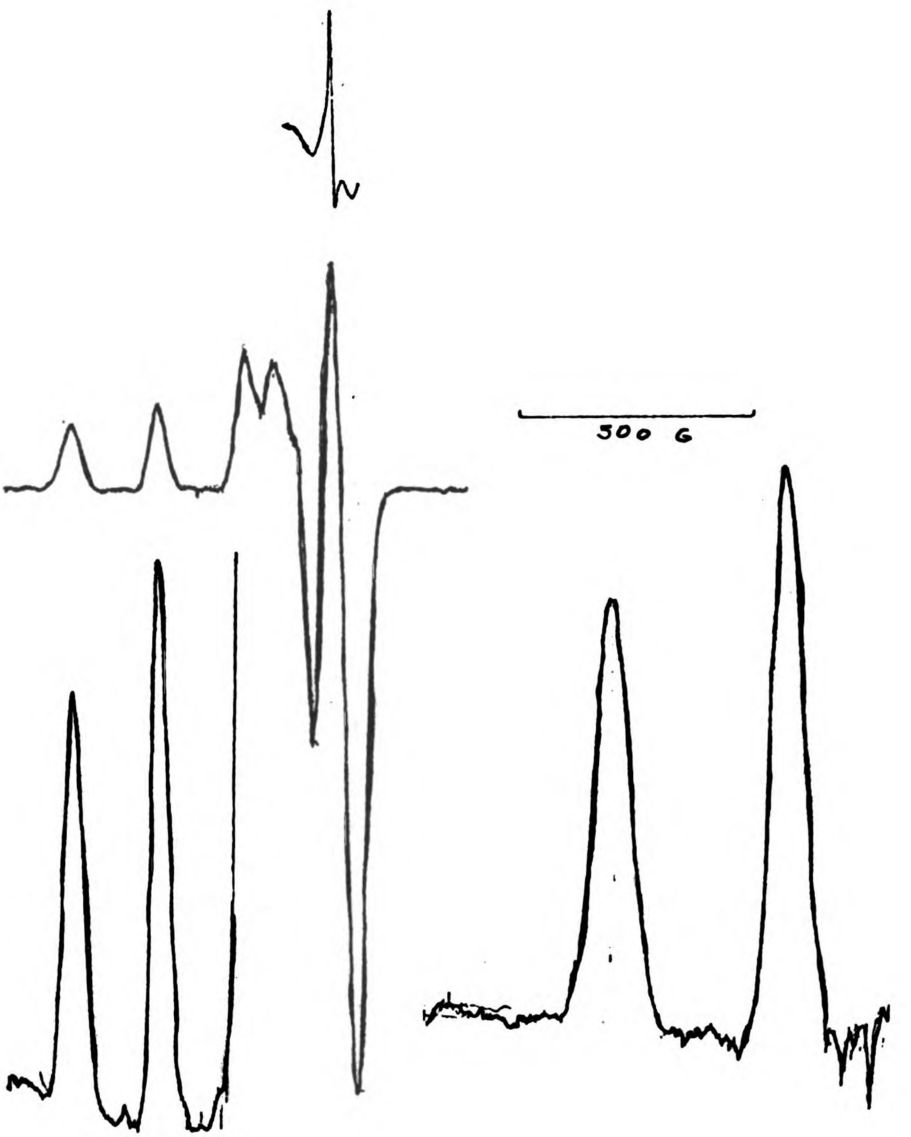


Fig. 4.--Esr spectrum at 77°K for a 4.0:1.0 molar ratio of $H_2NCH_2CH_2NH_2$ and $CuCl_2 \cdot 2H_2O$ in a methanol glass.

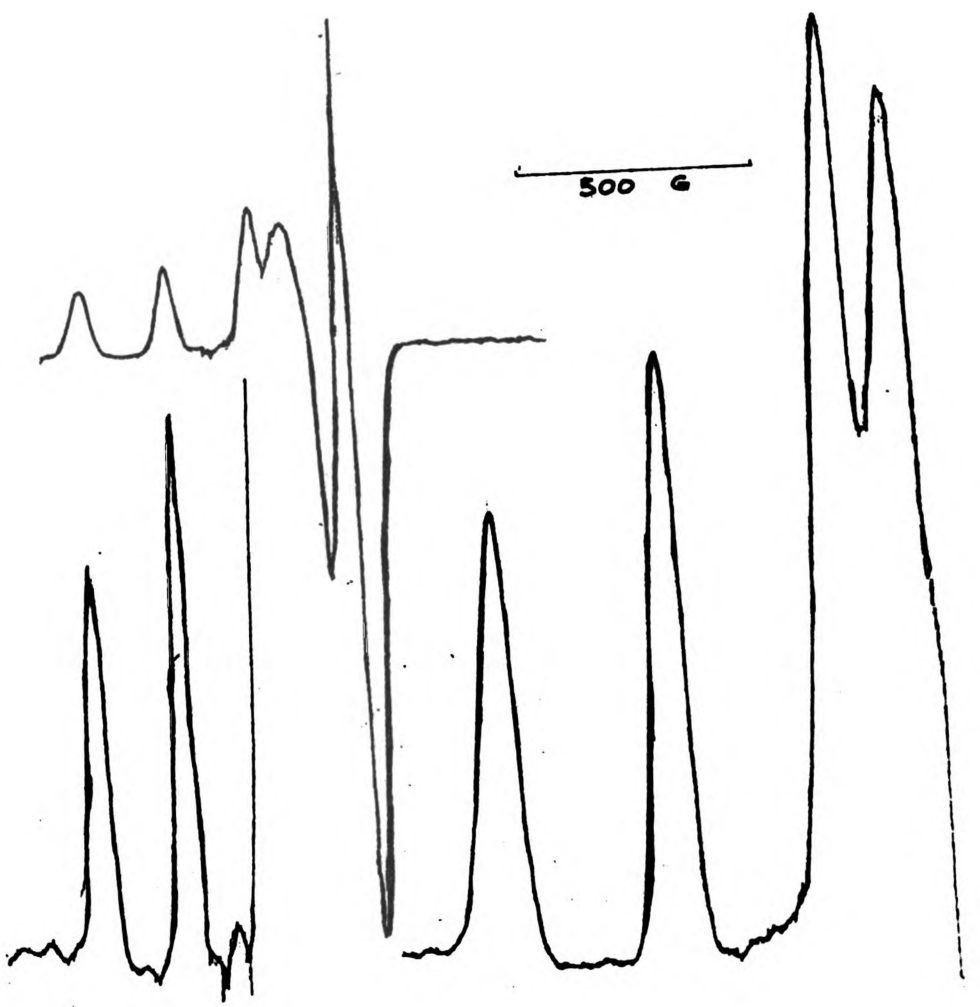


Fig. 5.--Esr spectrum at 77°K for a 10.0:1 molar ratio of $H_2NCH_2CH_2NH_2$ and $CuCl_2 \cdot 2H_2O$ in a methanol glass.

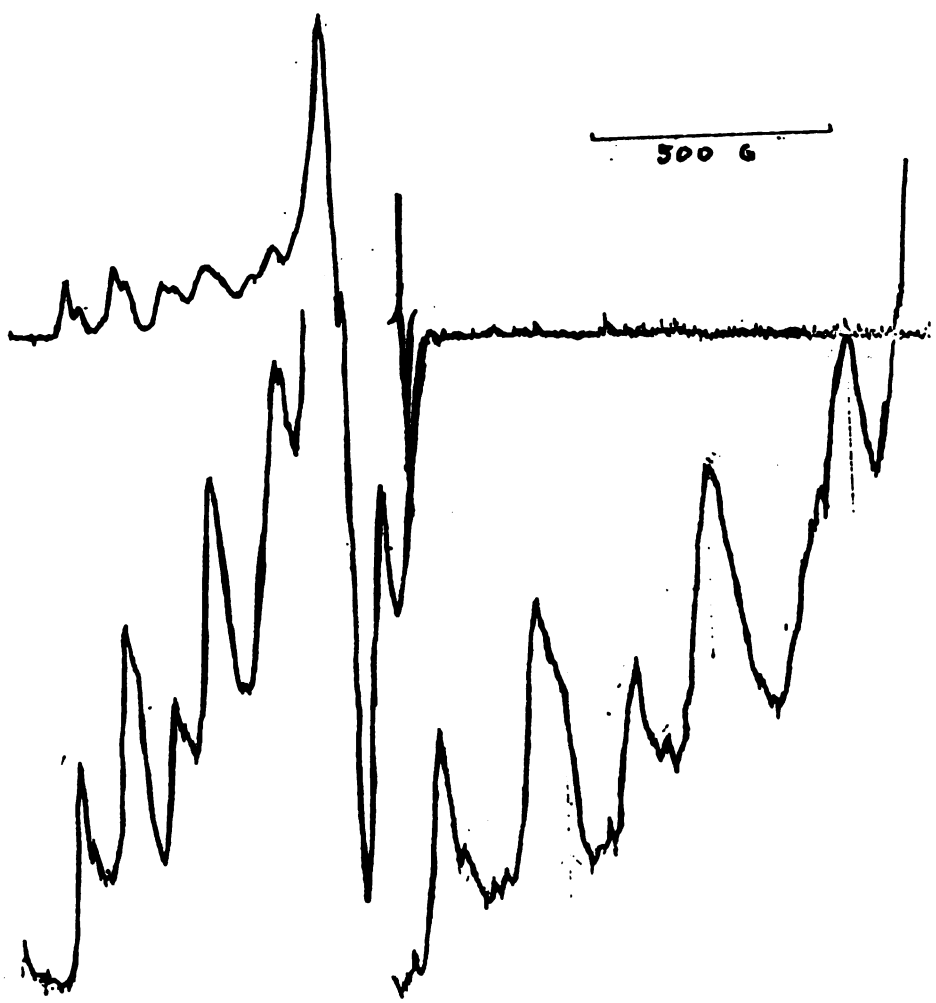


Fig. 6.--Esr spectrum at 77°K for a 0.5:1 molar ratio of $(MeO)_3Si\ CH_2CH_2CH_2NHCH_2CH_2NH_2$ and $CuCl_2 \cdot 2H_2O$ in a methanol glass.

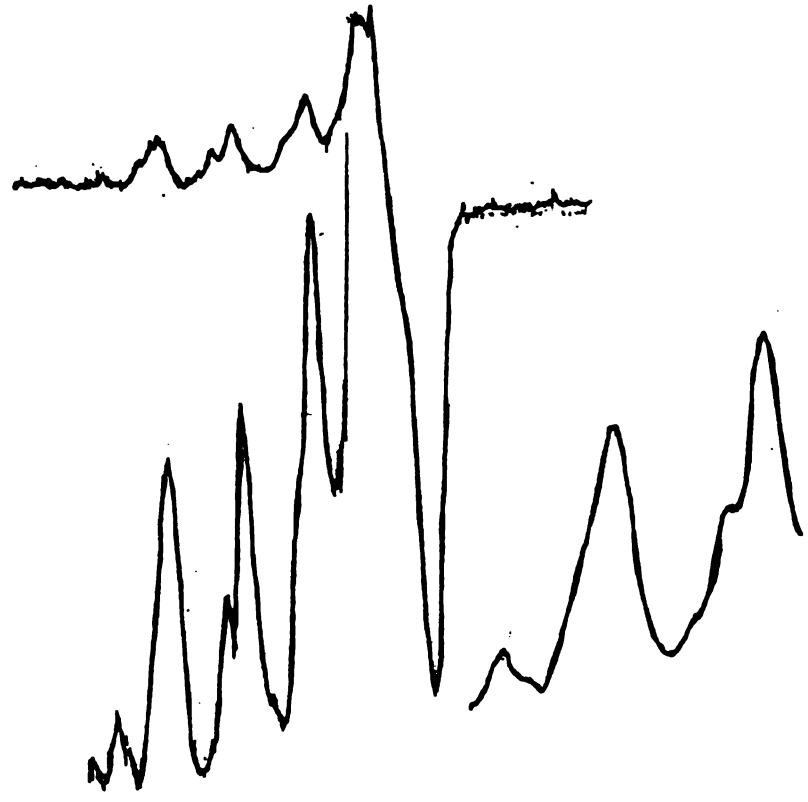


Fig. 7.--Esr spectrum at 77°K for a 1.0:1.0 molar ratio of $(MeO)_3Si\ CH_2CH_2CH_2NHCH_2CH_2NH_2$ and $CuCl_2 \cdot 2H_2O$ in a methanol glass.

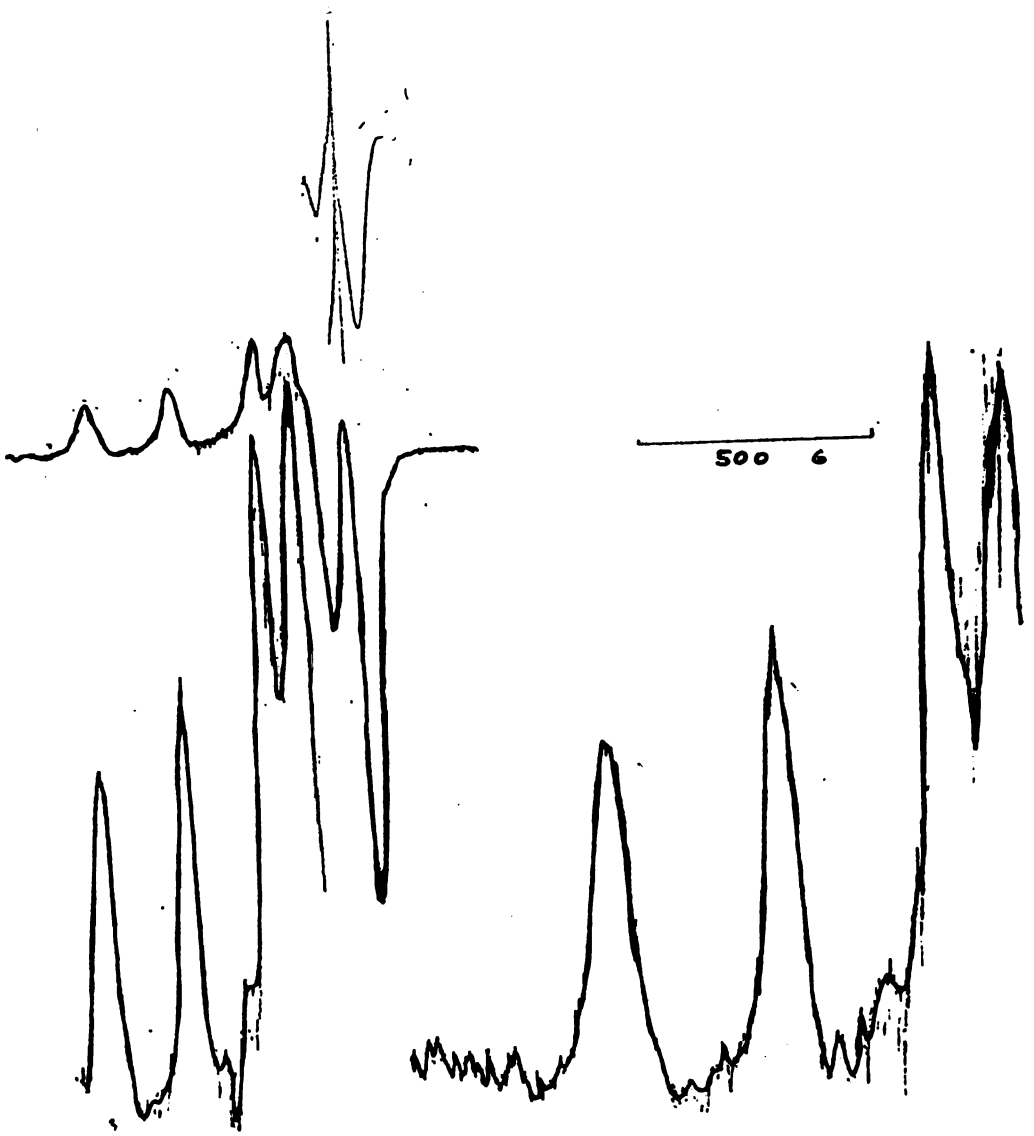


Fig. 8.--Esr spectrum at 77°K for a 2.0:1.0 molar ratio of $(MeO)_3Si\ CH_2CH_2CH_2NHCH_2CH_2NH_2$ and $CuCl_2 \cdot 2H_2O$ in a methanol glass.

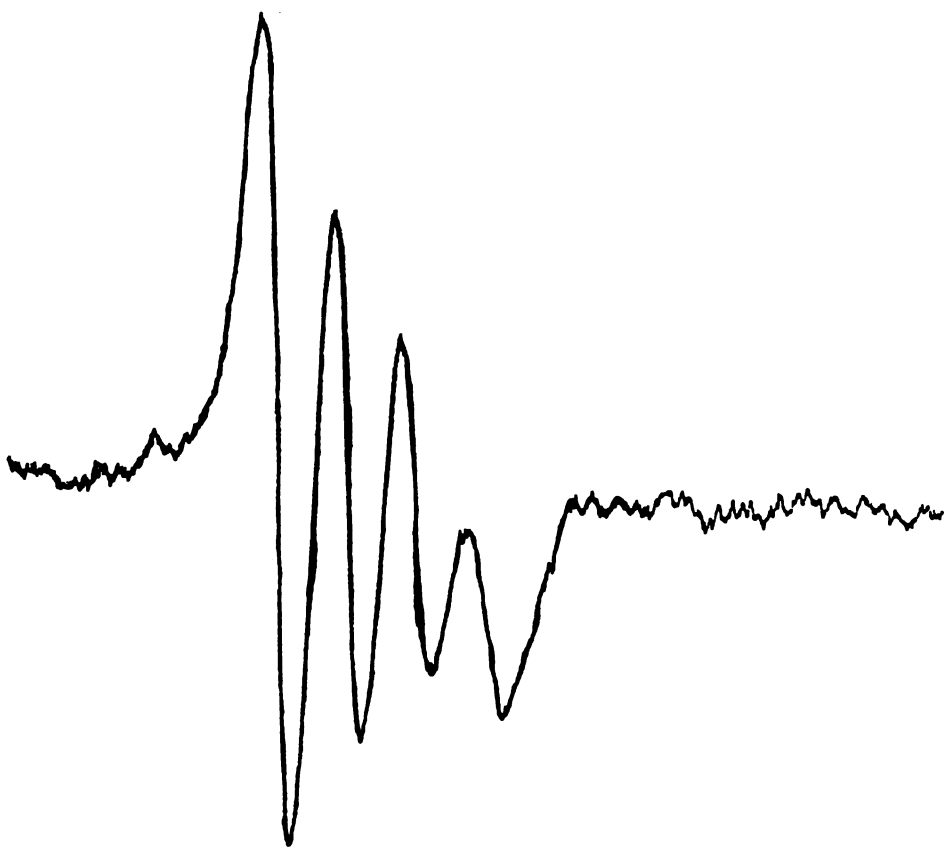


Fig. 9.--Esr spectrum at 300°K for a 2.0:1.0 molar ratio of $(MeO)_3Si\ CH_2CH_2CH_2NHCH_2CH_2NH_2$ and $CuCl_2 \cdot 2H_2O$ in methanol.

Z6020. These data show that both the Z6020 and en behave in a similar manner toward Cu (II).

Analysis of copper chloride in a methanol glass by esr shows two different forms of copper are present. The coupling constants vary only slightly for the parallel component, but the different $g_{||}$ values of nonequivalent copper ions are well resolved. A possible explanation for different forms of copper would be the presence of both $Cu^{II} \cdot 2H_2O$ and $Cu^{II} \cdot H_2O \cdot MeOH$. The latter form of copper would result from displacement of water of hydration by the solvent. Alternatively the following equilibrium could account for the spectrum observed in Figure 10.

$$Cu^{+2} + 2Cl^- \leftrightarrows CuCl^+ + Cl^- \leftrightarrows CuCl_2$$

B. Copper Immobilized on Silica Gel

Silica gel was treated with a 5% aqueous solution of aminoalkylsilane and washed with boiling water to obtain a monolayer of silane. The resulting aminofunctional silica gels and an untreated silica gel were mixed with 1 M $CuCl_2$ and washed exhaustively with distilled water to rid the silica gel of any free $CuCl_2$. Analysis of the silica gels by esr are summarized in Table 2 and Figures 11-14. Comparison of Cu (II) immobilized on a silica surface with the Cu (II) amine complexes immobilized in a methanol glass at 77°K shows distinct amine complexes are formed on the silica surface. The environment of the

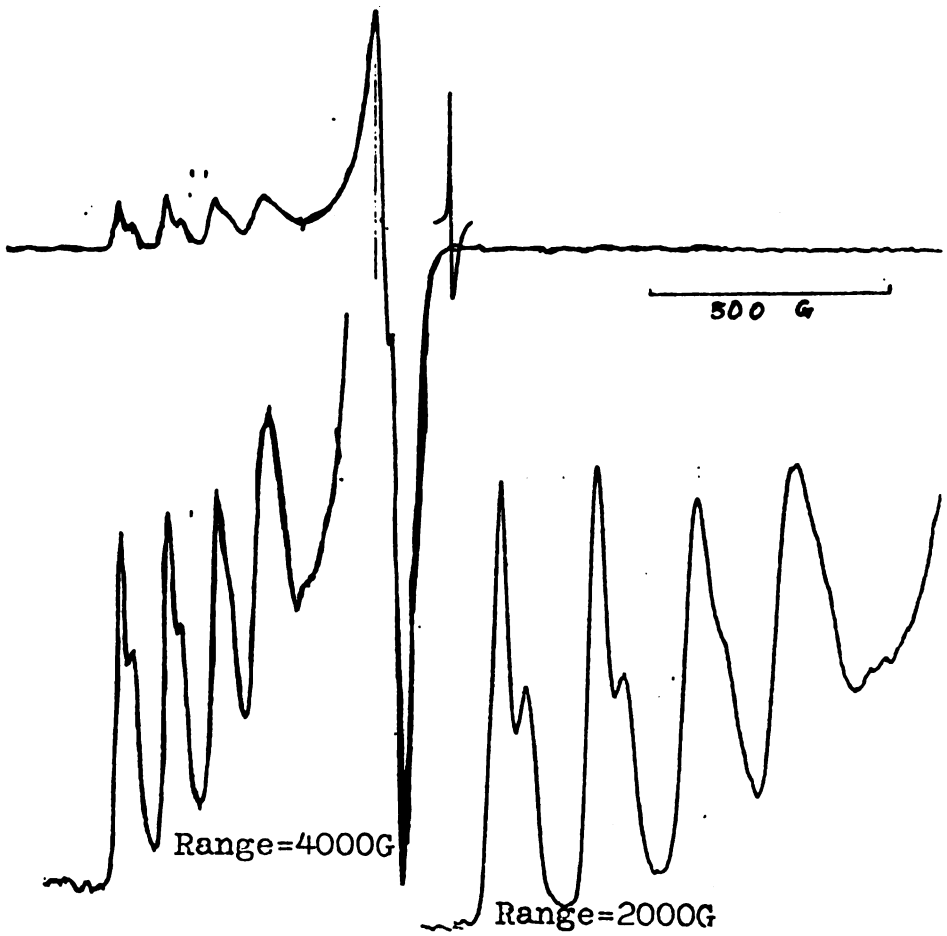
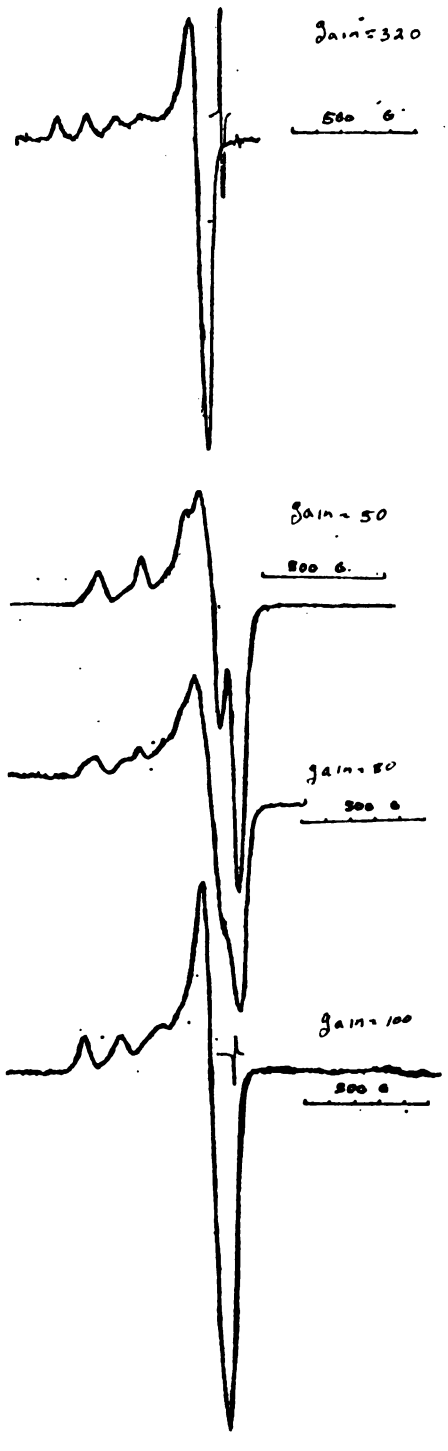


Fig. 10.--Esr spectrum at 77°K for a 3 x 10^{-3} M $CuCl_2 \cdot 2H_2O$ in a methanol glass.

Table 2.--Esr parameters for Cu^{+2} immobilized on silica gel and a layered silicate.

SAMPLE	$H_o^{\parallel}$ GAUSS	$g_{\parallel}$	$Ax10^4$ cm^{-1}	$H_o^{\perp}$ GAUSS	$g_{\perp}$	$\Delta H_{\perp}$ GAUSS	Temp °K	g_{ave}
1. Cu (II) on Silica Gel	2797	2.36	138	3182	2.07	50	77	2.17
2. Cu (II)-Z6020 on Silica Gel H_2O Wash at 25°C	3040	2.17	182	3270	2.02	170	77	2.07
3. Cu (II)-*Z6020 on Silica Gel	3005	2.19	194	3245	2.03	160	77	2.08
	2960	2.23	179					2.10
"	3090	2.19	189	3325	2.04	150	300	2.09
"	3015	2.24	173					2.11
4. Cu (II)-**A1100 on Silica Gel	2935	2.25	173	3250	2.03	105	77	2.10
	2986	2.27	167	3300	2.05	110	300	2.12
5. Cu (II)-*Z6020 on the BuN+ form of Hectorite Washed at 25°C	3027	2.18	195	3222	2.05	190	77	2.09

*Z6020 = $(MeO)_3$ Si $CH_2CH_2CH_2NHCH_2CH_2NH_2$ **A1100 = $(Eto)_3$ Si $CH_2CH_2CH_2NH_2$



A. Silica gel alone. Water washed at 100°C.

B. Silica gel treated with Z-6020 and the Cu(II) complex water washed at 25°C.

C. Same as B except washed at 100°C.

D. Silica gel treated with A-1100 and the Cu(II) complex water washed at 100°C.

Fig. 11.--First derivative esr spectra of Cu^{+2} on silica gel at 77°K.

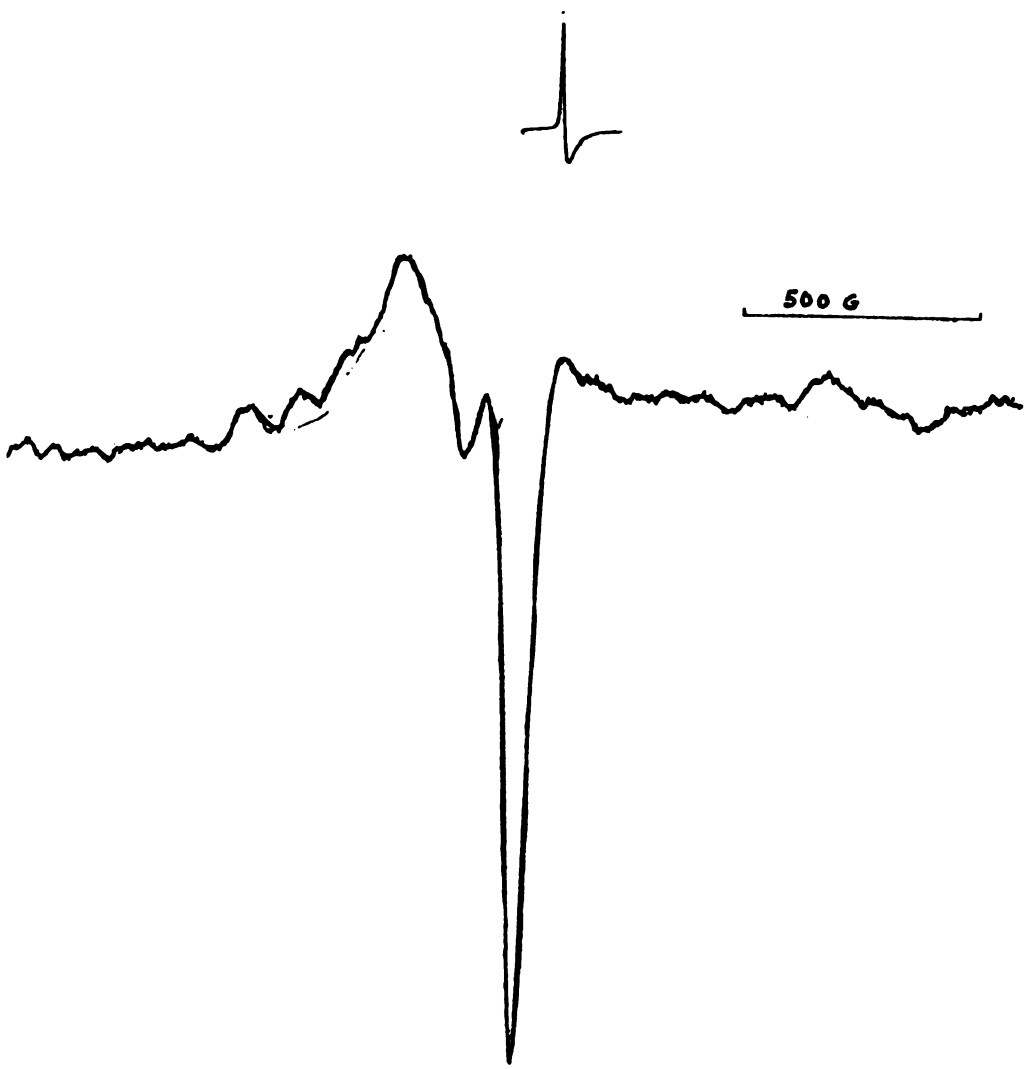


Fig. 12.--First derivative esr spectra of Cu^{+2} on untreated silica gel at 300°K.

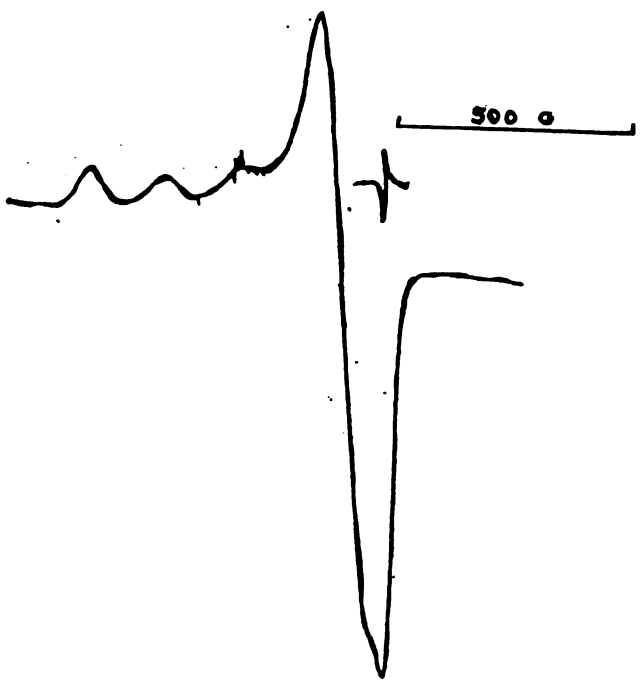


Fig. 13.--First derivative esr spectra at 300°K of Cu^{+2} on silica gel treated with A-1100.

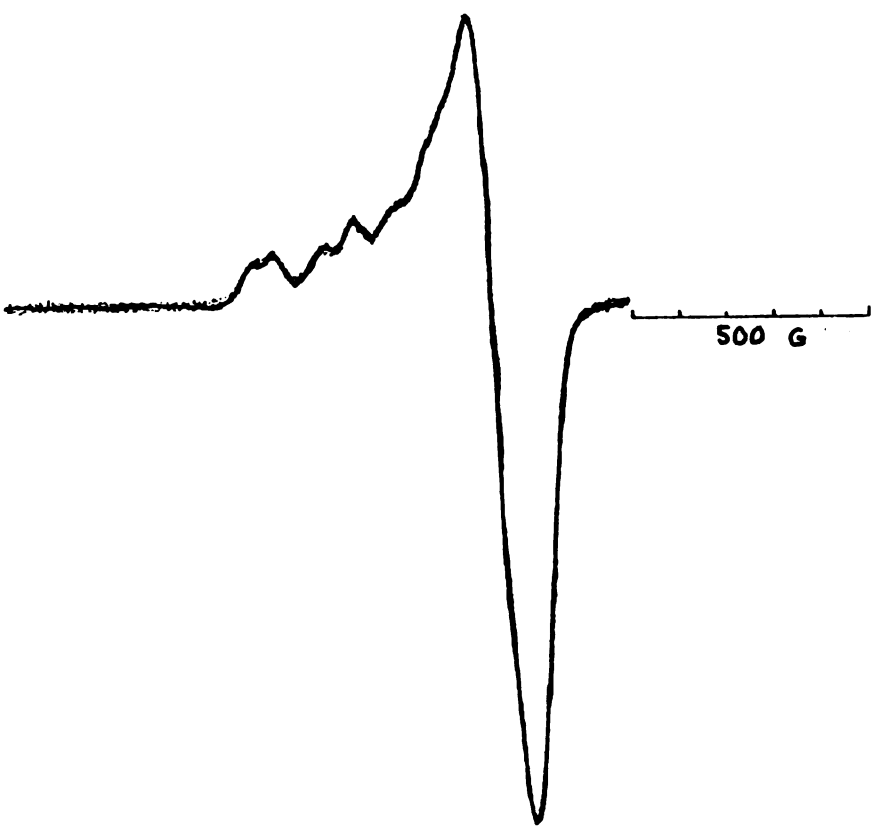


Fig. 14.--First derivative esr spectra at 300°K of Cu^{+2} on silica gel treated with Z6020 and washed with H_2O at 100°C after complexation.

copper depends on the silylating agent used and the conditions of complexation.

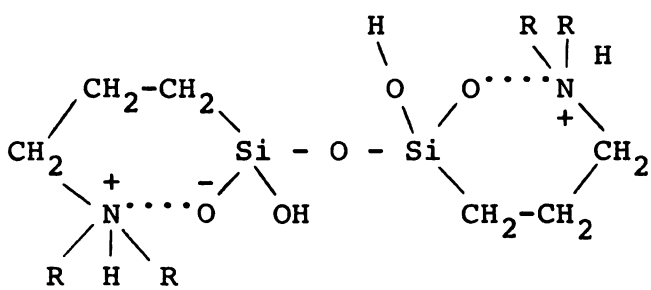
Without any coupling agent present the g_{11} component of Cu^{+2} at 77°K is resolved into a quartet with a value close to that of $CuCl_2 \cdot 2H_2O$ in a methanol glass. Comparison of Figure 11A with Figure 12 shows that a poorly resolved g_{11} component is observed at 300°K, where a quarter was observed at 77°K. This indicates that although Cu (II) is not removed by the washing technique, it is able to spin and/or slowly tumble on the silica surface at 300°K.

Copper immobilized with N-(β-amino-ethyl)-γ-aminopropyltrimethoxysilane on silica gave esr parameters which show the copper is immobilized as bis (N-β-amino-ethyl-γ-aminopropylsilyl) complex surrounded by four nitrogen atoms. Analysis of the immobilized Cu (II) at 300°K shows little change in the esr spectra from 77°K. Although the lines have broadened slightly, the g_{11} component is clearly observed.

When the copper complexed with bis (N-β-amino-ethyl-γ-aminopropylsilyl) treated silica surface is washed at 100°C a change is observed in the esr spectrum. Interpretation of the spectrum obtained at 77°K showed copper in two different forms, the original form and copper surrounded by two nitrogen atoms. Values of g_{11} for the new form of copper agree with the one to one complex between

Cu^{II} and N-(β-amino-ethyl)-γ-aminopropyltrimethoxysilane. Analysis of the sample at 300°K showed little change in the esr spectrum indicating the Cu^{II} was not free to tumble. It appears that the water wash in the presence of Cu^{+2} at 100°C caused desorption of the coupling agent.

The same treatment of silica gel with γ-aminopropyltriethoxysilane gave Cu (II) which was complexed by bis (γ-aminopropylsilyl) groups. Analysis at both 77°K and 300°K gave esr parameters which show the copper complexed with two nitrogen atoms and restricted mobility at 300°K ($g_{||}$ = 2.27, A = 0.0167 cm^{-1}). The esr parameters are consistent with axial symmetry. Smaller $g_{||}$ values and larger values of A relative to Cu (II) in a methanol glass are indicative of increased covalency of the amine complexes. Predominately bis (alkylammoniumsilyl) complexes with γ-aminopropylsilyl and N-(β-amino-ethyl)-γ-aminopropylsilyl on silica gel support the proposed dimeric structure of γ-aminopropylsilane in aqueous solution.



C. Copper on Clays

Layered silicate minerals known as smectites have a layered structure which is shown in Figure 15. An octahedral layer is positioned between two tetrahedral silica sheets and a negative charge originates from a positive charge deficiency in the octahedral layer. Cations, which balance the negative charge and occupy a layer between the silicate sheet, can be exchanged by treating an aqueous suspension of the silicate with an excess of another cation.[9] Hectorite and montmorillonite were fractionated by a sedimentation technique to give a fraction with a particle size <2μ. This fraction was isolated from suspension by centrifuging and freeze drying. Montmorillonite (Upton, Wyoming) and hectorite (Hector, California) were converted to the tetrapropylammonium form and tetrabutylammonium form respectively. Idealized unit cell formulas are given below:

Montmorillonite

$$(Pr_4N)_{0.64}[Al_{3.06}Fe_{0.32}Mg_{0.66}](Al_{0.10}Si_{7.90})O_{20}(OH)_4$$

Hectorite

$$(Bu_4N)_{0.42}[Mg_{5.42}Li_{0.68}Al_{0.02}](Si_{8.00})O_{20}(OH,F)_4$$

Both forms were silylated with N-(β-amino-ethyl-γ-aminopropyl)-trimethoxysilane (Z6020), washed at 25°C and a copper complex prepared. Analysis of the tetrapropylammonium form of montmorillonite gave broad signals

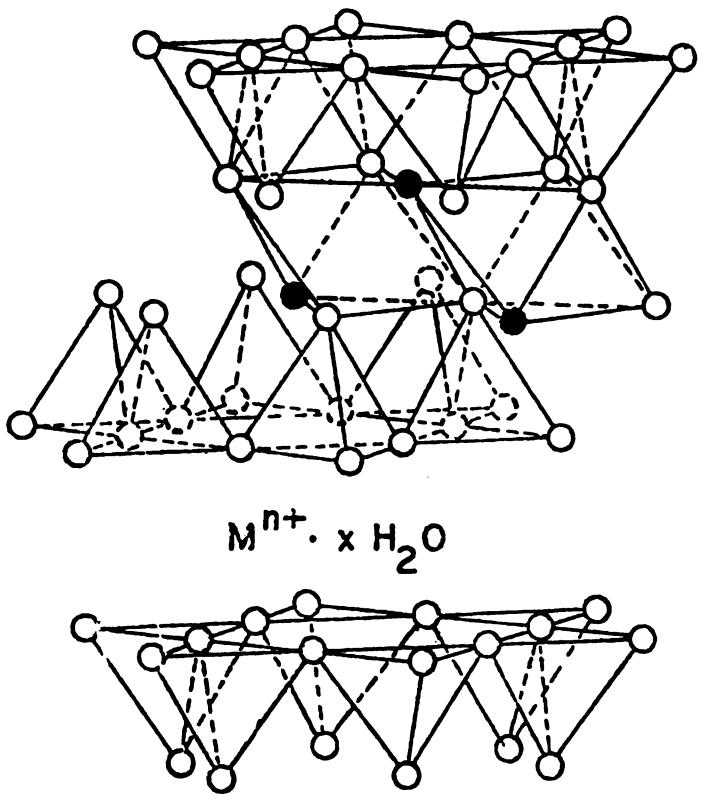
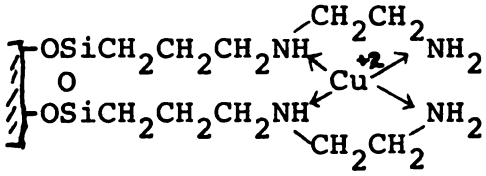
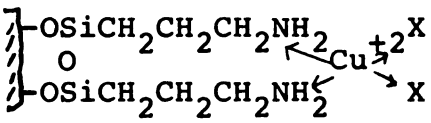


Fig. 15.--Oxygen (o) and hydroxyl (●) network of layered silicates. $M^{n+} \cdot x\ H_2O$ are the solvated interlayer exchange cations.

at both 300°K and 77°K. However, the hectorite sample gave an esr spectrum which was clearly resolved into a $g_{\parallel}$ and $g_{\perp}$ component (Figure 16) at both 77°K and 300°K. Significant amounts of iron are present in montmorillonite and probably cause line broadening by decreasing the relaxation time of the free electron of Cu (II) in the interlayer. The iron signal at g = 4.6 is much more intense in the esr spectrum of montmorillonite than in the hectorite sample. Esr parameters for Cu (II) immobilized on hectorite with N-(β-amino-ethyl)-γ-aminopropyltrimethoxysilane are almost the same as those given in Table 2 for silica gel. This suggests that copper is in a similar environment when immobilized on a microcrystalline silicate or an amorphous silica gel and is probably in an environment similar to that shown below.



Copper immobilized with N-β-amino-ethyl-γ-aminopropylsilyl



Copper immobilized with γ-aminopropylsilyl

Another property of the swelling clays is their ability to form oriented films when suspensions are allowed to evaporate. The covalent bonding theory of coupling agents requires the formation of a covalent bond between the metal oxide surface and the coupling agent.[1] The only

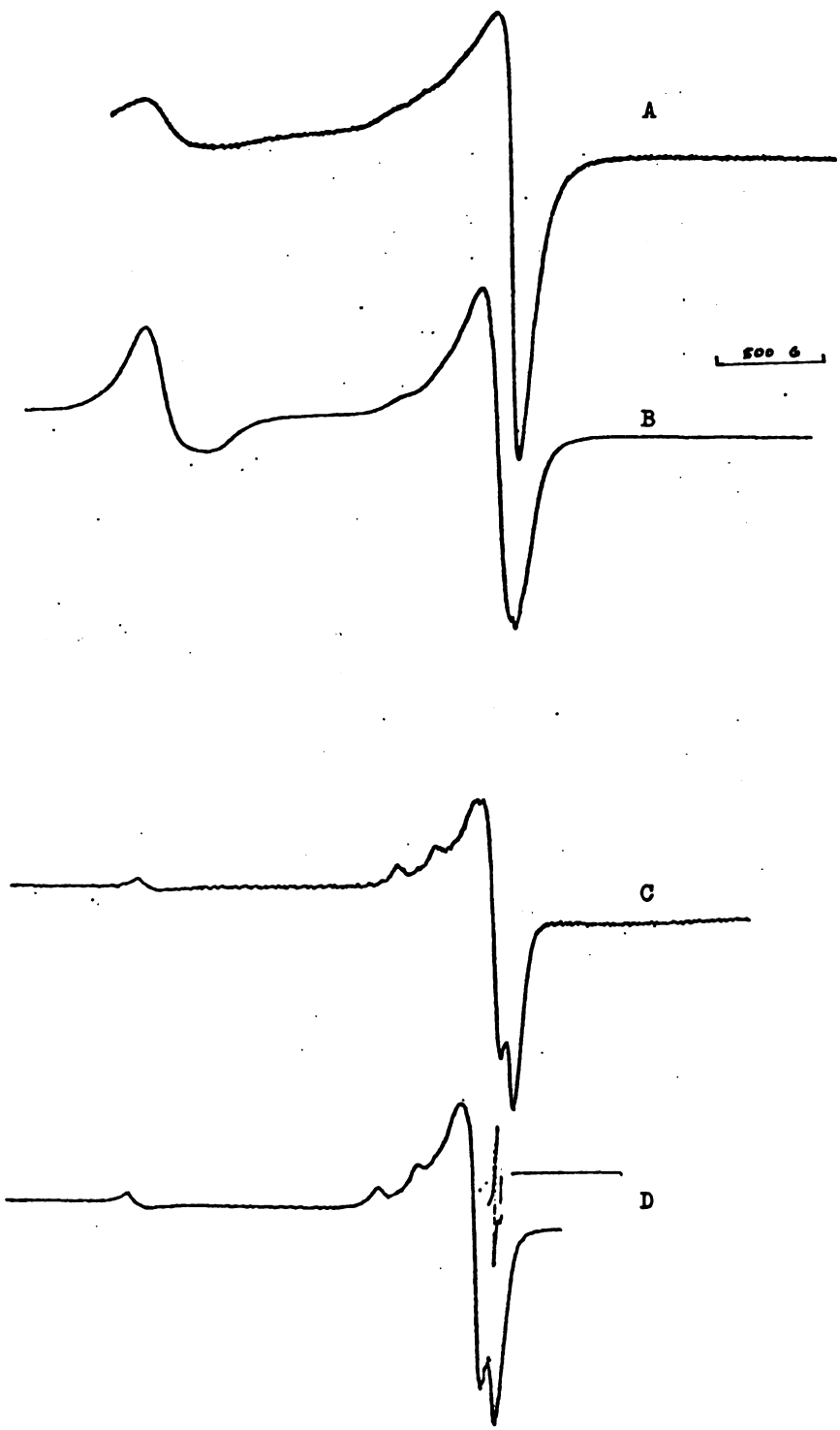


Fig. 16.--First derivative esr spectra for Cu (II) - Z6020 complex on Pr_4N^+ form of Montmorillonite at (A) 300°K and (B) 77°K and the same complex on BuN+ form of Hectorite at (C) 300°K and (D) 77°K.

accessible silanols present in the silicate sheet are located at the fractured edge of the silicate crystal, therefore, one would expect silylation to take place at the edge of the microcrystal. Oriented films of montmorillonite which had been silylated with N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane and treated with Cu (II) were fractured and analyzed for Cu on the surface and the edge by microprobe. These analyses are compared to oriented films of Cu^{II} saturated montmorillonite and the results are given in Figure 17 and 18 for the edge and surface of the films respectively.

Microprobe analysis is a surface analysis technique where a sample is bombarded with an electron beam and characteristic x-rays which fluoresce from the sample are measured. When copper is being analyzed by this technique the intensity of Cu K_α and L_α can be monitored as the sample is scanned. Copper saturated montmorillonite gave about the same average x-ray fluorescence on the edge as the silylated montmorillonite indicating the edge copper concentrations are approximately equivalent. Differences between the CuK_α and CuL_α fluorescence suggest a deeper section is being analyzed in the copper saturated montmorillonite. Analysis of the surface of each film shows the intensity of x-rays caused by copper are much more intense in the copper saturated montmorillonite than the sample where copper is immobilized with a silylating agent.

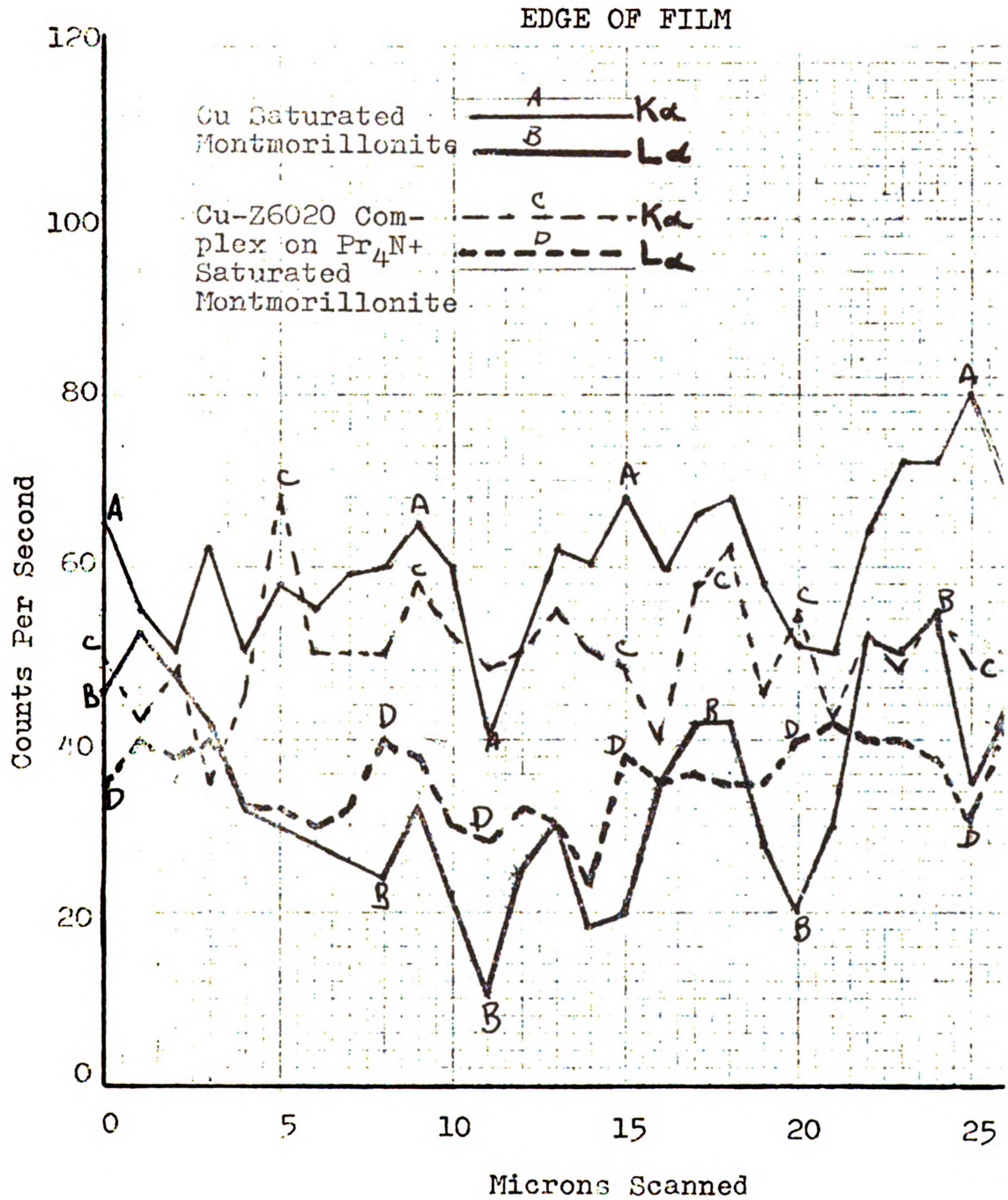


Fig. 17.--Microprobe scan on edge of oriented films of montmorillonite.

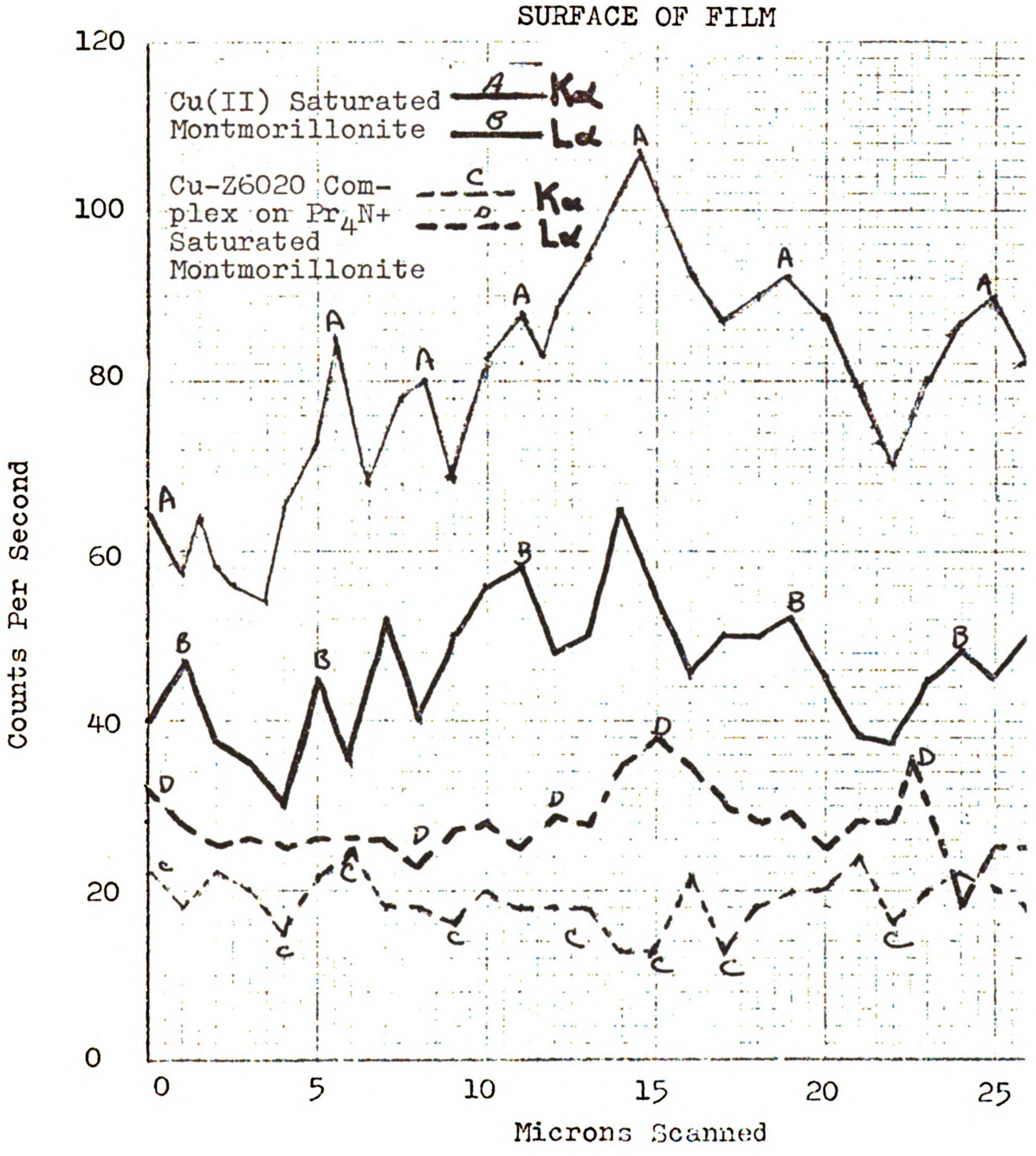


Fig. 18.--Microprobe scan on surface of oriented films of montmorillonite.

X-ray diffraction patterns of both samples show first order diffraction in the 001 planes of 14.5 Å and 12.4 Å for the tetrapropylammonium montmorillonite and copper montmorillonite respectively as would be expected. Total copper analysis showed 2.45% Cu in the copper saturated montmorillonite and 0.34% Cu in the montmorillonite which was treated with the silylating agent. These data are consistent with silylation taking place at the edge of the montmorillonite and the capacity of interlayer copper is six times greater than the capacity of copper immobilized on the edge by silylation. The relative amount of interlayer copper to edge copper will depend on the particle size of the clay and the thickness of the copper complex at the edge.

D. Trimethylsilylation of Clays

Trimethylsilylation of silica and silicates under acidic and basic conditions have been described.[10] Conditions of high or low pH in the system cause degradation of the silicate structure. Attempts to preserve the layered structure by trimethylsilylating the clays at near neutral pH resulted in poorly defined products. Weak infrared absorptions near 1250, 1395 and 795 cm^{-1} are assigned to Me_3Si-O. Attempts to increase the degree of silylation by use of polar solvents were complicated by side reactions of the solvent. The purpose of this silylation was to deactivate the polar silanol groups on

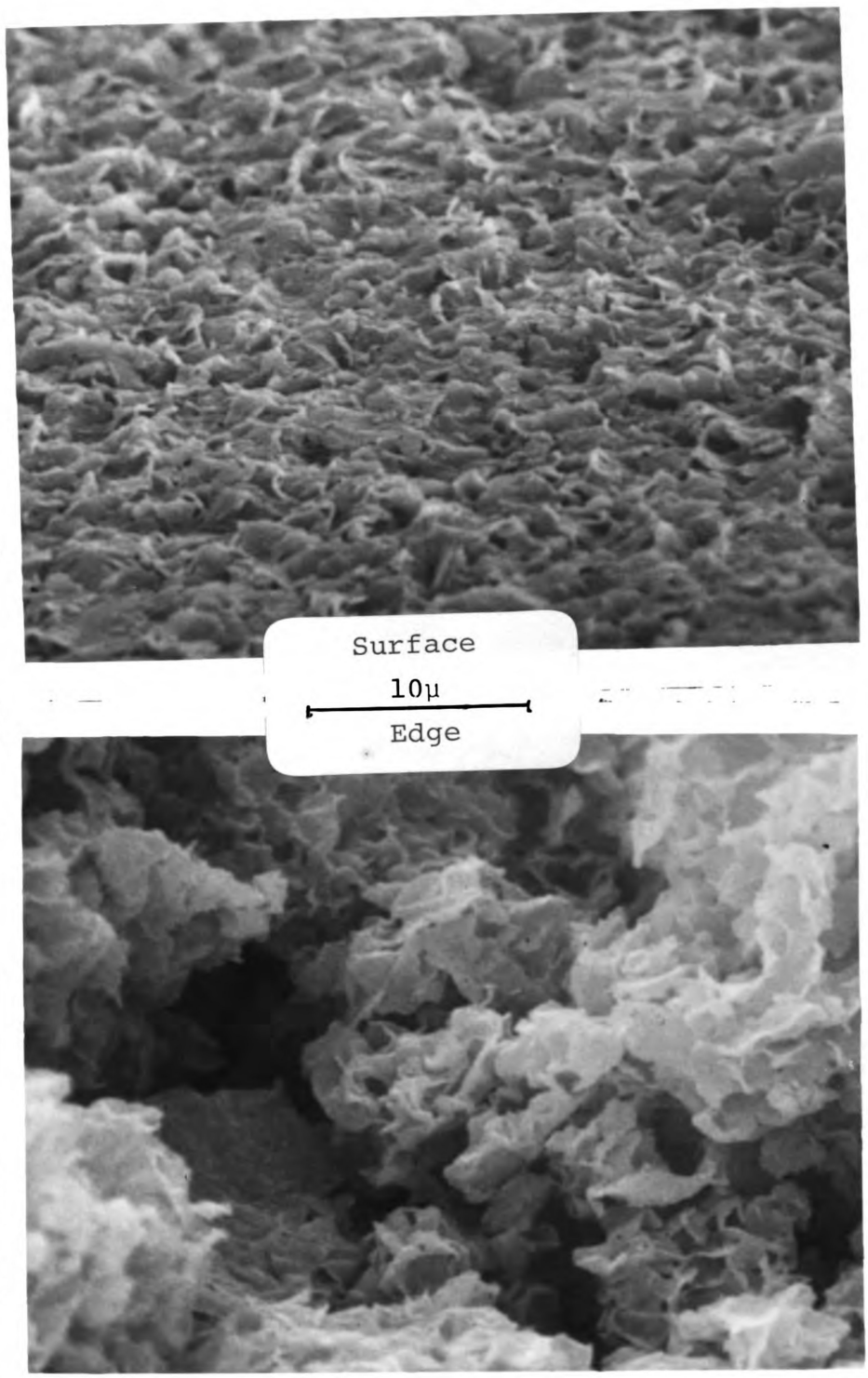


Fig. 19.--SEM of Pr_4N+ form of montmorillonite which was treated with Z6020 and complex with Cu^{+2} at 2600 X.

the edge of the silicate structure with trimethylsilyl groups while the layered structure of the silicate structure was to be preserved. This would require silylation at mild pH.

Trimethylsilylation of montmorillonite with mixtures of Me_3SiCl and $(Me_3Si)_2NH$ in dioxane gave an unexplained carbonyl band at 1610 cm^{-1} (Figures 20 and 21). When the reaction was attempted with Me_3SiCl and pyridine a band at 1490 cm^{-1} suggested pyridine was intercallated between the silicate sheets. However weak bands at 1250 cm^{-1}, 795 cm^{-1} and 1395 cm^{-1} suggested silylation took place (see Figure 22).

These results are too inconclusive for any lengthy discussion but might be useful for future studies. Smaller particle size clay would be better for such a study since the amount of edge silanol is greater and the products would be easier to characterize by infrared.

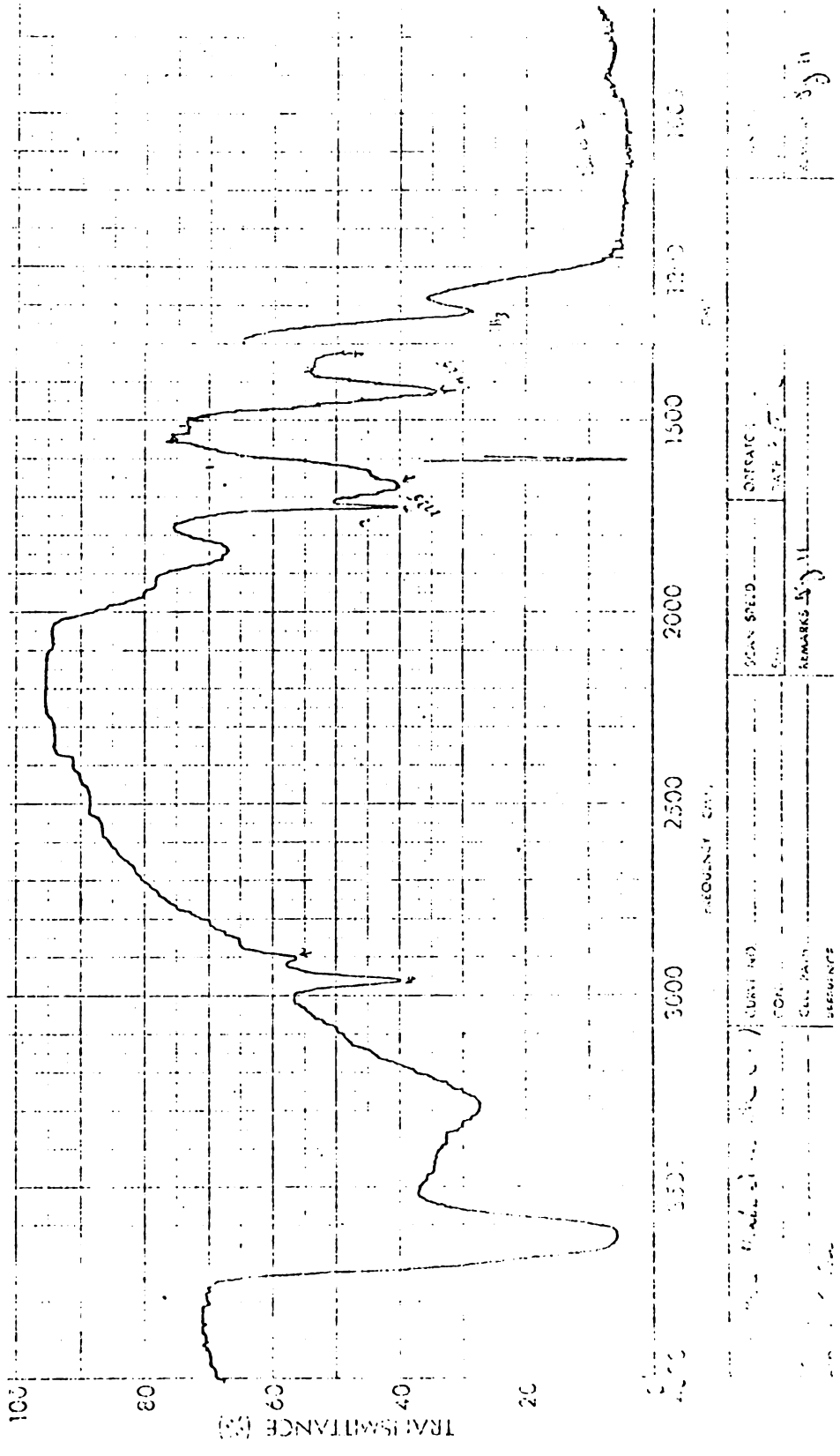


Fig. 20.--Infrared spectrum of montmorillonite silylated with Me_3SiCl and $(Me_3Si)_2NH$ at a molar ratio of 2.0 in dioxane.

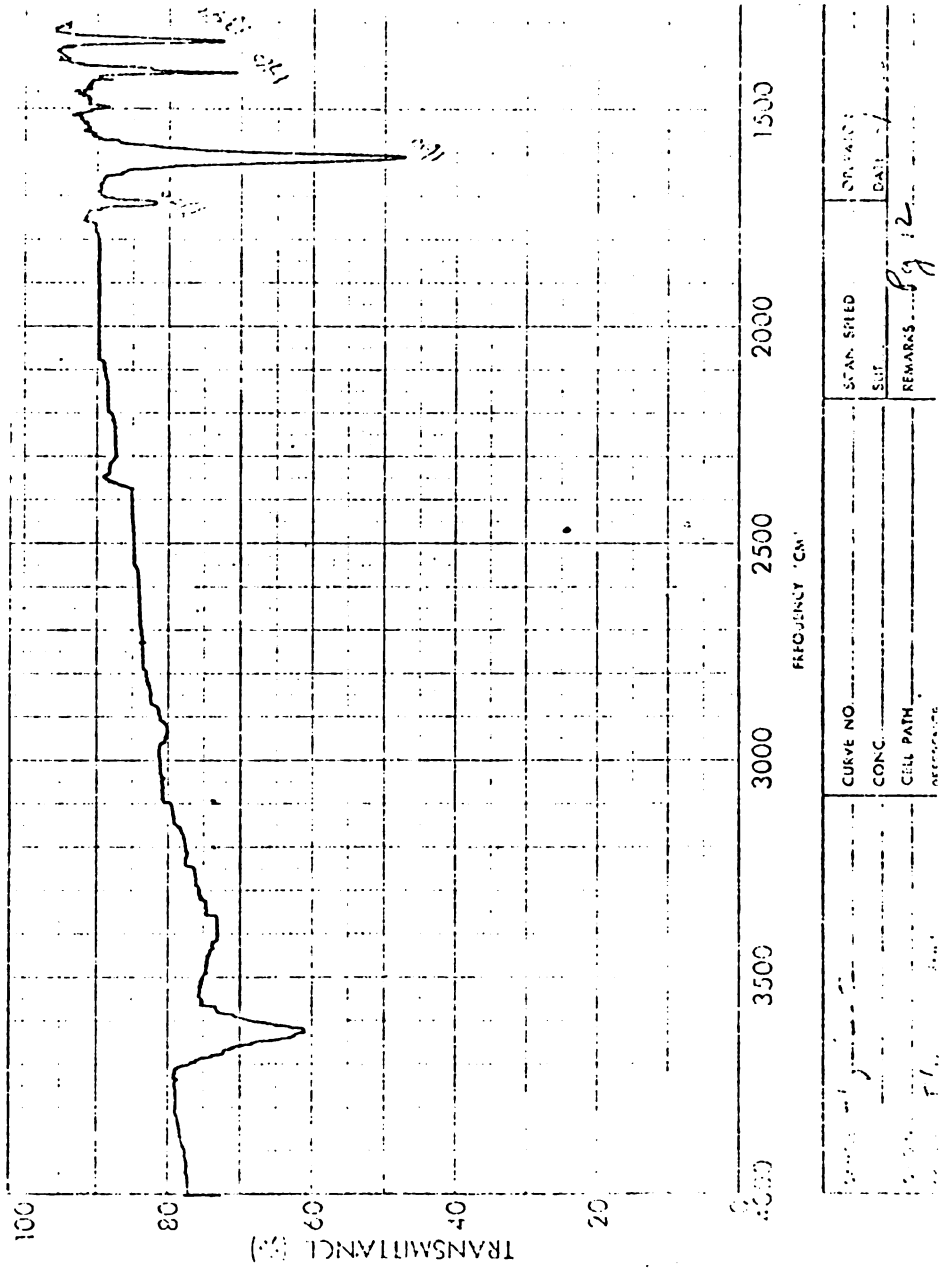


Fig. 21.--Infrared spectrum of montmorillonite silylated with Me_3SiCl and $(Me_3Si)_2NH$ at a molar ratio of 0.5 in dioxane.

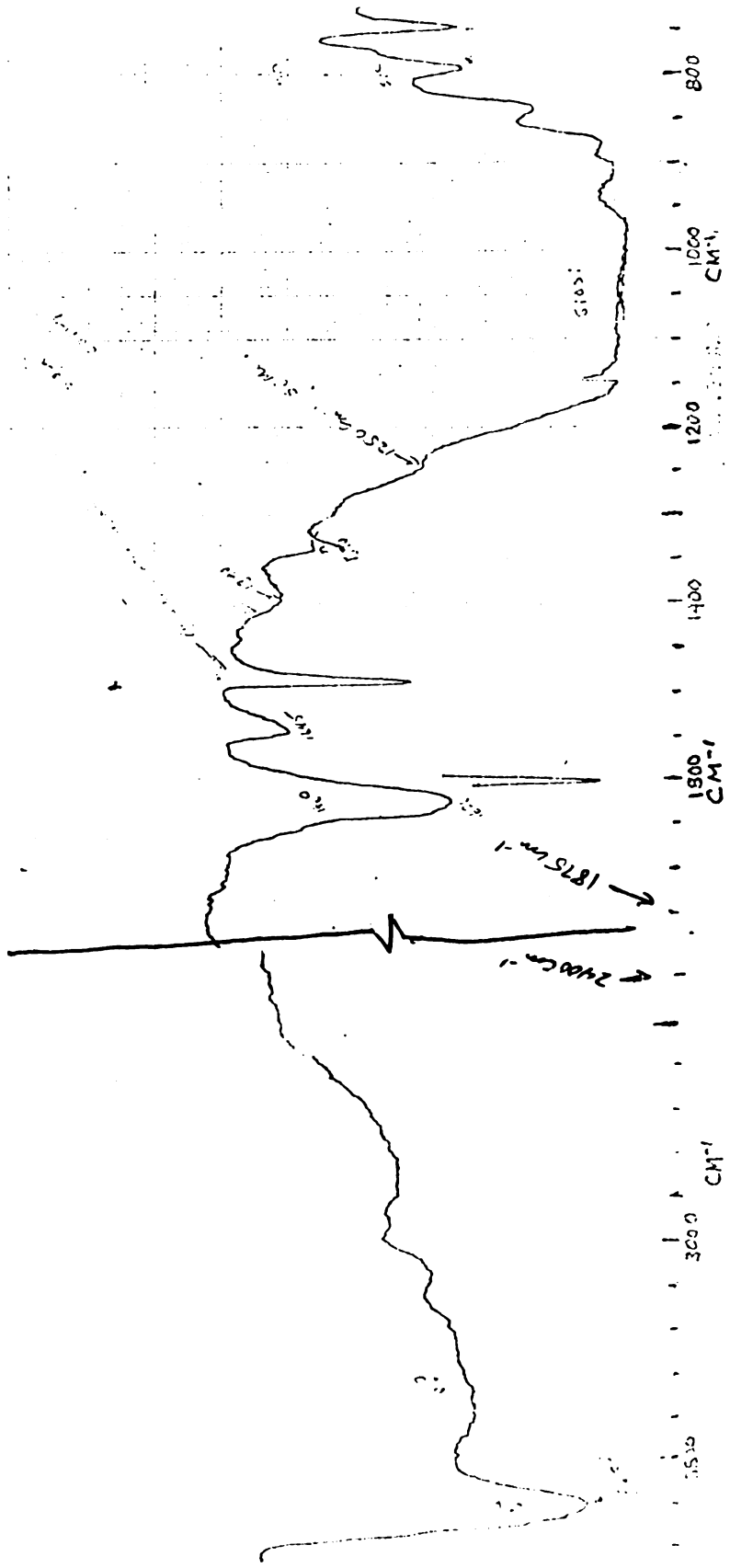


Fig. 22.--Infrared spectrum of montmorillonite silylated with Me_3SiCl in pyridine.

III. CONCLUSIONS

1. The environment of copper on clays and silica gel depends on the method of deposition. Esr is a useful tool for detecting the difference in the metal ion's environment.
2. Cu (II) amine complexes in a methanol glass at 77°K resemble immobilized Cu (II) amine complexes on silica surfaces.
3. Silylation of clays occurs on the edge of the silicate crystal where silanols are present, as suggested by the covalent bonding theory of coupling agents.
4. On montmorillonite Cu interlayer/Cu edge is equal to 6.3.

IV. EXPERIMENTAL

A. Fractionation of Montmorillonite

About 6 kg of a 2.5 wt % aqueous suspension of Na-montmorillonite (Upton Wyoming, Source Clay) was allowed settle in graduated cylinders. After 16 hours of sedimentation the top 17.5 cm of suspension (50 volume %) was siphoned, centrifuged at 9250 rpm and the buff colored product freeze dried to give 29.5 g of clay. Analysis by infrared showed ν_{OH} 3200-3700 cm^{-1}, ν_{HOH} 1626 cm^{-1} and ν_{SiOSi} 850-1200 cm^{-1}. BET surface area of 9 m^2/g was obtained by N_2 adsorption after 2 hrs of degassing at 180°C.

B. Preparation of Cation Exchange Forms of Clays

Cation exchange forms of the <2μ fraction of montmorillonite were prepared by adding excess halide salt to a 2.5% aqueous suspension of <2μ montmorillonite, removing the clay by centrifuging, washing the clay twice with a 1 M solution of the halide salt and finally washing with distilled water until no halide was detected in the supernate. The exchange form of the clay was then freeze dried.

Thus, n-Pr_4N + montmorillonite (2.56 g) was prepared from 3.5 g of <2μ fraction of montmorillonite. Analysis by infrared showed $\nu_{OH\ free}$ 3620 cm^{-1}, ν_{CH} 2890, 2950 and 2980 cm^{-1}, ν_{CH} 1360, 1380, 1460 and 1480 cm^{-1}, and a weak band at 1630 cm^{-1} caused by H_2O deformation. Heating the clay in air to 110°C for 1 hr did not cause disappearance of the band at 1630 cm^{-1}. Analysis of the powder by x-ray diffraction gave a first order spacing of the 001 plane of 14.2 Å.

The copper exchange form (2.38 g) was prepared from 3.00 g of <2μ fraction of montmorillonite. The infrared spectrum of the product showed ν_{OH} 3620, ν_{OH} 1622 and ν_{SiOSi} 850-1200 cm^{-1}. Chemical analysis showed 2.15% Cu present or 67.6 meq/100 g. Analysis of an oriented film by x-ray diffraction gave a first order spacing in the 001 plane of 12.4 Å.

The <2μ fraction of baroid hectorite (2 g) was treated with excess Bu_4NI in methanol (400 ml). The product was washed free of halide, filtered, and air-dried. Analysis of the product by x-ray diffraction gave a first order spacing in the 001 plane of 15.2 Å.

C. Silylation of Pr_4N + Montmorillonite with N-(β-Amino-Ethyl)-γ-Aminopropyl-trimethoxysilane (Dow Corning® Z6020 Silane)

The Pr_4N+ exchange form of montmorillonite (1.225 g) was suspended in 75 g of a 0.4% aqueous solution of Dow

Corning® Z6020 Silane, stirred for 15 min and freeze dried. A portion of the product (0.946 g) was washed with 50 ml portions of H_2O until the supernate gave no color change with Cu^{+2} (total of 4 washes). The washed clay was suspended in 50 ml of 0.10 M $CuCl_2$ for 10 minutes, washed until no Cu^{+2} was detected in the supernate and freeze dried. The product (0.706 g) gave infrared spectrum similar to the starting clay. However the absorptions ν_{CH} 2850-2970 cm^{-1} were broader and more intense. An oriented film was prepared by evaporation of a suspension of the product. Analysis by scanning electron microscopy and microprobe are presented in Figures 17, 18, and 19. Analysis of Cu^{+2} by esr is presented in Figure 16. Chemical analysis showed 0.34% Cu present or 10.8 meq/100 gm of clay. Analysis of x-ray diffraction gave a first order spacing of 14.5 Å.

D. Silylation of Bu_4N^+ Hectorite and Its Cu^{+2} Complex

The Bu_4N^+ exchange form of Hectorite (0.831 g) was dispersed in 60 ml of H_2O. A 3% aqueous solution of Dow Corning® Z6020 Silane (10 ml) was added, and the mixture was stirred for 30 min. The clay was washed until the supernate gave a negative amine test with $CuCl_2$ solution, and the resulting clay was suspended in 50 ml of 0.10 M $CuCl_2$ solution for 10 minutes. Excess copper was removed by repeated washing with distilled H_2O. After air drying,

the product (0.592 g) was analyzed by esr. The results can be found in Table 2.

E. Silylation of Silica Gel with Aminoalkylsilanes

Silica gel (10.0 g, BET surface area 540 m^2/g) was mixed with a 5% aqueous solution (42 g) of Dow Corning® Z6020 Silane or Union Carbide® A1100 Silane for 1 hr at room temperature. The solution was decanted, and the silica gel was washed twice with H_2O (100 ml), once with boiling H_2O (100 ml for 30 min) and finally at room temperature with 100 ml H_2O. The products were dried for 10 hrs at 95°C to give 9.0 and 8.7 g of product respectively.

F. Copper (II) Complexes of Silylated Silica Gels

Silica gel (1.00 g) which contained the functionalizing group indicated below was stirred with aqueous 0.10 M $CuCl_2$, washed twice with 100 ml of H_2O and allowed to air dry.

Functional Group	Temp of Wash	Recovered Silica Gel	Color
$\equiv Si(CH_2)_3NH(CH_2)_2NH_2$	100°C	0.90 g	Dark Blue
$\equiv Si(CH_2)_3NH(CH_2)_2NH_2$	25°C	0.80 g	Blue
$\equiv Si(CH_2)_3NH_2$	100°C	0.80 g	Light Blue
None	100°C	0.83 g	Greenish White

Esr data for each sample is presented in Table 2.

G. Copper Amine Complexes

Dow Corning® Z6020 Silane and ethylenediamine were added to 3 x 10^{-3} M $CuCl_2 \cdot 2H_2O$ in methanol to give various molar ratios of amine to Cu^{+2} as summarized in Table 1. The solutions were analyzed by esr. The spectra are shown in Figures 1-10 and Table 1.

H. Trimethylsilylation of Clay

1. Na+ Montmorillonite with Me_3SiCl and $(Me_3Si)_2NH$ in Dioxane.--A round bottom flask fitted with a stirrer, reflux condenser and N_2 purge was loaded with 1.00 g of <2μ montmorillonite and 24 g of dioxane. After stirring the mixture for 20 min, Me_3SiCl (1.072 g, 9.88 mole) and $(Me_3Si)_2NH$ (0.799 g, 4.96 mole) were added and the mixture was refluxed for 4 1/2 hrs. The cooled mixture was stirred an additional 17 hrs, and 1 M NaCl (70 ml) was added to the slurry. The product was washed with distilled H_2O until a negative halide test was obtained with $AgNO_3$. The infrared spectrum of the freeze dried clay (0.655 g) (Figure 20) showed ν_{OH} 3630, 3360 and 1630 cm^{-1}, ν_{CH} 2960 (weak), 1425 and ν_{SiOSi} 975-1150 cm^{-1}. A weak band at 1730 cm^{-1} (possibly C=O) was also present.

The procedure was repeated with Me_3SiCl (0.715 g, 6.59 m mole) and $(Me_3Si)_2NH$ (2.121 g, 13.17 m mole). Analysis of the product (0.877 g) by infrared showed ν_{OH} 3625, and 3400 cm^{-1}, ν_{CH} 2940, 1500, 1420 and 1350,

$\nu_{C=O}$ 1610 and 1720 cm^{-1}. The band at 1610 cm^{-1} was very strong as shown in Figure 21.

2. Na+ Montmorillonite with Me_3SiCl and $(Me_3Si)_2NH$ in Bulk.--The <2μ fraction of Na-montmorillonite (1.00 g) Me_3SiCl (4.48 g, 62.2 m mole) and $(Me_3Si)_2NH$ (20.0 g, 124 m mole) were refluxed for 18 hrs as previously described. The clay was removed by centrifuging, washed twice with hexane (30 ml) and once with 1 M NaCl (30 ml). After washing the clay free of chloride it was freeze dried to give 0.6943 g of product whose infrared spectrum was the same as montmorillonite, except that weak bands at ν_{CH} 2910 and 2850 cm^{-1}, ν 850 cm^{-1} were detected. No band due to SiMe deformation (1250-1270 cm^{-1}) was detected.

3. Na+ Montmorillonite with Me_3SiCl in Pyridine.--The formation of a light blue color was observed when Na-montmorillonite (1.00 g) and pyridine (23 ml) were stirred for 3 hrs in a N_2 atmosphere. After refluxing the mixture with Me_3SiCl (2.74 g, 25.2 m mole) for 18 hrs the clay turned dark blue. The product was recovered by decanting the supernate. It was washed with EtOH (50 ml), then with H_2O (100 ml), and finally with EtOH (100 ml). Oven drying at 100°C for 1 1/2 hrs gave a white product (0.950 g) whose infrared showed ν_{OH} 3600 and 3100-3500 cm^{-1}, ν_{H_2O} 1625 cm^{-1}, $\nu_{pyridine}$ 1490 cm^{-1} and ν_{SiOSi} 950-1200 cm^{-1}. Weak

bands at 1250 cm^{-1}, 795 and 1395 cm^{-1} could be attributable to SiMe (Figure 22).

4. Pr_4N+ Montmorillonite with Me_3SiCl and $(Me_3Si)_2NH$ in MeCN.--A flask as previously described was loaded with the Pr_4N+ exchange form of montmorillonite (0.400 g) and acetonitrile (9.0 ml). After 30 min of stirring, Me_3SiCl (0.543 g, 5.00 m mole) and $(Me_3Si)_2NH$ (0.808 g, 5.02 m mole) were added, and the mixture was refluxed for 11 hrs. The product was washed with water until no chloride was detected with $AgNO_3$. After drying at 110°C for 4 hrs analysis of the product (0.321 g) by infrared showed the same absorptions observed with the starting clay, but weak absorptions at 1255 and 840 cm^{-1} could be attributed to SiMe.

I. Intercalation of Silica in Na+ Montmorillonite

Two separate aqueous suspensions (2.4 wt %) of Na-montmorillonite and Cabosil® S-17 fumed silica were prepared by mixing with distilled water and dispersing in an ultrasonic disruptor for 4 min at 55 watts. About 14.2 g of a 1.41% solution of $[(MeO)_3Si(CH_2)_3NMe_3]^+Cl^-$ was added to the silica dispersion and it was treated again with the ultrasonic disruptor. Both suspensions were diluted to 2.00 wt % and mixed as shown below. After 6 hrs the products were centrifuged at 9000 rpm for 30 min, decanted and freeze dried.

Sample	Ml 2% Clay	Ml 2% Functionalized Clay	% Clay	Appearance of Supernate	Grams After Freeze Drying	BET Surface Area m^2/g
1	2.0	18.0	10%	Clear	0.373	334
2	6.7	13.3	33%	Clear	0.383	187
3	10.0	10.0	50%	Clear	0.397	137
4	13.3	6.7	67%	Clear	0.374	100
5	16.0	4.0	80%	Cloudy	0.223	65
6	18.0	2.0	90%	Cloudy	0.165	26
7	0.0	20.0	0%	Clear	0.269	276
8	20.0	0.0	100%	Cloudy	0.170	15

I. General

A varian E-4 electron spin resonance spectrometer fitted with a liquid nitrogen dewar was used to obtain esr spectra. Typical conditions for obtaining spectra are given in figure 1. Copper K_α and L_α radiation was measured with an ARL scanning electron microprobe instrument at 15.5 kv and 0.018 μ A.

BIBLIOGRAPHY

1. E. P. Pleuddemann in Composite Material, Vol. 6, L. J. Broutman and R. H. Krock, eds., Academic Press, New York (1974).

2. M. E. Schrader, I. Lerner, and F. J. D'Oria, Mod. Plas., 45, 195 (1967).

3. O. K. Johanson, F. O. Stark, G. E. Vogel, and R. M. Fleischman, J. Comp. Material, 1, 278 (1967).

4. H. Tominaga, Y. Ono, and T. Keii, J. of Catalysts, 40, 197 (1975).

5. R. L. Burwell, Chemtech, 370, June (1974).

6. D. M. Clementz, T. J. Pinnavaia, M. M. Mortland, J. Phys. Chem., 77, No. 2, 198 (1973).

7. D. E. Leyden and G. H. Luttrell, Anal. Chem., 47, 1612 (1975).

8. D. E. Leyden and G. H. Luttrell and T. A. Patterson, Anal. Letters, 8, 51 (1975).

9. R. M. Barrer and K. Brummer, Trans. Faraday Soc., 59, 959 (1962).

10. C. W. Lentz, Inorg. Chem., 3, 574 (1964).