

EFFECT OF SOLVENTS AND COMPLEX IONS ON
PROPERTIES OF SMECTITE

Dissertation for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
VAUGHN ELWOOD BERKHEISER
1976



This is to certify that the

thesis entitled

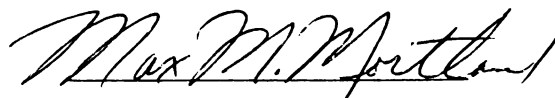
EFFECT OF SOLVENTS AND COMPLEX IONS ON
PROPERTIES OF SMECTITE

presented by

VAUGHN ELWOOD BERKHEISER

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Soil Chemistry


Major professor

Date Aug. 13, 1976



5/20/73

ABSTRACT

EFFECT OF SOLVENTS AND COMPLEX IONS
ON PROPERTIES OF SMECTITE

By

Vaughn Elwood Berkheiser

Full and reduced charge smectite saturated with Na(I), Ca(II), Cu(II), or tetralkylammonium ions were swollen by a series of solvents of various bulk physical properties. Swelling occurred in all solvents regardless of the exchange ion or the initial water content in the full charge smectites. Charge differences did not usually result in differential swelling of the smectite. Little correlation was found between the degree of swelling and the Gutmann donor numbers, bulk dielectric constants, bulk surface tensions, or dipole moments of the solvents. The intensities of the high field (Fe(III) resonance ($g=3.6$) in the esr spectra of full charge smectite swollen in various solvents reflected variability in exchange ion positions and depended upon the Gutmann donor number of the solvent. Considerable variety in the stereochemistry of Cu(II)-solvent complexes was revealed by esr spectra of the swollen systems.

Characteristics and properties of complexes of a smectite (hectorite) with 1,10-phenanthroline (phen) chelates

with iron or copper, were determined by a variety of physical and chemical measurements. The complex ions showed high selectivity for the hectorite surface. Basal spacings of $17.4 \text{ \AA}$ were produced by Fe(II) or Cu(II) analogues of M(phen)_3^{2+} hectorite. Adsorption of gases and vapors by the M(phen)_3^{2+} hectorite complex revealed large surface areas and reflected intrinsic characteristics of the complex ions. Lower surface areas were found for Cu(phen)_3^{2+} hectorite than Fe(phen)_3^{2+} hectorite because of the loss of a ligand from the Cu(II) ion. ESR spectra confirmed that appreciable Cu(II) existed as the bis-phen complex under certain conditions. An increase in the oxidation potential of the Fe(phen)_3^{2+} - Fe(phen)_3^3 couple above that in pure solvent was noted when these complexes were supported by the mineral surface.

EFFECT OF SOLVENTS AND COMPLEX IONS
ON PROPERTIES OF SMECTITE

By

Vaughn Elwood Berkheiser

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Crop and Soil Sciences

1976



ACKNOWLEDGEMENTS

Great appreciation is expressed to Dr. Max M. Mortland for his expert guidance and patience during the author's graduate work. His insistence on accurate and concise interpretation of experimental results will remain as a constant guideline in the future.

Dr. Thomas J. Pinnavaia deserves special thanks for advice particularly in the area of magnetic resonance spectroscopy and its applications to the study of clay mineral surfaces.

Thanks are also extended to Dr. Thomas A. Vogel and Dr. Boyd G. Ellis for serving on the author's advisory committee. Gratitude is also expressed to Dr. James F. Hoffman, Dr. Leon J. Halloran, and Mr. William H. Quayle for suggestions and assistance in laboratory matters of experimentation.

The author is most grateful to his wife, Ava, and daughter, Shauna, for their love and companionship during this period in Michigan.

TABLE OF CONTENTS

	Page
LIST OF TABLES	iv
LIST OF FIGURES	v
INTRODUCTION	1
PART I: Variability in Exchange Ion Position in Smectite: Dependence on Interlayer Solvent	3
A. Introduction	4
B. Experimental	5
C. Results and Discussion	8
D. Conclusions	29
PART II: Properties of Hectorite Containing Cu(II)- and Fe(II)-1,10-phenanthroline Chelates as Exchange Ions	31
A. Introduction	32
B. Experimental	33
C. Results and Discussion	36
D. Conclusions	64
SUMMARY AND CONCLUSIONS	66
LIST OF REFERENCES	67

LIST OF TABLES

Table	Page
PART I	
1. Solvents used and their properties.....	7
2. d-spacings of smectite saturated with various cations swollen with selected solvents (A)	9
3. Basal spacings (A) of full charge Upton montmorillonite in selected solvents after heat treatments.....	11
4. Electron spin resonance data for Cu(II) in smectite treated with various solvents	21
PART II	
1. X-ray basal spacings of Na(I) hectorite exchanged at various levels with $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Cu}(\text{phen})_3^{2+}$	43
2. Summary of calculated and observed BET surface areas of $\text{Fe}(\text{phen})_3^{2+}$ hectorite.....	55
3. Summary of oxidation-reduction reactions of Fe and Cu phen complexes on clay and in ClO_4^- salts.....	57
4. ESR parameters for $\text{Cu}(\text{phen})_3^{2+}$ hectorite complexes.....	63

LIST OF FIGURES

Figure	Page
PART I	
1. Orientation dependence in esr spectra of structural Fe(III) in a film of Ca(II) smectite solvated with pyridine. The vertical bar indicates $g=3.88$	13
2. ESR spectra of structural iron in oriented films of Na(I) smectite after heat treatment and solvation. The downward arrow indicates $g=3.6$	16
3. ESR spectra of structural iron in oriented films of Na(I) smectite swollen by various solvents. Numbers in parentheses are Gutmann Donor Numbers, while the other numbers are the (001) spacings. The downward arrow indicates $g=3.6$	18
4. ESR spectra of structural iron (left) and exchangeable Cu(II) (right) in oriented films of Cu(II) smectite solvated in DMSO and PY. Cu(II) spectra are shown for two orientations of the films with respect to the magnetic field. The vertical bar indicates $g=3.88$; the free electron signal indicates $g=2.0028$	22
5. ESR spectra of structural iron and exchangeable Cu(II) in oriented films of Cu(II)-doped Ca(II) smectite solvated in NIB and PY. Cu(II) spectra are shown for two orientations of the films with respect to the magnetic field. The vertical bar indicates $g=3.88$; the free electron signal indicates $g=2.0028$	26

PART II

1. Adsorption isotherms of $\text{Fe}(\text{phen})_3\text{Br}^2$ and $\text{Cu}(\text{phen})_3\text{SO}_4$ on $\text{Na}(\text{I})$ -hectorite and cetylpyridinium bromide on montmorillonite.....	37
2. Exchange isotherms for three ions on $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Cu}(\text{phen})_3^{2+}$ hectorite systems.....	41
3. Data for adsorption of N_2 on $\text{Fe}(\text{phen})_3^{2+}$ hectorite plotted according to BET, Langmuir, and Huttig equations.....	45
4. Specific surface areas of hectorite $2+$ fractionally saturated with $\text{M}(\text{phen})_3$ calculated from the BET equation.....	48
5. Adsorption isotherms of H_2O and benzene vapors on $\text{M}(\text{phen})_3^{2+}$ hectorite at 20°C	51
6. ESR spectra of oriented thin films of $\text{Cu}(\text{II})$ in $\text{Cu}(\text{phen})_3^{2+}$ hectorite at different levels of hydration. The free electron signal indicates $g=2.0028$; films were oriented parallel ($\parallel$) and perpendicular ($\perp$) to the magnetic field H	60

INTRODUCTION

Solvate and chelate complexes of exchange ions in smectite are of interest in environmental studies and in industrial applications. Clay minerals, with their inherent negative charge and exchangeable cations, serve as important substrates for processes which occur in natural systems as well as on an industrial scale. In addition to chemical reactions and complex formation on the silicate surface, the swelling ability of certain clay minerals remains an important phenomenon in soil mechanics, petroleum engineering, and in other fields which utilize the high surface area exposed in the swollen mineral. A unifying principle which describes the swelling phenomenon remains an elusive pursuit in studies of clay mineral properties. Recently, the use of smectite-bound homogeneous catalysts has promoted interest in the behavior of interlamellar exchange cations in the mineral swollen by non-aqueous solvents.

In natural systems where water predominates as the solvent, chelates of metal ions with naturally occurring organic species are common. Clay minerals, being ubiquitous constituents of natural environments, may be important sinks for the deactivation of these metal ion pollutants. The resulting properties of the chelated ion clay complex may be different

from those minerals containing only hydrated ionic species.

This study is an attempt to elucidate some of the factors underlying these properties. By the use of electron spin resonance spectroscopy, structural and dynamical parameters of paramagnetic ions on smectite surfaces is evaluated. This spectroscopic technique is especially applicable to investigation of ionic environments in fully solvated systems in which the ion serves as a probe of the character of the surface environment. In addition, other properties of smectite complexes were studied and included swelling properties of smectite with various layer charges, stereochemistry and positions of some exchange ion solvates, the adsorption of complex ion chelates by hectorite, properties of the complex ion-hectorite complex, and stereochemistry of the Cu(II) ions in various solvate and chelate systems.

PART I

VARIABILITY IN EXCHANGE ION POSITION IN SMECTITE:
DEPENDENCE ON INTERLAYER SOLVENT

(Previously published in Clays and Clay
Minerals, Copyright © 1975, The Clay
Minerals Society)

INTRODUCTION

Crystalline swelling of clays has been related to the charge density of the clay surface, to the nature of the exchange ions present on the clay surface, and to the dielectric constant of the interlayer medium (Norrish, 1954). Cation movement from the clay surface to positions midway between the clay sheets is generally believed to occur upon swelling as in the case of Mg-vermiculites (Walker, 1961). However, on the basis of conductometric measurements, the fraction of ions remaining at the surface of the clay was shown to be related to the nature of the cations and the kind of interlayer solvent (Shainberg and Kemper, 1966). Barshad (1952) has suggested that for solvents of low coordinating strength, the cations in swollen smectite reside in the surface hexagonal holes.

This paper reports an investigation of the relationship between exchange cation position as indicated by electron spin resonance spectroscopy, and the Gutmann donor number of the interlayer solvent. In addition the effect of a number of factors on smectite swelling is reported. These include charge density, nature of the interlayer cations, and the bulk dielectric constants, dipole moments, and surface tensions of the added solvent. The Gutmann donor number is the negative molar enthalpy of the reaction between a particular solvent and SbCl_5 in 1,2-dichloroethane (Gutmann, 1968). Since ion solvation is an important phenomenon in smectite

swelling (Norrish, 1954), this parameter might be of use in describing clay-solvent interactions. Relationships between crystalline swelling and charge density may be obtained from full and reduced charge smectites swollen in the selected solvents. Application of the methods of Clementz, Pinnavaia, and Mortland (1973) to the present systems allow electron spin resonance investigation of the stereochemistry of the Cu(II)-solvent complexes.

EXPERIMENTAL

Preparation of reduced charge smectite. Li(I) saturated Upton, Wyoming montmorillonite (A.P.I. H-25) was heated 220°C for 24-hr to produce reduced charge smectite, according to the method of Brindley and Ertem (1971). Cation exchange capacities were found to be 27 and 87 me/100g for the reduced and full charge clay, respectively, by conductometric titration of Cu(II) according to the method of Clementz et al. (1974).

Cation exchange forms. The high and low charge smectites were washed in a large excess of 0.5 N chloride 95% ethanol solutions of Na(I), Ca(II), Cu(II), and tetramethylammonium (TMA) cations. Excess salts were removed with 95% ethanol until a negative Cl^- test with AgNO_3 was obtained after which they were dried at 110°C. Smectite containing about 10 mole % Cu(II) doped into Ca(II) was prepared by washing the clay 5 times with a chloride solution of 10 mole % Cu(II) and 90 mole % Ca(II); excess

salts were removed by dialyzing against deionized water until Cl^- free. After evaporation from aqueous suspensions, the clays were stored air-dried until used.

Solvents. Reagent grade solvents were used throughout as they were received from the distributor without further purification. Homoionic clays from above were heated for two hours at 110°C and then placed into sealed beakers containing each solvent. The clays were in contact with the solvents for 10 days at which time measurements were taken. Selected properties of the solvents used in this study are given in Table 1. Abbreviations for solvent names will be used.

X-ray diffraction measurements. The (001) basal spacings were measured on a Philips X-ray Diffractometer using Ni filtered Cu-K_α radiation. In most samples three orders of reflections were detectable while each clay was kept wet with its respective solvent during the measurement.

Electron spin resonance measurements. A Varian E-4 ESR spectrometer operated at a proximal frequency of 9.47 GHz was used for recording broad-line spectra. Thin films of the clay specimens were oriented in quartz tubes, heated overnight, and then solvents added. After 10 days of equilibration, the excess solvent was removed with a syringe and the spectra of the structural Fe(III) resonances at $g=4.2$ and $g=3.6$ and of Cu(II) on exchange sites were recorded. McBride, et al., 1975 (in press), have shown that the intensity of the $g=3.6$ resonance is

Table 1. Solvents used and their properties.

Solvent Name	Abbrevi- ation	Gutmann Donor Number*	Dielectric Constant	Dipole Moment, Debye
1,2-dichloroethane	DCE	0.0	10.1	1.19
Nitrobenzene	NIB	4.4	34.8	4.27
Acetonitrile	AN	14.1	38.0	3.84
Diethylcarbonate	DC	16.4	89.0	1.10
Methylacetate	MA	16.5	6.7	1.72
Diethylether	DE	19.2	4.3	1.15
N,N-dimethylformamide	DMF	26.6	36.7	3.82
Dimethylsulfoxide	DMSO	29.8	45.0	4.3
Ethanol	EtOH	31.5	24.3	1.69
Water	H ₂ O	33.	81.0	1.85
Pyridine	PY	33.1	12.3	2.26
N-methylformamide	MF	--	182.4	3.83

* Donor numbers are taken from Gutmann (1968) except for water which was taken from Ehrlich *et al.* (1970). Dielectric constants and dipole moments are taken from Handbook of Chemistry and Physics.

sensitive to the distance between the exchange ion charge and the silicate surface.

RESULTS AND DISCUSSION

It is seen from Table 2 that for smectite dehydrated at 110°C, little relationship exists between the degree of swelling and the Gutmann Donor Number of the solvent except for the Cu(II) system which was significantly correlated at the 5% level of confidence. Similar negative results for all systems were obtained when the basal spacings were plotted against bulk dielectric constants and surface tensions of the solvents. When the basal spacings were plotted against dipole moments of the above solvents, those with moments above 2.3 Debye tended to swell the TMA saturated smectites, whereas solvents with dipole moments of below 2.3 Debye tended not to swell the TMA-smectite beyond that defined by the organic cation itself (13.8 Å). Swelling of high and low charged smectites saturated with inorganic cations showed little relationship to dipole moment.

In most cases, there is little differential swelling due to charge density differences. This effect could be explained on the basis of balancing of the osmotic swelling force and the force of attraction between the negatively charged silicate surfaces and the interlayer cations which results in spacings not greatly different for both the reduced and fully charged systems.

Table 2. d-spacings of smectite saturated with various cations swollen with selected solvents (Å).

Solvent	Reduced charge smectite				Full charge smectite			
	Na(I)	Ca(II)	Cu(II)	TMA ⁺	Na(I)	Ca(II)	Cu(II)	TMA ⁺
DCE	12.6-13.0*	13.8*	9.8-13.0*	13.8	12.6-13.0*	14.7	13.0	13.8
NIB	14.8*	14.9*	15.1*	21.2	15.0	15.0	14.7	21.0
AN	19.6	19.8	20.0*	20.1	19.6	19.6	20.0*	20.5
DC	13.0*	14.7*	13.0	13.8	13.6	13.2*	13.2	13.8
MA	16.0	15.0	15.0	14.7	15.5	15.5	15.1	14.5
DE	19.4	18.0	16.4*	13.8	15.5	15.8	16.1	13.8
DMF	19.3	19.3	14.5-17.7*	16.7*	19.0	19.1	13.0-16.7*	17.7*
DMSO	19.0	18.8	18.8	15.0*	18.8	18.8	18.4	17.3*
EtOH	17.4*	17.5	17.8	14.0	17.0	17.2	17.0	14.0
H ₂ O	9.8*	19.2*	21.0*	13.8*	>20	19.4	18.8	14.5
PY	19.6	19.9	18.5*	14.7	19.6	19.6	19.4	14.7
MF	12.8-17.7*	17.0*	12.6-17.0*	13.0*	>20	17.4	17.3	15.5*

* Denotes an interstratified system.

Most interesting is the anomalous behavior of Na(I)-smectites in water. The full charge smectite swelled to such large spacings in water that no diffraction peaks were observed, whereas the reduced charge smectite remains largely unswollen in water in accordance with the results of Brindley and Ertem (1971). In addition to their results, information obtained here indicated that swelling of the reduced charge smectite occurs in a wide range of solvents.

It should be noted that there are varying amounts of water remaining on the smectite depending upon the cation present and the temperature of dehydration. Van Olphen and Deeds (1962) reported the effects of mixed PY-H₂O systems upon Na-smectite swelling. Thermogravimetric analyses show that at 110°C the clay contains on the average 6-8 water molecules per Cu(II) ion, 3-4 molecules per Ca(II) ion and about 1 molecule per Na(I) ion based upon 225°C heated clay. If water were propping the interlayers open, the effect of this remaining coordinated water would be to facilitate entry of solvent molecules into the interlayer space which induces swelling. However, as shown in Table 3, the initial water content has little effect upon the amount of swelling. These homoionic clays were thermally dehydrated and then placed into three solvents. For each solvent and a given cation the basal spacing remains almost constant regardless of the degree of dehydration before treatment, which indicates that the

Table 3. Basal spacings ($\text{\AA}$) of full charge Upton montmorillonite in selected solvents after heat treatments.

Exchange ion	Solvent added	Heat treatment				
		25°C	110°C	140°C	180°C	225°C
Na(I)	H ₂ O ^Δ	12.3	9.8	--	--	9.8
	DCE	13.0*	12.6-13.0*	--	12.6	12.6
	NIB	15.0	15.0	15.0	15.0	15.0
	PY	19.6	19.6	19.6	19.6	19.6
Ca(II)	H ₂ O ^Δ	15.2	--	--	--	9.5 [†]
	DCE	15.0	14.7	14.7	14.7	14.7
	NIB	15.0	15.0	15.0	15.0	15.0
	PY	20.3	19.6	19.6	19.6	19.6
Cu(II)	H ₂ O ^Δ	12.4	12.0	--	--	--
	DCE	13.2	13.0	13.0	13.0	--
	NIB	15.0	14.7	14.7	14.7	--
	PY	19.4	19.4	19.4	18.6*	--

* Denotes interstratified system.

[†] Taken from Norrish (1954).

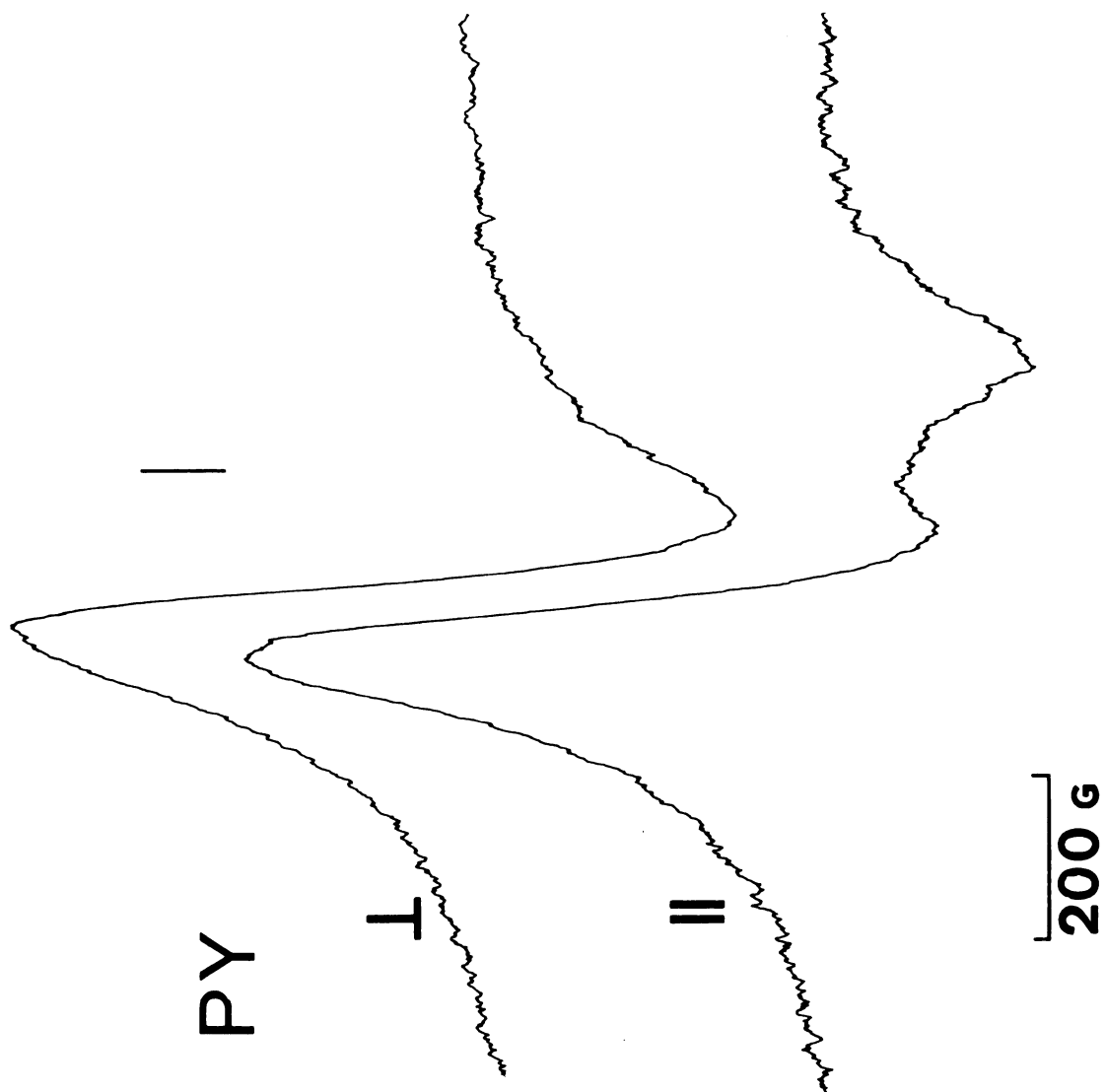
^Δ Adsorbed from atmosphere after heat treatment.

added solvent determines the interlayer spacing.

Exchange cation positions. Even though the clays are swollen in each solvent, cations do not necessarily move to positions midway between the clay sheets. This effect was observed by recording the esr spectra of the structural iron in Upton montmorillonite after the same treatment as in Table 3. McBride et al. (1975) by using powder samples have shown that the intensity of the high field Fe resonance ($g=3.6$), increases as the distance between the exchange cation and the Fe(III) associated with Mg(II) in the octahedral layer increases.

When observed in oriented thin films, this high field Fe(III) resonance at $g=3.6$, is strongly anisotropic as is shown by a Ca(II) montmorillonite solvated in PY in Figure 1. This anisotropy suggests that the $g=3.6$ resonance originates from Fe(III) whose magnetic axes lie in different planes than those of the Fe(III) which gives the strong $g=4.2$ resonance. Absence of the $g=3.6$ resonance in the fully reduced charge smectite suggests this site becomes magnetically similar to the $g=4.2$ site upon entry of Li into the octahedral layer. Since the $g=3.6$ signal intensity is maximized when the clay sheets are parallel to the magnetic field, this orientation was used throughout the study. When decreases in intensities of the $g=3.6$ resonances are observed, the exchange cations are thought to approach the smectite surface. Figure 2 illustrates this effect for Na(I) full charge smectite. Before adding the

Figure 1. Orientation dependence in esr spectra of structural Fe(III) in a film of Ca(II) smectite solvated with PY. The vertical bar indicates $g=3.88$.



solvents and after heating, the ions approach the smectite surface more closely as the degree of dehydration increases which results in a corresponding decrease in intensities of the high field Fe(III) resonances. At 225°C the Na(I) ions reside in hexagonal holes as the basal spacing is only 9.8Å. Swelling by solvents of differing Gutmann donor numbers causes a regain of this high field Fe(III) resonance to various degrees depending upon initial water content and the solvent. For DCE the high field Fe(III) resonance intensity decreases as dehydration increases and almost disappears at 110°C [225°C in the case of Ca(II)]. The important point here is that after solvent treatment, the cation position varies with initial water content even though the clay is swollen to equivalent spacings as previously suggested by Barshad (1952). From the difference in signal intensity, it appears that NIB keeps the cations at a greater distance from the clay surface on the average than DCE since it coordinates a given cation somewhat more strongly than DCE. In PY the high field Fe(III) resonance intensity is even greater, probably due to the combined effects of increased cation solvation and the higher basal spacing. These results qualitatively agree with those of Shainberg and Kemper (1966) who showed that the fraction of relatively immobile ions residing at the clay surface in pastes increased in the series $H_2O < \text{methanol} < \text{ethanol}$. In the case of Cu(II) smectite, the minimum temperature of dehydration at which the high field Fe(III) resonance

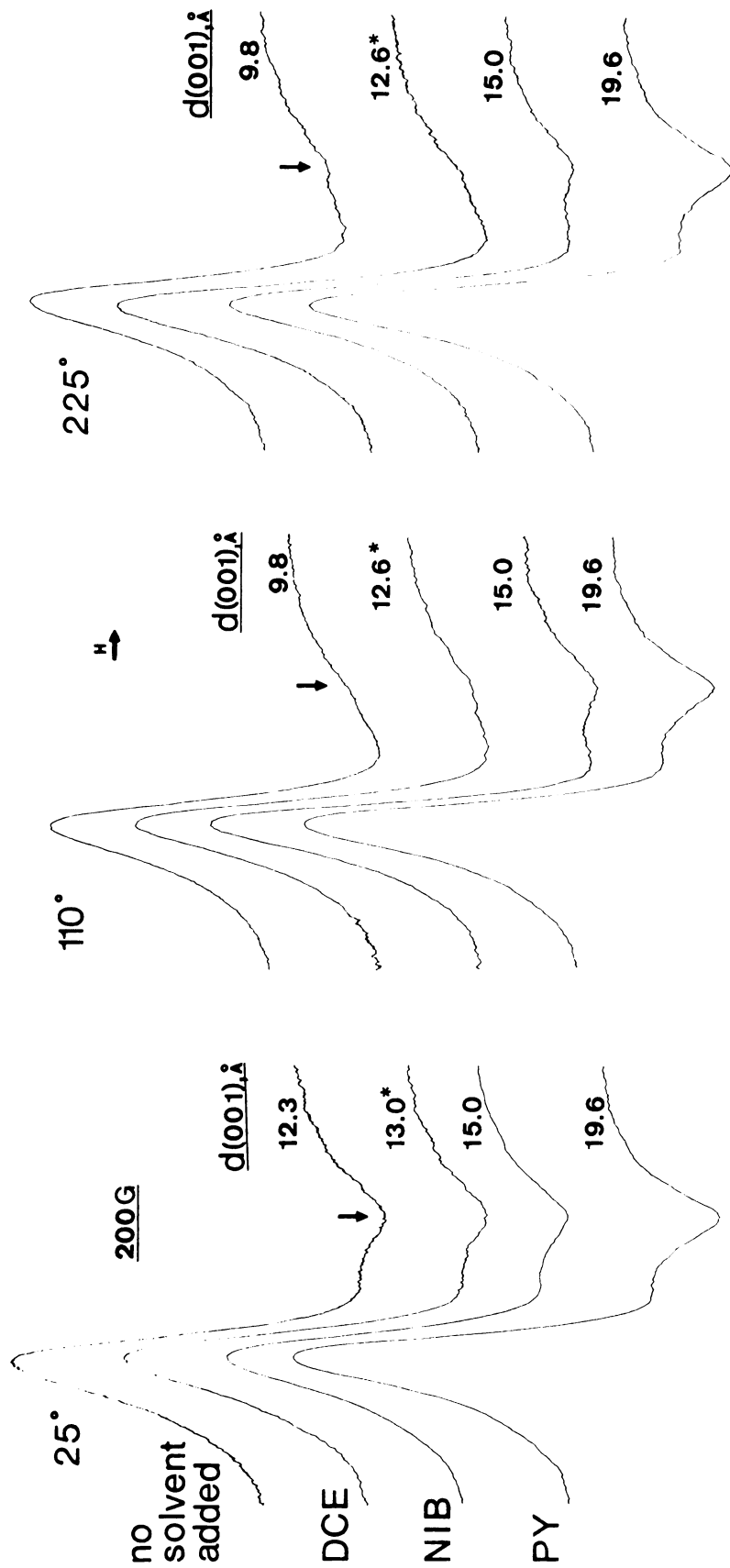
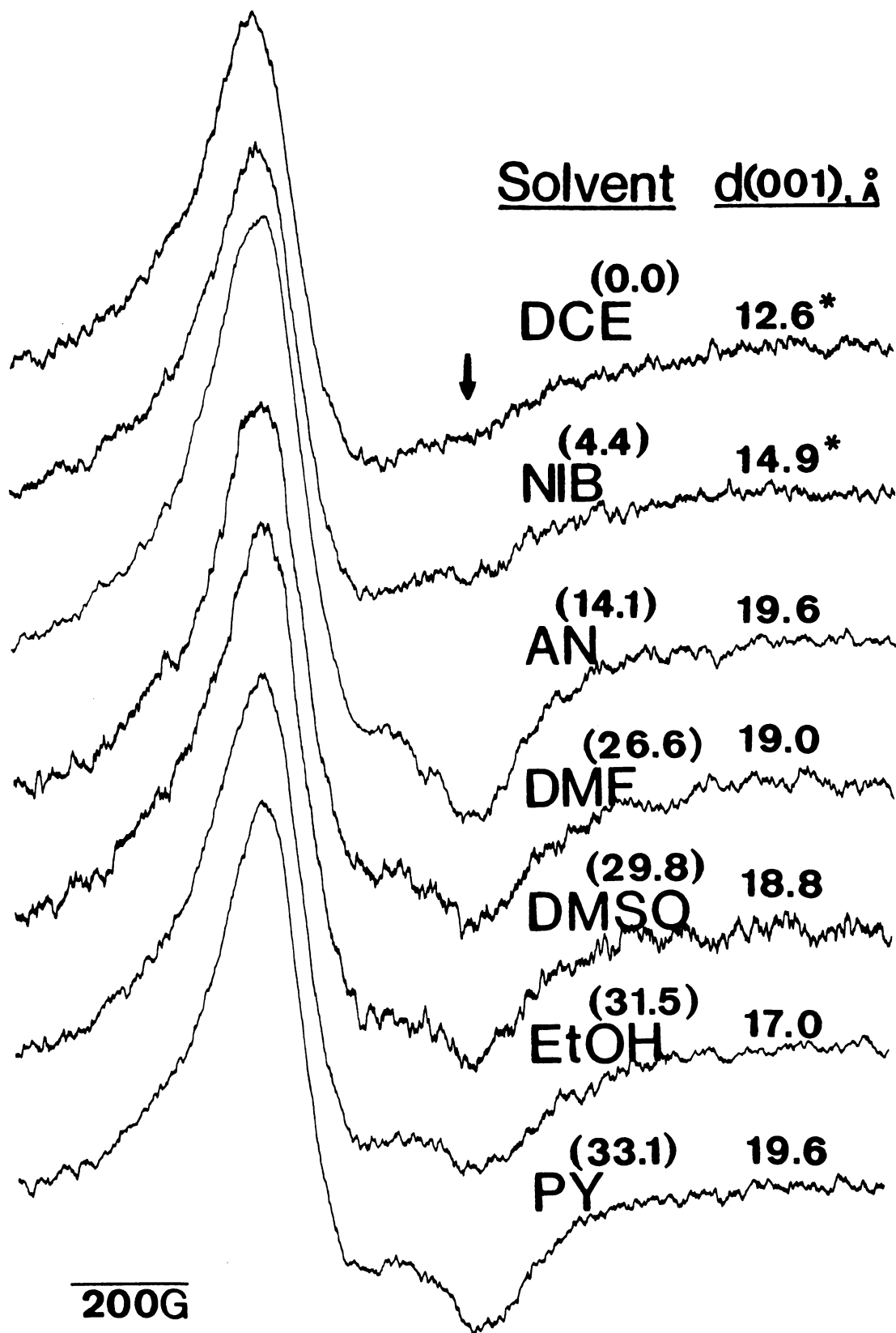


Figure 2. ESR spectra of structural iron in oriented films of Na(I) smectite after heat treatment and solvation. The downward arrow indicates $g=3.6$.

disappears is 140°C for both DCE and NIB whereas for Ca(II) smectite in NIB, the high field resonance Fe signal remains even after the 225°C heat treatment and resolvation.

The degree to which the ion is removed from the smectite surface (or hexagonal hole) appears to be related to the Gutmann Donor Number of the solvent and the nature of the exchangeable cation. Figure 3 shows that for Na(I) smectite dehydrated at 110°C and resolvated with the indicated solvents, a Gutmann Donor Number of about 14 is required for complete solvation of Na(I) which results in its removal from the surface. Above this value, the sodium ions appear to be fully solvated as indicated by the high field Fe(III) resonance intensities. However, the same experiment (i.e., dehydration at 110°C) conducted with Ca(II) and Cu(II) saturated montmorillonite indicates that these divalent ions retain some coordination water which keeps the ion away from the surface, since the high field Fe(III) resonance was clearly visible even in DCE and NIB and supported by infrared spectra indicating the presence of water. Since exchange of a low donor number solvent molecule (DCE or NIB) for a coordinated water molecule on the cation is unlikely, the size of the cation-water complex precludes penetration of the ion into the hexagonal hole in the silicate surface in contrast with the case of unsolvated Na(I) ion. Consequently, the Fe(III) in the $g=3.6$ site is not perturbed by Ca(II) - and Cu(II) -water complexes as much as by dehydrated Na(I) .

Figure 3. ESR spectra of structural iron in oriented films of Na(I) smectite swollen by various solvents. Numbers in parentheses are Gutmann Donor Numbers, while the other numbers are the (001) spacings. The downward arrow indicates $g=3.6$.



Stereochemistry of Cu(II)-solvent complexes. Results from esr spectra of Cu(II) smectite in the solvents shown in Table 4 and x-ray diffractograms indicate that the stereochemistry of the Cu(II)-solvent complexes depends largely upon the nature of the interlayer solvent. The esr data in Table 4 illustrate the variation in types of spectra obtained. Spectra from Cu(II) saturated montmorillonite heated to 110°C and solvated with DMSO and PY are shown in Figure 4 as examples of the shapes of Cu(II) spectra obtained. Spectra of the high field Fe(III) resonance accompany the Cu(II) spectra to illustrate the positions of the Cu(II) ions, and the basal spacings are given in Table 2. As mentioned previously, these high field Fe(III) resonances indicate that the Cu(II) ions are solvated and are located away from the surface.

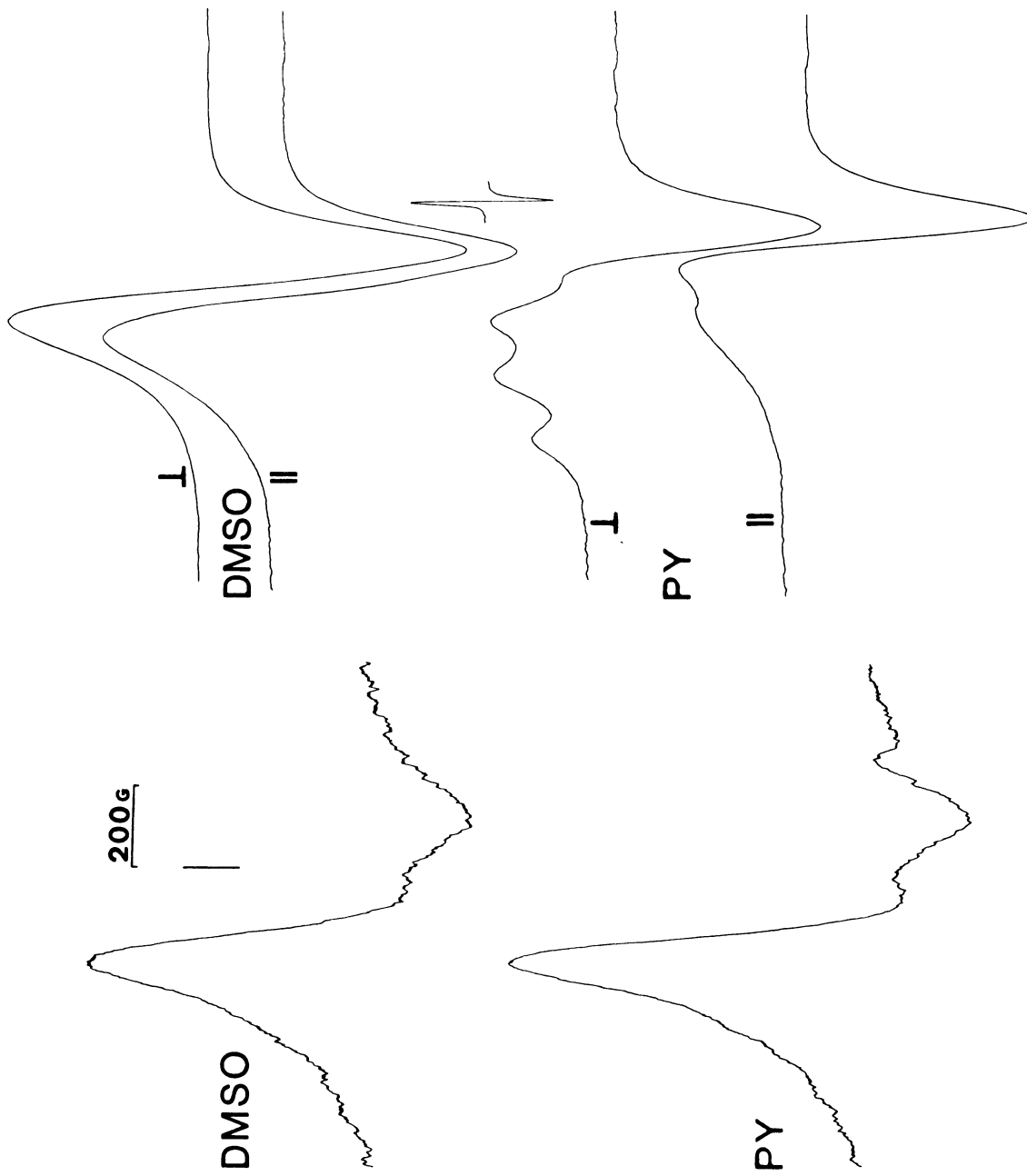
Spectra similar to that for DMSO were also obtained for EtOH, and together with the basal spacings, the spectra indicate that the Cu(II)-solvent complexes are rapidly tumbling in the interlayer either by rotation of the Cu(II)-solvent complex or by rapid Jahn-Teller dynamics which averages the anisotropic components of the g-tensor to give g_{iso} near 2.15. Similar isotropic spectra were previously observed in fully water solvated Cu(II) smectites (Clementz et al., 1973). In the case of PY, the esr spectra showed the presence of tetragonally distorted octahedral complexes of Cu(II) as indicated by the orientation dependence of the $g_{\parallel}$ and $g_{\perp}$ components of the g-tensor. Similar spectra were

Table 4. Electron spin resonance data for Cu(II) in smectite treated with various solvents.*

Exchange ion	Added solvent	$\epsilon_{ }$	$\epsilon_{\perp}$	ϵ_{iso}	$A_{ }, \text{cm}^{-1}$
Cu(II)	DCE	2.30	2.10	--	0.0132
	NIB	--	--	2.14	--
	AN	2.27	2.07	--	0.0140
	DMF	2.29	2.09	--	0.0142
	DMSO	--	--	2.14	--
	EtOH	--	--	2.16	--
	PY	2.24	2.06	--	0.0139
Ca(II)*Cu(II) (9:1 mole ratio)	DCE	No observable spectrum			
	NIB	No observable spectrum			
	AN	2.27	2.06	--	0.0140
	DMF	--	--	2.11	--
	DMSO	--	--	2.11	--
	EtOH	--	--	2.11	--
	PY	2.24	2.05	--	0.0154

* Smectite was heated to 110°C before solvents were added.

Figure 4. ESR spectra of structural iron (left) and exchangeable Cu(II) (right) in oriented films of Cu(II) smectite solvated in DMSO and PY. Cu(II) spectra are shown for two orientations of the films with respect to the magnetic field. The vertical bar indicates $g=3.88$; the free electron signal indicates $g=2.0028$.



obtained for AN. The lower values for $g_{||}$ in PY and AN probably indicate the increased covalent nature of the Cu-nitrogen bond over the Cu-oxygen bond in those solvents with oxygen donor atoms (Kivelson and Neiman, 1961). The x-ray basal spacing of these two systems would allow space for four PY or AN molecules in equatorial positions and two water molecules in axial positions in each complex with the $H_2O-Cu-H_2O$ axis oriented perpendicular to the silicate sheets. These observations do not preclude the existence of a Cu(II) complex in which some of the PY in equatorial positions is linked to the Cu(II) ion through water molecules as suggested by Farmer and Mortland (1966).

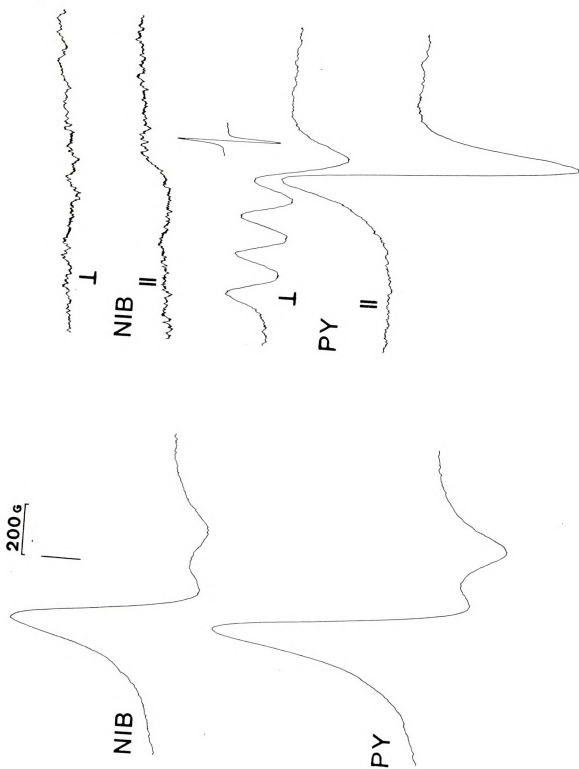
The spectra of the DMF system indicate a mixture of tetragonally distorted octahedral complexes whose z -axes are not perpendicular to the clay sheets and square planar complexes which lie parallel to the smectite sheets. Clementz et al. (1973) noted similarly oriented octahedral complexes in hydrated Cu(II)-vermiculite in which both $g_{||}$ and $g_{\perp}$ components of the g -tensor were resolved when the clay sheets were oriented either perpendicular or parallel to the magnetic field. This interpretation is consistent with the $13.0-16.7^{\circ}$ basal spacing when the presence of mixed Cu(II)- H_2O -DMF is taken into account in which distorted octahedral complexes occupy the more swollen interlayers and the square planar complexes occupy less expanded interlayers.

Esr spectra of Ca(II)-montmorillonite doped with

10 mole % Cu(II), heated to 110°C, and treated with solvents were recorded for both Cu(II) and the high field Fe(III) resonance which are exemplified by spectra shown in Figure 5. The high field Fe(III) resonances indicate that in all cases most, if not all, interlayer ions are away from the surface of the silicate. Spectra of Cu(II) in this doped smectite solvated with AN, DMSO, EtOH, and PY were similar to the corresponding Cu(II) spectra in the fully Cu(II) saturated smectite as Table 4 indicates. The spectrum of Cu(II) in the doped smectite solvated with DMF was isotropic in shape which indicated averaging of the $g_{||}$ and $g_{\perp}$ components. This spectrum was not orientation dependent as was that of the fully saturated Cu(II)-smectite solvated in DMF, probably because of the higher basal spacing in the doped smectite (19.1Å versus 16.7Å interstratified in the Cu(II)-smectite).

With DCE and NIB as the added solvents, spectra of Cu(II) in fully saturated Cu(II)-smectite and Cu(II)-doped Ca(II)-smectite dehydrated at 110°C before solvent treatments, reveal differences in the rigidities of Cu(II)-solvent complexes in the interlayer space. The spectra of Cu(II) in fully saturated Cu(II)-smectite solvated with DCE are similar to those in Figure 4 for PY, thus indicating that the Cu(II)-solvent complex in DCE is tetragonally distorted with its z -axis perpendicular to the clay sheets. These observations are consistent with the basal spacing of 13.2Å in which there is a square planar complex of hydrated

Figure 5. ESR spectra of structural iron and exchangeable Cu(II) in oriented films of Cu(II)-doped Ca(II) smectite solvated in NIB and PY. Cu(II) spectra are shown for two orientations of the films with respect to the magnetic field. The vertical bar indicates $g=3.88$; the free electron signal indicates $g=2.0028$.



Cu(II) ions. In NIB, the fully saturated Cu(II)-smectite swells to $14.7\text{\AA}$ which allows the Cu(II)-H₂O complex to tumble in the interlayer. This greater degree of tumbling averages the $g_{\parallel}$ and $g_{\perp}$ components of the g-tensor to give an isotropic spectrum similar to that in Figure 5 for DMSO.

In the case of the Cu(II)-doped-Ca(II)-smectite, dehydrated at 110°C and treated with DCE and NIB, no Cu(II) spectrum is observed. Since the spectra reappear at 77°K , rapid spin relaxation mechanisms are apparently operating which broaden the Cu(II) signal beyond recognition at room temperature. Since the Cu(II) is hydrated even in the presence of excess NIB or DCE because of the low Gutmann donor number of DCE and NIB, the Cu(II)-water complex could be spinning rapidly in the solvent and relaxed through anisotropic g-tensor and spin-rotational relaxation mechanisms (Wilson and Kivelson, 1966; Atkins and Kivelson, 1966). The differences between the spectra of Cu(II) in the fully Cu(II) saturated clay and the Cu(II)-doped-Ca(II) clay (both solvated by DCE and NIB) may be explained on the basis of different dehydration levels of the two clays. The lack of an observable Cu(II) spectrum in the Cu(II)-doped-smectite indicates that water associated with a given Cu(II) ion in the Cu(II)-doped-Ca(II) interlayer (where there are 3-4 water molecules per ion) apparently interacts less with another cation-water complex than does a given Cu(II)-water complex in the fully Cu(II) saturated clay (where there are 6-8 water molecules per ion). Since this interionic-complex

interaction may be less in the Cu(II)-doped clay, the complex is freer to tumble or rotate, and the electron spin is thus relaxed to a greater degree. Water structure is apparently better developed in the fully Cu(II) saturated clay; hence, the complexes are more rigid and unable to cause extreme broadening of the esr signal. Similar observations were made in other Cu(II)-doped smectites (McBride et al., 1975).

CONCLUSIONS

(1) Little relationship is found between the crystalline swelling of smectite and various bulk properties of the interlayer solvent. These properties include dielectric constant, dipole moment, surface tension, and Gutmann donor number.

(2) Crystalline swelling is not necessarily accompanied by cation movement to positions midway between the silicate sheets. The removal of Na(I) ions from hexagonal holes in the silicate surface requires a solvent with a Gutmann donor number of about 14 or greater.

(3) No relationship between crystalline swelling and charge density is found except in the case of water as the solvent. Anomalous behavior occurred in the reduced charge Na(I) saturated smectite systems in that water was the only solvent in which the smectite did not swell.

(4) Esr data indicate considerable variety in the stereochemistry of Cu(II) ions in the interlayers in

concurrence with Olejnik, Posner, and Quirk (1974).

Factors influencing this stereochemistry include; (a) the nature of the added solvent, (b) the initial water content of the interlayer and its strength of interaction with the added solvent, (c) the basal spacing. Where complex formation is non-homogenous, mixed spectra are obtained. The results from x-ray diffraction and esr spectroscopy reported here illustrate the complexity of smectite swelling.

PART II

PROPERTIES OF HECTORITE CONTAINING Cu(II)-
AND Fe(II)-1,10-PHENANTHROLINE CHELATES
AS EXCHANGE IONS

INTRODUCTION

Adsorption of molecular 1,10-phenanthroline (hereafter designated as phen) has been used to determine surface areas of various clay mineral species (Lawrie, 1961; Bower, 1962). Although metal ion complexes of phen have been known for many years (Blau, 1898) no reports were found concerning the interaction of these complexes with clay minerals. Complexes of phen with transition metal ions are noted for their high formation constants in aqueous solution and in some cases for their high molar absorptivity. Of particular note is the tris-phen iron (II) complex which finds usefulness as an indicator in oxidimetry because of its high molar absorptivity (10^4), its high stability in strongly acid solutions, and its reversible high oxidation potential (1.06 V) (review by Schilt, 1969). In addition to their oxidation-reduction properties, the geometry of the $M(\text{phen})_3^{n+}$ (where M=metal ion in oxidation state n+) complexes could make them useful as molecular props in the interlayer space of layer silicate minerals. Consequently, large areas of the smectite surface should be exposed for the adsorption of small molecules. These phen-clay complexes should produce interlayer spaces on the order of $8 \text{ \AA}$ in contrast to tetramethylammonium cations (Clementz and Mortland, 1974) and tetraethylenediammonium dications (Mortland and Berkheiser, 1976) which give interlamellar thicknesses of $4.0 \text{ \AA}$ and $4.6 \text{ \AA}$, respectively. When supported on the layer silicate surface, these transition metal

complexes could also find application in reactions which are catalyzed by outer-sphere electron transfers.

In the present study adsorption characteristics and properties of the Cu(II) and Fe(II) phen complexes on Na(I) hectorite have been examined. These included solution selectivities with other ions, adsorption of water and benzene, qualitative oxidation-reduction reactions, and a study of the stereochemistry of the Cu(II)-phen complex on the clays.

EXPERIMENTAL

Preparation of 1,10-phenanthroline-metal complexes. The ligand used was purchased as reagent grade compound and was further purified by recrystallization from water before use. In preparation of all complexes the 1,10-phenanthroline (phen) was added to aqueous solutions of the metal chloride or sulfate salt in the required stoichiometric ratios; some complexes were precipitated from solution by adding the Na salt of the anion desired. $\text{Fe(phen)}_3\text{Br}_2 \cdot 3\text{H}_2\text{O}$ was prepared according to Blau (1898). $\text{Fe(phen)}_3(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ was prepared according to procedures given by Schilt and Taylor (1959) and was wrapped in Al foil to prevent photoreduction and stored over anhydrous CaCl_2 . $\text{Ni(phen)}_3\text{Cl}_2$ was prepared according to Inskeep (1962) but was not crystallized from solution. $\text{Cu(phen)}_3(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ was prepared after Inskeep (1962) and stored as the pale blue powder. $\text{Cu(phen)}_2\text{ClO}_4$ was prepared after the method of Schilt and Taylor (1959)

and was stored as the dark violet powder.

Preparation of metal-complex exchange forms of hectorite.

For experiments that required thin films, the metal-phen complex was dissolved in 95% EtOH and the Na-exchange form of the smectite was placed in the solution. In order to accelerate the exchange, the closed beaker was placed in an oven at 75°C until the exchange was complete (determined by observing the disappearance of the colored complexes from solution). Acetonitrile solutions of $\text{Fe(phen)}_3(\text{ClO}_4)_3$ and $\text{Cu(phen)}_2\text{ClO}_4$ were used to prepare hectorite films containing these complexes. Nitrogen gas was bubbled through the solution in order to exclude H_2O and to prevent oxidation of the Cu(I) complex. Both metal-phen complexes were used immediately after preparation.

Ion exchange and selectivity experiments. Ion exchange isotherms were developed for the adsorption of Fe(phen)_3^{2+} and Cu(phen)_3^{2+} on Na-hectorite by adding the appropriate amount of metal complex aqueous standard solution to 100.0 mg Na-hectorite and bringing the suspension volume to 50.00 ml. The amount of metal complex adsorbed by the clay was calculated after the analyzing the supernatant solution for the metal complex concentration by UV-VIS spectrophotometry. Equilibrium was established after 24 hours; supernatant concentrations were stable up to one month. Adsorption isotherms were repeatable to within experimental error as determined by checking selected points on the isotherms three times.

Ion exchange selectivity curves were produced by adding appropriate volumes of standard solutions of MgCl_2 , tetra-n-propylammonium bromide, or $\text{Ni(phen)}_3\text{Cl}_2$ to fully saturated Fe(phen)_3^{2+} or Cu(phen)_3^{2+} hectorite. The hectorite in this case was prepared by adding 1.00 symmetry of each metal complex to 100.0 mg 100°C dried Na-hectorite in water suspension, mixing overnight, and washing free of excess salts.

Surface area measurements. Na-hectorite partially exchanged with Fe(phen)_3^{2+} and Cu(phen)_3^{2+} from zero to one equivalent fraction were freeze-dried and dehydrated at 150°C overnight under flowing He gas. Surface areas were then determined with a Perkin-Elmer Model 212B Sorptometer at liquid N_2 temperature using data plotted according to the BET equation. Approximately 50 mg of adsorbent were used for each determination.

Oxidation-reduction experiments. Qualitative experiments were performed on both Cu and Fe phen hectorite complexes. In all cases reagent grade chemicals were used as received from the supplier.

Spectral measurements. Ir, UV-VIS, and ESR spectra were taken of selected complexes. IR spectra were recorded on a Beckman Model IR-7 spectrophotometer using a Pyrex glass cell equipped with NaCl windows. UV-VIS spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer using either 1 cm quartz cells for solutions or fused quartz discs for thin films. ESR spectra were recorded at X-band on a Varian E-4 EPR spectrometer using



quartz tubes containing thin films. Standard pitch served as a standard for which $g=2.0028$.

Adsorption isotherms. Water adsorption isotherms were developed by placing fully saturated $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Cu}(\text{phen})_3^{2+}$ hectorite (freeze dried and dehydrated at 150°C overnight) in atmospheres of varying relative humidity provided by H_2SO_4 and saturated salt solutions at 20°C . The weight gain was compared to the 150°C dried material. Benzene adsorption isotherms at 25°C were developed using calibrated quartz helices in a high vacuum system.

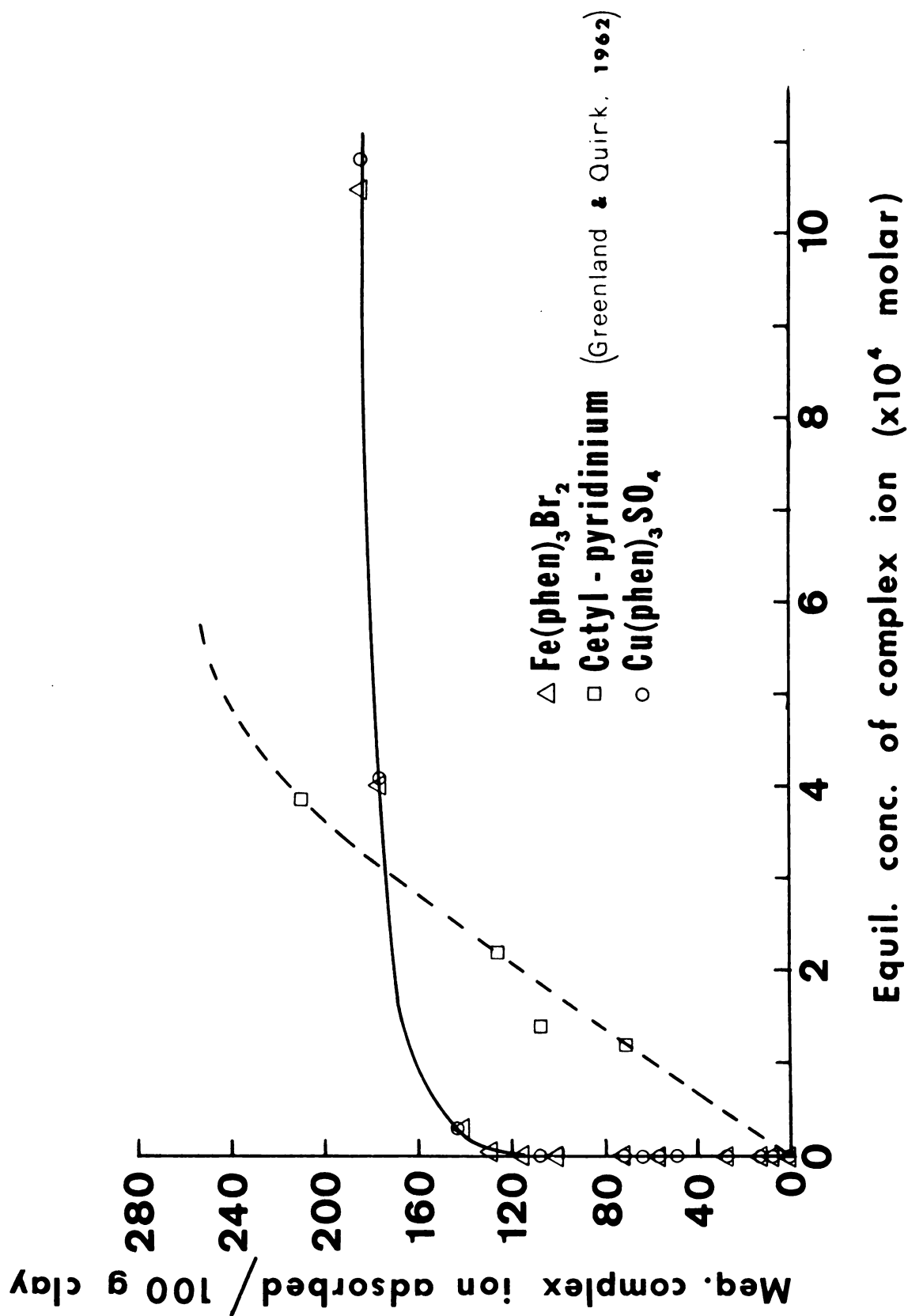
X-ray diffraction measurements. Thin films were mounted in a Phillips X-ray diffractometer using Ni filtered $\text{Cu-K}\alpha$ radiation. Diffractograms were usually recorded to four orders of reflections. When higher orders of reflections were present, the average of the (001) spacings determined by the orders was taken.

Preparation of hectorite. The hectorite used was obtained from Baroid Division, National Lead Company as a centrifuged and spray dried powder. Exchangeable Na(I) in the raw material was 84.2 me per 100 g; Cu(II) saturation and conductimetric titration of Cu(II) with NaOH gave a CEC of 70. me/100g.

RESULTS AND DISCUSSION

Ion adsorption and selectivity. Both $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Cu}(\text{phen})_3^{2+}$ exhibit a marked affinity for the mineral surface in aqueous solution (Figure 1) when exchanged onto a

Figure 1. Adsorption isotherms of $\text{Fe}(\text{phen})_3\text{Br}_2$ and $\text{Cu}(\text{phen})_3\text{SO}_4$ on Na(I)-hectorite and cetylpyridinium bromide on montmorillonite.

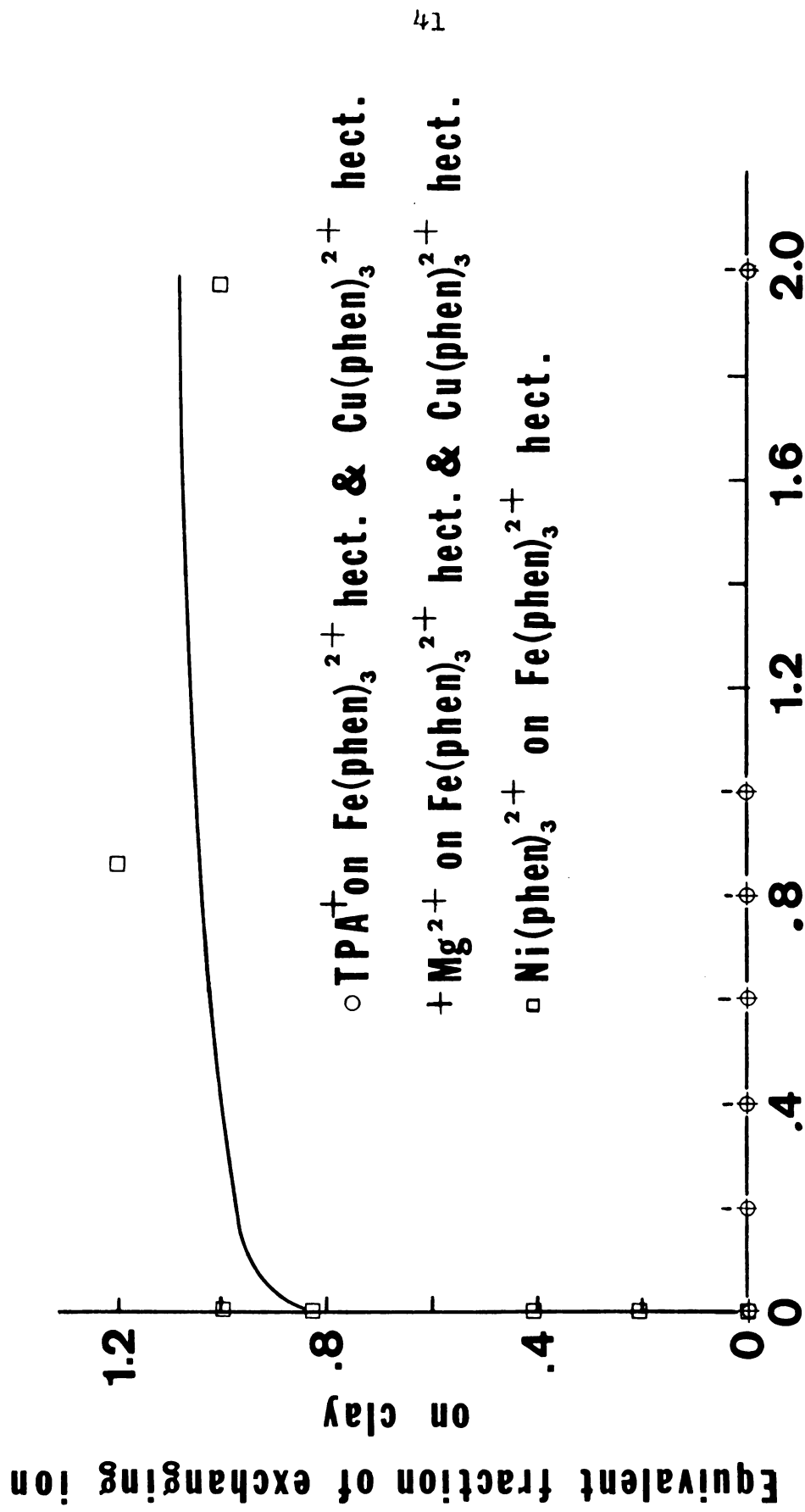


Na(I) hectorite. Stronger coulombic attraction in the divalent complex than that of the Na(I) ion as well as van der Waals interactions between the complex and the clay surface, probably account for the preference. Amounts of $M(\text{phen})_3^{2+}$ adsorbed beyond the exchange capacity are presumably adsorbed as the molecular complex (the bromide or sulfate salt) in much the same manner as long chain 1-n-alkyl pyridinium bromides in Na(I)-bentonite (Greenland and Quirk, 1962). Compared to the cetyl pyridinium bromide, the phenanthroline complexes show a more distinct selectivity most likely due to the divalent character of the phenanthroline complexes.

Although cetyl pyridinium produces a clay complex with a 42Å basal spacing which is stable against washing with water or benzene, the phenanthroline clay complex was not stable against washing. When the hectorite adsorbed the complexes in excess of the exchange capacity almost all of the non-coulombic bound complex was removed by washing with water. Analysis of $\text{Fe}(\text{phen})_3^{2+}$ in the clay-complex after washing indicated that 83 ± 5 meq/100g remained on the clay. A lower level of van der Waals interaction between organic ions in the $M(\text{phen})_3^{2+}$ complex, in comparison with the cetyl pyridinium complex, may account for this difference. In addition, the $M(\text{phen})_3^{2+}$ adsorption isotherms were reproducible within experimental error in contrast to the reported cetyl pyridinium adsorption data. Hydrolysis of the cetyl pyridinium complexes may explain the erratic

behavior of those systems (Greenland and Quirk, 1962). The $M(\text{phen})_3^{2+}$ complexes were stable over the course of the investigation with no observable change in the molar absorptivity of the complexes in solution. Moreover, X-ray basal spacings of the air dry complexes which contained more than one symmetry of $M(\text{phen})_3^{2+}$ were not significantly different than those of clay-complexes with one symmetry. In addition, no peaks were observed for the free salt. All those observations suggest that the excess molecular complexes are weakly bound by the clay and occupy remaining available space.

Additional experiments were performed to test the selectivity of the $M(\text{phen})_3^{2+}$ cations versus other cations for the clay surface. Figure 2 shows that when the hectorite is first saturated with the $M(\text{phen})_3^{2+}$ cation neither large monovalent organic cations (molecular weight of TPA=186) nor small divalent cations $[Mg(II)]$ exchanged the $M(\text{phen})_3^{2+}$ cation from the clay. However, when $Ni(\text{phen})_3^{2+}$ was used to exchange $Fe(\text{phen})_3^{2+}$ from the clay, a great deal of the $Ni(\text{phen})_3^{2+}$ was adsorbed while only a small fraction of the $Fe(\text{phen})_3^{2+}$ was released. The adsorption curve of $Ni(\text{phen})_3^{2+}$ on $Fe(\text{phen})_3^{2+}$ hectorite levels off at about one symmetry. However, analysis of the supernatant solution showed that in the plateau region of the adsorption curve only about 0.2 symmetries of $Fe(\text{phen})_3^{2+}$ were released, indicating most of the $Ni(II)$ complex was adsorbed by non-coulombic forces. This



Equivalent fraction of exchanging ion in solution

Figure 2. Exchange isotherms for three ions on $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Cu}(\text{phen})_3^{2+}$ hectorite systems.

observation agrees with data showing the excess adsorption of Fe(phen)_3^{2+} on Na(I)-hectorite beyond the exchange capacity. Van der Waals forces appear to be responsible for adsorption of M(phen)_3^{2+} complexes on hectorite beyond the exchange capacity.

X-ray diffraction studies. Thin films of Na(I)-hectorite containing fractional symmetries of Cu(phen)_3^{2+} or Fe(phen)_3^{2+} were observed in 95% EtOH solution and the solvent removed by drying in air. Basal spacings were determined at different levels of hydration and are shown in Table 1. The iron systems generally exhibited two peaks indicative of separate phases at $12 \text{ \AA}^{\circ}$ and $17.4 \text{ \AA}^{\circ}$. The intensity of the higher basal spacing in these systems increased with the amount of complex cation on the clay and at 80% saturation, the $12 \text{ \AA}^{\circ}$ spacing is a weak shoulder on the $17.4 \text{ \AA}^{\circ}$ peak. At 100% saturation only the $17.4 \text{ \AA}^{\circ}$ peak appeared and persisted to 350°C . On the other hand, diffractograms of the copper systems indicated more random interstratification of $12 \text{ \AA}^{\circ}$ layers with those at $17.4 \text{ \AA}^{\circ}$. Apparently, the strength of the van der Waals forces favors adsorption of the complexes in a given interlayer before adsorption occurs in succeeding interlayers. This adsorption results in a progression toward a higher proportion of $17.4 \text{ \AA}^{\circ}$ layers in both systems. If the complex cations were uniformly distributed over the clay surface, a constant $17.4 \text{ \AA}^{\circ}$ would be expected. The van der Waals interaction between initially exchanged metal complexes and

Table 1. X-ray basal spacings of Na(I) hectorite exchanged at various levels with Fe(phen)_3^{2+} and Cu(phen)_3^{2+} .

Ion in Complex	S*	Air dry	100°C	150°C
Fe(II)	0.0	13.6	11.8	11.8
	0.2	15.8, (13.2) ^a	(12.4), 16.0	12.4, 16.0
	0.4	16.4, 13.2	(16.7), 12.3	(17.0), 11.8
	0.6	(16.7), 13.2	17.5	(17.2), 11.8
	0.8	17.4 ^r	17.4 ^r	17.0 ^r
	1.0	17.4 ^r	17.4 ^r	17.2 ^r
Cu(II)	0.0	13.6	11.8	11.8
	0.2	12.6	12.4	11.8
	0.4	14.7	14.7	13.6
	0.6	15.8	15.5	15.5
	0.8	16.4	16.1	16.0
	1.0	17.5 ^r	17.5 ^r	17.1 ^r

* S denotes fraction of exchange sites occupied by complex ion. ^r denotes a rational system. ^a number in () indicates the more intense peak.

succeeding complex ions may be an important driving force in promoting segregation. The X-ray results are in accord with molecular dimensions of the tris-phenanthroline complexes. Space-filled models of the complexes show that the cations are approximately $8 \text{ \AA}$ thick (i.e., along the C_3 symmetry axis). When the C_3 axis is perpendicular to the silicate sheets, a $17.6 \text{ \AA}$ spacing should result and is in agreement with the data. Interstratification is more pronounced in the Cu systems than in the Fe systems presumably because of the slightly greater lability of the phenanthroline ligands on Cu(II) than on Fe(II). This point is discussed further in the next section. As expected from the geometry of the large complex cations, the basal spacings changed very little upon dehydration.

Adsorption of N_2 and surface area determinations.

$Cu(phen)_3^{2+}$ and $Fe(phen)_3^{2+}$ hectorite systems were prepared by adding 1.00 symmetry (based on a CEC of 0.70 meq/g) of the complex ion to Na(I)-hectorite. After heating 18 hr at $160^\circ C$ under He adsorption isotherms were obtained. Figure 3 shows data from N_2 adsorption isotherms plotted according to BET, Langmuir, and Hüttig equations (Adamson, 1967).

Langmuir's model of adsorption assumes that adsorption occurs as a monolayer and that the heat of adsorption is independent of surface coverage. The Langmuir equation may be written as $p/v_{ads} = 1/bv_m + p/v_m$ where p =pressure of the adsorbate, v_{ads} =volume of gas adsorbed at pressure p and v_m

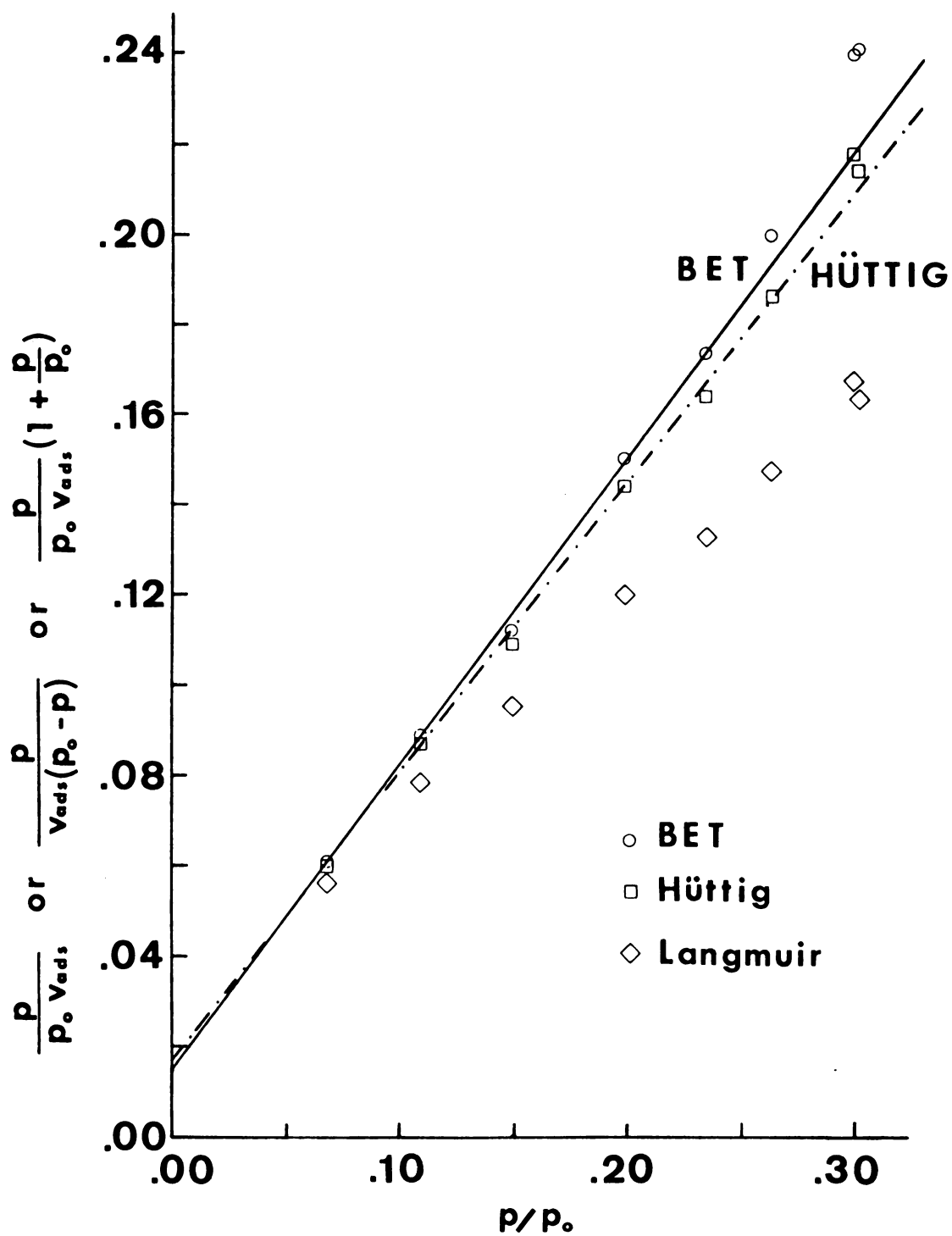


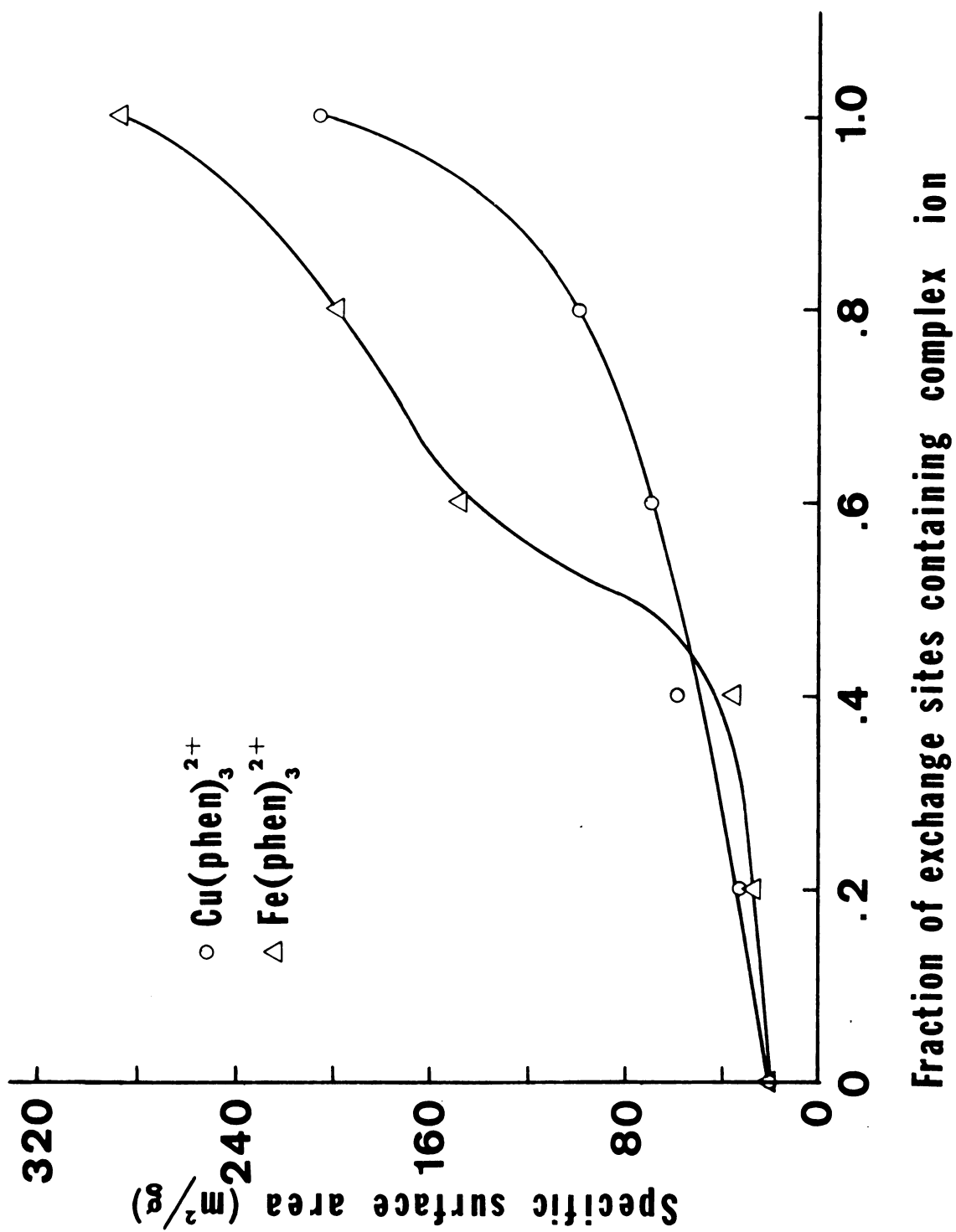
Figure 3. Data for adsorption of N_2 on $Fe(phen)_3^{2+}$ hectorite plotted according to BET, Langmuir, and Hüttig equations.

the volume adsorbed at the monolayer point, b =ratio of rates of evaporation and condensation at the surface. The BET model assumes that the Langmuir equation applies to each layer of a multilayer film and also assumes that the heat of adsorption of the first monolayer may have some special value but the heat of adsorption of each succeeding layer equals the heat of vaporization of the liquid adsorbate. This model may be represented by the equation $x/v_{ads}(1-x) = 1/cv_m + (c-1)x/cv_m$ where $x=p/p_0$, v_{ads} and v_m as before, and c =constant. Hüttig's model is similar to the BET model except that it assumes that each layer acts as an independent Langmuir film. This model is represented algebraically as $x(1+x)/v_{ads} = 1/cv_m + x/v_m$ where the symbols are the same for the BET model. Thus, a model of the $M(phen)_3^{2+}$ hectorite complex in which the silicate layers are propped apart by $\sim 8 \text{ \AA}$, allows for multilayer adsorption in areas unoccupied by the complex ions. In these systems it seems that the BET and Hüttig models provide a more satisfactory picture of the N_2 surface areas than the Langmuir model which was appropriate for monolayer adsorption on the more contracted tetramethyl-ammonium saturated smectites (Clementz and Mortland, 1974). These models give surface areas of 416, 290, 304 m^2/g respectively for Langmuir, BET, and Hüttig equations, and when compared with total calculated areas expected (Table 2), the BET equation gives a more realistic surface area and was used for subsequent surface area calculations.

Figure 4 shows the increase in surface area with increasing saturation of the clay with $M(\text{phen})_3^{2+}$. These results together with the basal spacings suggest that the complex cations may not be regularly distributed in the interlayer space of the smectite, but rather localized sections of the interlayer tend to become $M(\text{phen})_3^{2+}$ saturated before appreciable quantities of complex cations enter other parts of the interlayers. If the $M(\text{phen})_3^{2+}$ cations were regularly distributed in the interlayer, the effect would be a positive deviation from a linear plot linking the homogenous systems. Negative deviation from a linear relationship between specific surface area and the fraction of exchange sites containing the $M(\text{phen})_3^{2+}$ (Figure 4) suggests that layers with higher charge density were filled with the complex ion before layers of lower charge density. Crowding of the large complex ions in some layers would occur and would reduce adsorption of N_2 in those regions. Although the charge heterogeneity was not determined independently in this study, such inhomogeneous charge distribution has been observed previously in smectites and vermiculites (Lagaly and Weiss, 1975).

The generally lower surface areas of the $Cu(\text{phen})_3^{2+}$ hectorite than the $Fe(II)$ analog may possibly be attributed to the partial collapse of some interlayers. ESR spectra indicate that some of the $Cu(II)$ -phenanthroline complexes may be bis complexes in which one of the phenanthroline ligands has been lost from the $Cu(II)$ ion. This is not

Figure 4. Specific surface areas of hectorite fractionally saturated with $\text{M}(\text{phen})_3^{2+}$ calculated from the BET equation.

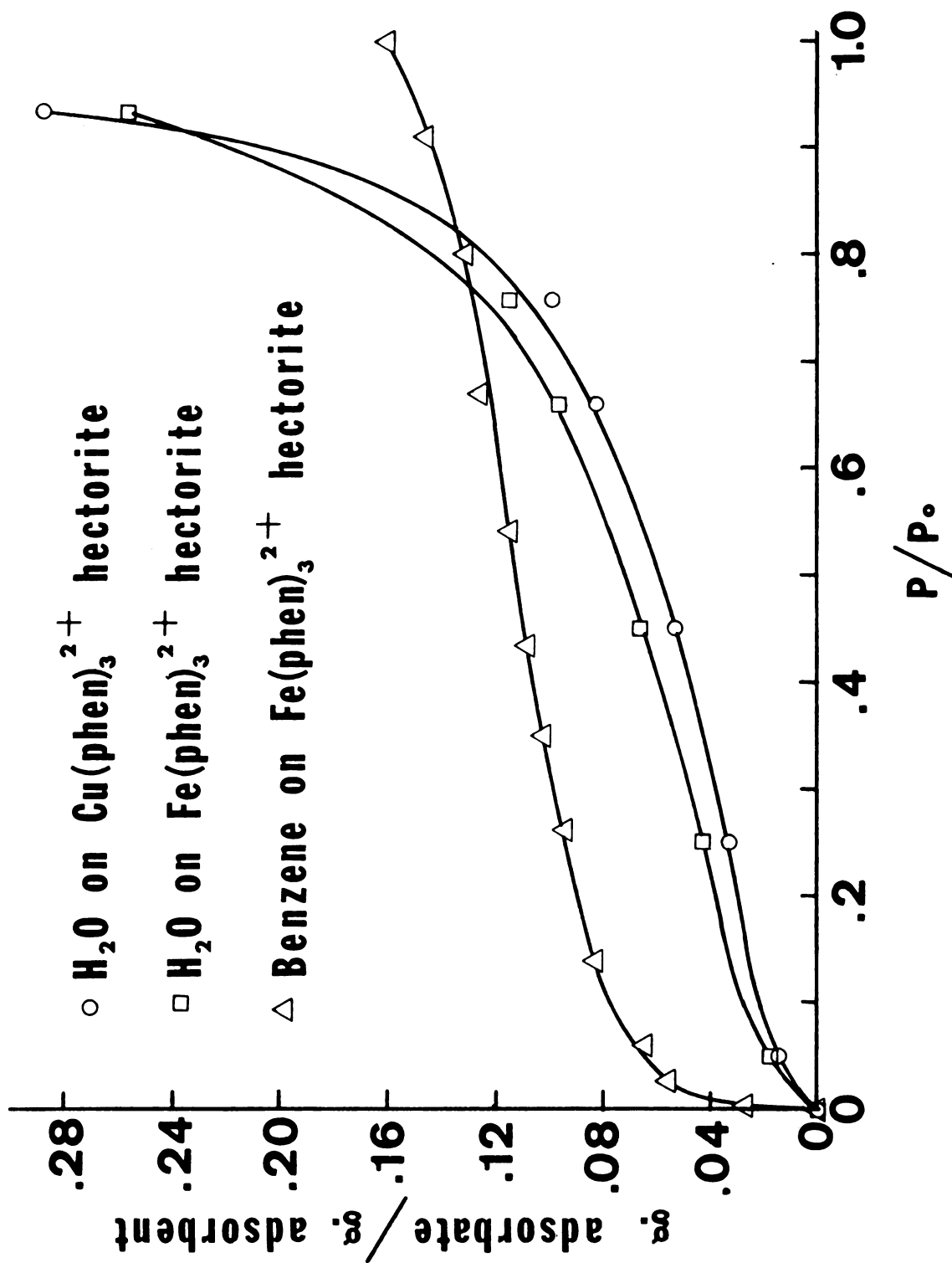


unexpected since the relative instability of the tris-phenanthroline Cu(II) compared with Ni(II) complex has been previously explained due to the absence of Jahn-Teller distortion in the tris-phenanthroline Cu(II) complex (James and Williams, 1961). Inskeep (1962) suggests that greater stability of the tris-phenanthroline Fe(II) complex compared to the Cu(II) species may arise from π -bonding of phen ligands peculiar to Fe(II) in the series Fe(II), Co(II), Ni(II), Zn(II).

Adsorption of water and benzene. Water and benzene adsorption isotherms are shown in Figure 5. Generally, the isotherms may be classed as Type II in Brunauer's classification. However, differences between the water and benzene isotherms are obvious. In the case of the water adsorption isotherms, the low amounts of water adsorbed at low p/p_0 compared to that adsorbed at high p/p_0 indicate that adsorbate-adsorbate interactions predominate over adsorbate-adsorbent interactions. The amount of water adsorbed at p/p_0 less than 0.7 is, however, about the same as that adsorbed by tetramethylammonium saturated bentonite (Gast and Mortland, 1971). Beyond $p/p_0 = 0.7$, approximately twice as much water is adsorbed on the $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Cu}(\text{phen})_3^{2+}$ hectorites as in the tetramethylammonium bentonite and presumably exists as physically bound H_2O in the interstices between the cations.

Water adsorption by $\text{Fe}(\text{phen})_3^{2+}$ hectorite was studied in more detail since this complex gave the highest specific

Figure 5. Adsorption isotherms of H_2O and benzene vapors
on $M(phen)_3$ hectorite at $20^\circ C$.



surface and the metal complex is more structurally stable than the Cu(II) complex. The O-H stretching regions of water were observed by IR spectroscopy at 50% r.h. and gave bands which indicated that there are apparently two different kinds of H_2O present in the $Fe(phen)_3^{2+}$ hectorite complex. The first of these produces a band at 3597 cm^{-1} which has been attributed previously to H_2O weakly hydrogen bonded to silicate oxygens (Farmer and Russell, 1967). The second band centered at 3400 cm^{-1} is indicative of H_2O coordinated to the metal cation and hydrogen bonded to other H_2O molecules in the second coordination sphere (Farmer and Russell, 1967). Other workers have also observed a band near 3400 cm^{-1} and attributed it to H_2O weakly coordinated to Fe(II) in $Fe(phen)_3^{2+}$ which had been dissolved in nitromethane solutions (Burchett and Meloan, 1972). If a model of the $Fe(phen)_3^{2+}$ hectorite is considered in which the complex cations are separated by a distance of about $12\text{ \AA}$, the adsorbed water could be bound to either the silicate surface or to the metal nucleus of the complex ion, the latter being more energetic. With this model a maximum of six water molecules would be allowed to coordinate to the complex cation (two water molecules in each void between phenanthroline planes) in a manner similar to a structure suggested by Jensen, Basolo, and Neumann (1958). The remaining water molecules in the hectorite complex would likely be weakly bound to the silicate sheet and at high p/p_0 would exist as interstitial water.

Because of the similarities in the structures and charges of the Fe(II) and Cu(II) phenanthroline complexes, the isotherms are expected to be closely similar and this appears to be the case. Even though the 150°C pretreatment of the clay-complex may have caused some collapse of Cu(phen)_3^{2+} complexes, the exposed ligand sites on the Cu(II) complex would adsorb water and thus compensate for an apparent loss in interlayer space compared to that of the Fe(II) analog.

Benzene adsorption is different from that of water in that the isotherm shows that adsorbate-adsorbent interactions are stronger than adsorbate-adsorbate interactions. This behavior is expected since the aromatic character of benzene is similar to the aromaticity of the phenanthroline ligands. At $p/p_o = 0.3$ there are 4.5 benzene molecules for every Fe(phen)_3^{2+} cation on the average. No pleochroism was observed in the IR spectra of oriented thin films containing adsorbed benzene at $p/p_o = 0.5$ (5.2 molecules benzene per cation). Benzene could adsorb on to the phenanthroline molecules via π -electron interaction which would produce orientations of the benzene parallel with the aromatic ligands.

Comparison of surface area requirements of the complex cations and adsorbates with the observed surface areas are in general agreement. These results are summarized in Table 2. The cross-sectional area of the Fe(phen)_3^{2+} cation was calculated from a space-filled molecular model,

Table 2. Summary of calculated and observed BET surface areas of $\text{Fe}(\text{phen})_3^{2+}$ hectorite.

Calculated area occupied by $\text{Fe}(\text{phen})_3^{2+}$ cations including both silicate surfaces of interlayer	548 m ² /g
Observed surface areas	
a) Nitrogen	290 m ² /g
b) Benzene	145 m ² /g
Total surface areas	
a) Complex cation + nitrogen surface area	838 m ² /g
b) Complex cation + benzene surface area	693 m ² /g

* Cross-sectional area of benzene was calculated from

$$\left(\frac{V_{\text{mole}}}{N} \right)^{2/3} \quad \text{where } V_{\text{mole}} = \text{volume of 1 mole benzene and}$$

$N = \text{Avagadro's number.}$

and was taken to be $130 \text{ \AA}^2$ (approximately circular). The higher surface area measured by N_2 adsorption can be rationalized from the smaller molecular dimensions of the N_2 molecule compared with benzene ($16 \text{ \AA}^2$ and $27.8 \text{ \AA}^2$, respectively) in that N_2 may be adsorbed in smaller spaces than benzene. Adsorption of either N_2 or benzene on the surface of the phenanthroline ligands would cause measured surface areas to be high since the area of the adsorbent includes both surface of cation plus mineral surface.

Oxidation-reduction reactions. Oxidation-reduction reactions of both copper and iron phen complexes on hectorite were studied qualitatively. Table 3 summarizes the reactions which were conducted. The most surprising result of this series of experiments was the instability of the Fe(phen)_3^{3+} cation on the clay surface in water. Water caused very rapid reduction of the Fe(III) species to the Fe(II) species. Conversely, neither Ce(IV) nor PbO_2 in $0.1 \text{ N H}_2\text{SO}_4$ with oxidation half-cell potentials near 1.7 volts oxidized the Fe(II)-phen complex on the clay to the Fe(III) form. The clay surface apparently causes an increase in the oxidation potential of the Fe(phen)_3^{2+} - Fe(phen)_3^{3+} couple above 1.06 volts normally observed in water (Hume and Kolthoff, 1943). The cause for this apparent increase in the oxidation potential for the iron complex on hectorite is unclear at this time. A possible explanation may be that interaction with the silicate surface causes destabilization of the oxidized form compared to the reduced form

Table 3. Summary of oxidation-reduction reactions of Fe and Cu phen complexes on clay and in ClO_4^- salts.

Metal ion in phen complex	Solvents or reagents added	Reaction observed*	
		Clay complex	ClO_4^- salt
Fe(III)	H_2O	Rn	N
	Methanol	Rn	N
	Ethanol	Rn	N
	n-butanol	Rn	Rn ^a
	Acetonitrile	N	N
	Acetone	N	N
	Methyl ethyl ketone	Rn	Rn
	Benzene	N	N ^a
	Cyclohexene	Rn	Rn ^a
	1-hexene	Rn	Rn ^a
Fe(II)	PbO_2 in 0.1 N H_2SO_4	N	Ox
	Ce(IV) in 0.1 N H_2SO_4	N	Ox
	Conc. HNO_3	Ox	Ox
Cu(II)	H_2O	N	N
	Acetonitrile	N	N
	Hydrazine	Rn	Rn
	Hydroquinone in 0.1 N NaOH	Rn	Rn
	Dithionite in 0.1 N H_2SO_4	Rn	Rn
Cu(I)	O_2 in air or in acetonitrile	Ox	Ox
	Quinone in 0.1 N H_2SO_4	Ox	Ox
	Ce(IV) in 0.1 N H_2SO_4	Ox	Ox

*Rn=reduction of metal ion, Ox=oxidation of metal ion, N= no reaction. ^a indicates that the ClO_4^- salt was solubilized with acetonitrile and added to the appropriate solvent.

in a manner similar to that observed in other studies (James and Williams, 1961). Increases in the redox potential of iron and copper complexes with substituted phen ligands were thought to be due to steric hindrance between ligands on the metal ion and to greater basicity of the chelates.

Other solvents also cause reduction of $\text{Fe}(\text{phen})_3^{3+}$ on hectorite and include the alcohols, olefins, and methyl ethyl ketone. No correlation was found between solvents causing reduction of $\text{Fe}(\text{phen})_3^{3+}$ on hectorite and solvent ionization potentials or dipole moments.

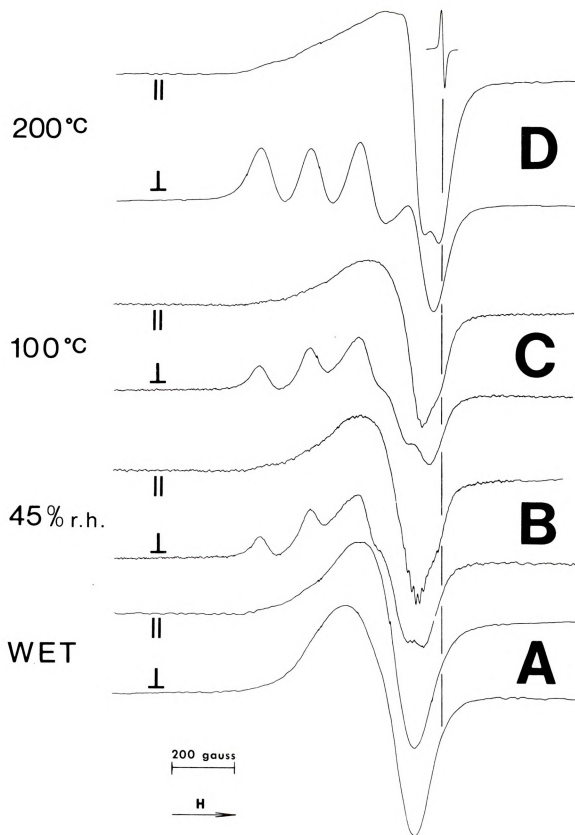
The copper tris-complex apparently loses a ligand upon reduction to Cu(I) . The resulting Cu(I) -phen species is dark violet in color which is characteristic of the $\text{Cu}(\text{phen})_2^{1+}$ species in aqueous solution (Schilt and Taylor, 1959). This reduced form of the copper complex exists on the clay surface presumably in tetrahedral coordination. Visible spectra of the reduced species on hectorite showed a band at 460 nm agreement with previous observations of tetrahedral $\text{Cu}(\text{phen})_2^{1+}$ (Hall, Marchant, and Plowman, 1963). Also, the addition of $\text{Cu}(\text{phen})_2^{1+}$ to Na(I) hectorite gave identical spectral results.

ESR spectroscopy. In order to determine the stereochemistry of the $\text{Cu}(\text{phen})_3^{2+}$ complex on hectorite, ESR spectra of Cu(II) in $\text{Cu}(\text{phen})_3^{2+}$ and $\text{Cu}(\text{phen})_2^{2+}$ were compared. The tris complex on the clay surface should show orientation independent spectra characteristic of other tetragonally

distorted Cu(II) complexes on clays; whereas, the bis complex on the clay should show orientation dependence as in other systems (Berkheiser and Mortland, 1975) where the Cu(II)-ligand plane is parallel to the silicate sheets. Thin films of the $\text{Cu}(\text{phen})_3^{2+}$ hectorite complex were prepared by the addition of one symmetry of the tris complex to Na(I) hectorite in 95% EtOH. The $\text{Cu}(\text{phen})_2^{2+}$ hectorite complex was formed by addition of a half symmetry of $\text{Cu}(\text{phen})_2^{1+}$ to Na(I) hectorite in acetonitrile, and subsequently oxidized to the $\text{Cu}(\text{phen})_2^{2+}$ species with O_2 . ESR spectra of these oxidized complexes are shown in Figure 6 at various levels of hydration. The increasing anisotropy of the spectra as dehydration increases (spectra A to D) is likely due to increasing loss of phen ligands from the coordinations spheres of the Cu(II) ions. Under wet conditions the X-ray basal spacing is $17.5 \text{ \AA}$ which may allow space for the $\text{Cu}(\text{phen})_2^{2+}$ to move rapidly enough in the interlayer space to average the g and A tensors sufficiently to provide the relaxation necessary to produce the observed spectrum. The spectra of the wet $\text{Cu}(\text{phen})_3^{2+}$ hectorite film are similar to spectra A. In this case Jahn-Teller distortion dynamics are probably rapid enough to average the g and A tensors to produce a somewhat isotropic spectrum similar to that observed in the nitrate salt (Allen, Kokoszka, and Inskeep, 1964).

At 45% relative humidity, the Cu(II) ion in both $\text{Cu}(\text{phen})_3^{2+}$ and $\text{Cu}(\text{phen})_2^{2+}$ hectorite becomes more

Figure 6. ESR spectra of oriented thin films of Cu(II) in Cu(phen)_2^{2+} hectorite at different levels of hydration. The free electron signal indicates $g = 2.0028$; films were oriented parallel ($\parallel$) and perpendicular ($\perp$) to the magnetic field H .



statically oriented in the interlayer as indicated by the four lines due to hyperfine splitting caused by interaction of the electron with the copper nucleus. The g -values taken from these spectra (Table 4) indicate that Cu(II) is coordinated predominantly by phen rather than water since g -values of hydrated Cu(II) are near 2.30. Perchlorate and nitrate salts of Cu(phen)_3^{2+} show g -values near 2.24 (Allen, Kokoszka, and Inskeep, 1964; Hathaway, Hodgson, and Power, 1974) as do Cu(II)-pyridine complexes in montmorillonite (Berkheiser and Mortland, 1975). At this level of hydration the Cu(II) ion probably exists as the $\text{Cu(phen)}_2(\text{H}_2\text{O})_2^{2+}$ species since on the average there are 8-10 H_2O molecules per Cu(II) ion. The interlayer spacing of $7 \text{ \AA}$ would accomodate this complex if it were oriented with the elongated axis perpendicular to the clay sheets as the spectra indicate.

As dehydration continues, more water is lost from the axial positions of the $\text{Cu(phen)}_2(\text{H}_2\text{O})_2^{2+}$ species, and the complexes becomes better oriented and homogeneous as the Cu(phen)_2^{2+} species. Spectra of the Cu(phen)_3^{2+} hectorite are identical to those shown in C-D which indicate that a phen ligand is lost from the Cu(II) ion. This loss is not entirely unexpected as noted in previous sections. The loss of the ligand would tend to allow some interlayers to collapse to the spacing determined by the bis complex and uncoordinated phen. This collapse is also suggested by the X-ray diffraction data where a higher degree of

Table 4. ESR parameters for $\text{Cu}(\text{phen})_x^{2+}$ hectorite complexes.

Treatment	g (± 0.005)	g (± 0.005)	g_{iso} (± 0.005)	$A \times 10^4$ cm^{-1} (± 2)	Nitrogen hyperfine, gauss (± 0.5)
$\text{Cu}(\text{phen})_3^{2+}$, wet with H_2O	--	--	2.10	a	a
$\text{Cu}(\text{phen})_3^{2+}$, 45% r. h. 18 hr	2.249	a	--	163	a
$\text{Cu}(\text{phen})_3^{2+}$, 100°C, 18 hr	2.248	a	--	168	a
$\text{Cu}(\text{phen})_3^{2+}$, 200°C, 18 hr	2.240	2.058	--	172	a
$\text{Cu}(\text{phen})_2^{2+}$, ox.*, wet with H_2O	--	--	2.10	a	a
$\text{Cu}(\text{phen})_2^{2+}$, ox., 45% r. h. 18 hr	2.246	2.052	--	168	14.0
$\text{Cu}(\text{phen})_2^{2+}$, ox., 100°C, 18 hr	2.248	2.042	--	170	13.5
$\text{Cu}(\text{phen})_2^{2+}$, ox., 200°C, 18 hr	2.234	2.060	--	167	a

a indicates that these parameters were not resolved.
 * ox. refers to $\text{Cu}(\text{phen})_2^{1+}$ oxidized to $\text{Cu}(\text{phen})_2^{2+}$ on the clay.

interstratification exists in the Cu(II) system than in the Fe(II) system and the surface area measurements where areas of the Cu(II) system are 50% lower than for the Fe(II) analogue.

In addition to hyperfine splitting due to interaction with Cu(II) nucleus, superhyperfine lines due to interaction of the electron with the ligand nitrogen atoms appear at intermediate levels of hydration. Their disappearance in the wet system is probably due to broadening caused by rapid molecular tumbling. Dehydration at 200°C may cause the complex to contact the clay surface where spin-lattice relaxation mechanisms cause broadening of the nitrogen hyperfine lines so that they do not appear.

CONCLUSIONS

(1) The complex cations $\text{Cu}(\text{phen})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ show marked affinity for exchange onto the Na(I)-hectorite surface. Van der Waals interactions appear to be responsible for the adsorption of the complex cations in excess of the exchange capacity. These interactions cause adsorption of $\text{Ni}(\text{phen})_3^{2+}$ on $\text{Fe}(\text{phen})_3^{2+}$ hectorite to behave in the same manner as observed for the adsorption of $\text{Fe}(\text{phen})_3^{2+}$ beyond the exchange capacity. The magnitude of the van der Waals forces is great enough for the complex cations on exchange sites to resist exchange by TPA^+ and $\text{Mg}(\text{II})$. These van der Waals forces may also comprise an important driving force which causes a complete interlayer to be saturated

before adsorption occurs in succeeding interlayers.

(2) Adsorption of gases onto dehydrated $M(\text{phen})_3^{2+}$ hectorite complexes probably occurs as multilayers on areas unoccupied by the complex ion. The high surface areas (up to $280 \text{ m}^2/\text{g}$) and X-ray diffraction data can be successfully interpreted in terms of the complex cation which is oriented in the interlayer with its C_3 symmetry axis perpendicular to the clay sheets, thus permitting adsorption in the interstices between complex ions. The nature of the complex ion in the interlamellar space of hectorite determines the observed adsorption behavior of gases and vapors.

(3) Qualitative estimates of the oxidation potential of the $\text{Fe}(\text{phen})_3^{2+}$ - $\text{Fe}(\text{phen})_3^{3+}$ couple showed that the smectite caused an increase in the potential in water and some alcohols above that in pure solvent. Those solvents not causing such an increase included benzene and acetonitrile. No increase in the oxidation potential was observed for the $\text{Cu}(\text{II})$ -phen-hectorite complex.

(4) ESR data show that $\text{Cu}(\text{phen})_3^{2+}$ loses a ligand phen molecule when situated in the interlayer space of hectorite under some conditions. Loss of the ligand causes a decrease in the surface area of the $\text{Cu}(\text{II})$ analogue compared to $\text{Fe}(\text{phen})_3^{2+}$ hectorite.

SUMMARY AND CONCLUSIONS

Properties of smectite can be altered with different solvents and by exchange with complex metal ions. By changing the swelling medium, the positions of the cations on the surface can be varied and the mobility of the interlayer cations can be altered. Swelling of smectite was found to be complex in nature and was not dependent upon bulk properties of the solvents. Charge density does not influence the degree of smectite swelling except in the case of water as the solvent. When the smectite contains $M(\text{phen})_3^{2+}$ cations, the interlayer spacing is determined by the geometry of the complex ion. In this case the cation exchange and vapor adsorption characteristics of the $M(\text{phen})_3^{2+}$ -clay complex are largely determined by the intrinsic properties of the complex ion. Oxidation potentials are increased in some systems. ESR spectra of both solvated and chelated Cu(II) ions show that the mobility of the Cu(II) ion varies widely depending upon the nature of the solvent or chelate which complexes the ion.

LIST OF REFERENCES

LIST OF REFERENCES

- Adamson, A. W. (1967) Physical Chemistry of Surfaces, pp. 585-589, Interscience Publishers, New York.
- Allen, H. C., Kokoszka, G. F., and Inskeep, R. G. (1964) The electron paramagnetic resonance spectrum of some tris-complexes of Cu(II): J. Amer. Chem. Soc. 86, 1023-1025.
- Atkins, P. W. and Kivelson, D. (1966) ESR linewidths in solution. II. Analysis of spin-rotational relaxation data: J. Chem. Phys. 44, 169-174.
- Barshad, I. (1952) Factors affecting the interlayer expansion of vermiculite and montmorillonite with organic substances: Soil Sci. Soc. Amer. Proc. 16, 176-182.
- Berkheiser, V. and Mortland, M. M. (1975) Variability in exchange ion position in smectite: Dependence on interlayer solvent: Clays and Clay Minerals 23, 404-410.
- Blau, F. (1898) Uber neue organische metallverbindungen: Monatsh. 19, 647-689.
- Bower, C. A. (1962) Adsorption of o-phenanthroline by clay minerals and soils: Soil Sci. 93, 192-195.
- Brindley, G. W. and Ertem, G. (1971) Preparation and solvation properties of some variable charge montmorillonites: Clays and Clay Minerals 19, 399-404.
- Burchett, s. and Meloan, C. E. (1972) Infrared studies of water bound to some extracted phenanthroline and phenanthroline chelates: J. Inorg. Nucl. Chem. 14, 1207-1213.
- Clementz, D. M. and Mortland, M. M. (1974) Properties of reduced charge montmorillonite: Tetra-alkylammonium ion exchange forms: Clays and Clay Minerals 22, 223-229.
- Clementz, D. M., Mortland, M. M., and Pinnavaia, T. J. (1974) Properties of reduced charge montmorillonites: Hydrated Cu(II) ions as a spectroscopic probe: Clays and Clay Minerals 22, 49-57.

- Clementz, D. M., Pinnavaia, T. J., and Mortland, M. M. (1973) Stereochemistry of hydrated Copper (II) ions on the interlamellar surfaces of layer silicates. An electron spin resonance study: J. Phys. Chem. 77, 196-200.
- Ehrlich, R. H., Roach, E., and Popov, A. I. (1970) Solvation studies of sodium and lithium ions by sodium-23 and lithium-7 nuclear magnetic resonance: J. Amer. Chem. Soc. 92, 4989-4990.
- Farmer, V. C. and Mortland, M. M. (1966) An infrared study of the coordination of pyridine and water to exchangeable cations in montmorillonite and saponite: J. Chem. Soc. (A) 1966, 344-351.
- Farmer, V. C. and Russell, J. D. (1967) Infrared absorption spectrometry in clay studies: Clays and Clay Minerals 5, 121-142.
- Gast, R. G. and Mortland, M. M. (1971) Self-diffusion of alkylammonium ions in montmorillonite: J. Colloid Interface Sci. 37, 80-92.
- Greenland, D. J. and Quirk, J. P. (1962) Adsorption of 1-n-alkyl pyridinium bromides by montmorillonite: Clays and Clay minerals 9, 484-499.
- Gutmann, V. (1968) Coordination Chemistry in Non-Aqueous Solvents, p. 19. Springer-Verlag, New York.
- Hall, J. R., Marchant, N. K. and Plowman, R. A. (1963) Coordination compounds of substituted 1,10-phenanthrolines and related dipyridyls: Aust. J. Chem. 16, 34-41.
- Hathaway, B. J., Hodgson, P. G. and Power, P. C. (1974) Single-crystal electronic and electron spin resonance spectra of three tris-chelate copper(II) complexes: Inorg. Chem. 13, 2009-2013.
- Hume, D. N. and Kolthoff, I. M. (1943) A revision of the oxidation potentials of the orthophenanthroline- and dipyridyl- ferrous complexes: J. Amer. Chem. Soc. 65, 1895-1897.
- Inskeep, R. G. (1962) Infrared spectra of metal complexes below 600 cm^{-1} : the spectra of the tris complexes of 1,10-phenanthroline and 2,2'-bipyridine with the transition metals iron(II) through zinc(II): J. Inorg. Nucl. Chem. 24, 763-776.

- James, B. R. and Williams, R. J. P. (1961) The oxidation-reduction potentials of some copper complexes: J. Chem. Soc. 1961, 2007-2019.
- Jensen, A., Basolo, F. and Neumann, H. M. (1958) Mechanism of racemization of complex ions. IV. Effect of added large ions upon the rates of dissociation and racemization of tris-(1,10-phenanthroline)-iron(II) ion: J. Amer. Chem. Soc. 80, 2354-2358.
- Kivelson, D. and Neiman, R. (1961) ESR studies on the bonding in copper complexes: J. Chem. Phys. 35, 149-155.
- Lagaly, G. and Weiss, A. (1975) The layer charge of smectite layer silicates: In Proc. International Clay Conf. 1975 (Edited by S. W. Bailey) Applied Publishing Ltd., Wilmette, IL, pp. 157-172.
- Lawrie, D. C. (1961) A rapid method for the determination of approximate surface areas of clays: Soil Sci. 92, 188-191.
- McBride, M. B., Pinnavaia, T. J., and Mortland, M. M. (1975) Perturbation of structural Fe^{3+} in smectites by exchange ions: Clays and Clay Minerals 23, 103-107.
- Mortland, M. M., Berkheiser, V. E., (1976) Triethylene-diamine-clay complexes as matrices for adsorption and catalytic reactions: Clay and Clay Minerals 24, (in press).
- Norrish, K. (1954) The swelling of montmorillonite: Trans. Faraday Soc., London 18, 120-134.
- Olejnik, S., Posner, A. M. and Quirk, J. P. (1974) Swelling of montmorillonite in polar organic liquids: Clays and Clay Minerals 22, 361-365.
- Shainberg, I. and Kemper, W. D. (1966) Conductance of adsorbed alkali cations in aqueous and alcoholic bentonite pastes: Soil Sci. Soc. Am. Proc. 30, 700-706.
- Schilt, A. A. (1969) Analytical Applications of 1,10-phenanthroline and Related compounds, Pergamon Press.
- Schilt, A. A. and Taylor, R. C. (1959) Infrared spectra of 1,10-phenanthroline metal complexes in the rock salt region below 2000 cm^{-1} : J. Inorg. Nucl. Chem. 2, 211-221.
- van Olphen, H. and Deeds, C. T. (1962) Stepwise hydration of clay-organic complexes: Nature, Lond. 194, 176-177.

Walker, G. F. (1961) Vermiculite minerals: In The X-ray Identification and Crystal structures of Clay Minerals, (Edited by Brown, G.) Mineralogical Society, London, pp.297-324.

Wilson, R. and Kivelson, D. (1966) Esr linewidths in solution-I. Experiments on anisotropic and spin-rotational effects: J. Chem. Phys. 44, 154-168.

MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 03057 8383