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HECTORITE COMPLEXES WITH Cu(II) AND Fe(II)–1,10-PHENANTHROLINE CHELATES*

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Abstract—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 Å 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 copper phen hectorite than iron phen hectorite probably 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.

INTRODUCTION

Adsorption of molecular 1,10-phenananthroline (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, 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 $M(phen)_3^{n+}$ (where M = metal ion is in oxidation state $n+$) complexes could make them useful as 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 Å in contrast to the tetramethylammonium cations (Clementz and Mortland, 1974) and tetraethylenediammonium dications (Mortland and Berkheiser, 1976) which give interlamellar thicknesses of 4.0 Å and 4.6 Å, respectively. When supported on the layer silicate surface, these transition metal complexes also could find application in reactions which are catalyzed by outer-sphere electron transfers.

In the present study, adsorption characteristics and properties of the copper and iron phen complexes exchanged 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 stoichometric ratios; some complexes were precipitated from solution by adding the Na salt of the anion desired. $Fe(phen)_3Br_2 \cdot 3H_2O$ was prepared according to Blau (1898). $Fe(phen)_3(ClO_4)_3 \cdot H_2O$ was prepared according to procedures given by Schilt and Taylor (1959) and was wrapped in Al foil to prevent photoreduction and stored over anhydrous $CaCl_2$. $Ni(phen)_3Cl_2$ was prepared according to Inskeep (1962) but was not crystallized from solution. $Cu(phen)_3(ClO_4 \cdot 3H_2O$ was prepared after Inskeep (1962) and stored as the pale blue powder. $Cu(phen)_2ClO_4$ 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

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solution). Acetonitrile solutions of $Fe(phen)_3(ClO_4)_3$ and $Cu(phen)_2ClO_4$ 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 analyzing the supernatant solution for the metal complex concentration by u.v.–vis spectrophotometry. Equilibrium was established after 24 hr; supernatant concentrations were stable up to 1 month. Absorption 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 $Ni(phen)_3Cl_2$ 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 100.00 mg 100°C dried Na–hectorite in water suspension, mixing overnight, and washing free of excess salts. Mg(II) was analyzed by atomic adsorption spectrometry. Bromide was analyzed volumetrically by precipitation with Ag^+.

Surface area measurements

Na–hectorite exchanged to various levels with $Fe(phen)_3^{2+}$ and $Cu(phen)_3^{2+}$ from zero to one equivalent fraction, were freeze-dried and then 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 temperatures 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

Infrared, u.v.–vis, and ESR spectra were taken of selected complexes. Infrared spectra were recorded on a Beckman Model IR-7 spectrophotometer using a Pyrex glass cell equipped with NaCl windows. Ultraviolet–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 $Fe(phen)_3^{2+}$ and $Cu(phen)_3^{2+}$ 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 powder diffraction measurements

Thin films were mounted in a Phillips X-ray diffractometer using Ni filtered Cu-Kα 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 mequiv./100 g; Cu(II) saturation and conductimetric titration of Cu(II) with NaOH gave a CEC of 70 mequiv./100 g.

RESULTS AND DISCUSSION

Ion adsorption and selectivity

Both $Fe(phen)_3^{2+}$ and $Cu(phen)_3^{2+}$ exhibit a marked affinity for the mineral surface in aqueous solution (Figure 1) when exchanged on to a Na(I) hectorite. Stronger coulombic attraction in the divalent complex than that of the Na(I) ion, size differences, as well as van der Waals interactions between the complex and the clay surface, probably account for the preference. Amounts of $M(phen)_3^{2+}$ adsorbed beyond

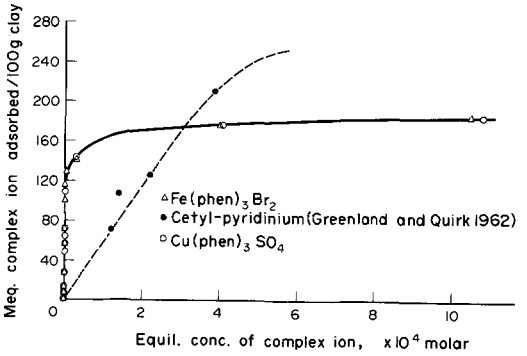


Figure 1. Adsorption isotherms of $Fe(phen)_3Br_2$ and $Cu(phen)_3SO_4$ on Na(I)–hectorite and cetylpyridinium bromide on montmorillonite.

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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. The cetyl pyridinium produces a clay complex with a 42 Å basal spacing which is stable against washing with water or benzene. In the case of the phenanthroline clay systems, the metal phen complexes adsorbed in excess of the exchange capacity were not stable against washing. Almost all of the non-coulombic bound complex was removed by washing with water. Analysis of $Fe(phen)_3^{2+}$ in the clay complex after washing 130 times with 15 ml aliquots of water indicated that 83 $\pm$ 5 mequiv./100 g remained on the clay. A lower level of van der Waals interaction between organic ions in the $M(phen)_3^{2+}$ complex, in comparison with the cetyl pyridinium complex, may account for this difference. In addition, the $M(phen)_3^{2+}$ 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 behaviour of those systems (Greenland and Quirk, 1962). The $M(phen)_3^{2+}$ 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 $M(phen)_3^{2+}$ were not significantly different from those of clay-complexes with one symmetry. In addition, no diffraction lines were observed for free salt. All those observations suggest that the excess molecular complexes are weakly bound by the clay and occupy remaining available interlamellar space.

Additional experiments were performed to test the selectivity of the $M(phen)_3^{2+}$ cations versus other cations for the clay surface. Hectorite samples containing one symmetry of $M(phen)_3^{2+}$ cations were equilibrated with various concentrations of $MgCl_2$, tetrapropylammonium (TPA) bromide, and $Ni(phen)_3Cl_2$. The amounts of iron and copper phen complexes released to solution were measured as well as the amount of exchanging ion remaining in solution. Results indicated no $Fe(phen)_3^{2+}$ or $Cu(phen)_3^{2+}$ were exchanged by Mg(II) at any concentration, nor was any $MgCl_2$ adsorbed. The TPA^+ displaced no $Fe(phen)_3^{2+}$ from hectorite at any concentration however trace quantities of TPABr were absorbed. In the $Cu(phen)_3^{2+}$ system, trace quantities were exchanged by TPA^+ and 0.2 symmetries of TPABr adsorbed when 2 symmetries of TPABr were present. However, when $Ni(phen)_3^{2+}$ was used to exchange $Fe(phen)_3^{2+}$ from the clay, a great deal of the nickel complex was adsorbed (about one symmetry maximum) while about 0.2 symmetries of $Fe(phen)_3^{2+}$ were displaced from the clay. Thus, while a small portion of the $Ni(phen)_3^{2+}$ actually exchanged some of the $Fe(phen)_3^{2+}$ from exchange sites, the greater portion was adsorbed by the same non-coulombic forces which were responsible for the adsorption of excess $Fe(phen)_3^{2+}$ complex beyond the exchange capacity as shown in Figure 1.

X-ray powder diffraction studies

Thin films of Na(I)–hectorite containing fractional symmetries of $Cu(phen)_3^{2+}$ or $Fe(phen)_3^{2+}$ were examined with X-ray powder diffraction. Basal spacings were determined at different levels of heating and are shown in Table 1. The iron systems generally exhibited two peaks indicative of separate phases near 12 Å and at 17.4 Å. 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 Å spacing is a weak shoulder on the 17.4 Å peak. At 100% saturation only the 17.4 Å peak appeared and persisted to 350°C. On the other hand, diffractograms of the copper systems indicated more random interstratification of 12 Å layers with those at 17.4 Å. Apparently, the strength of the van der Waals forces favors adsorption of the complexes in a given interlayer before adsorption occurs in succeeding interlayers. If the complex cations were uniformly distributed over the clay surface, a constant 17.4 Å would be expected at all levels of saturation. The van der Waals interaction between initially exchanged metal complexes and 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 Å thick (i.e. along the C_3 symmetry axis). When the C_3 axis is perpendicular to the silicate sheets, a 17.6 Å spacing should result and is in agreement with the data. As expected from the geometry of the large complex

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 (Å)	100°C (Å)	150°C (Å)
Fe(II)	0.0	13.6	11.8	11.8
	0.2	15.8, (13.2)	16.0, (12.4)	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 brackets indicates the more intense peak.

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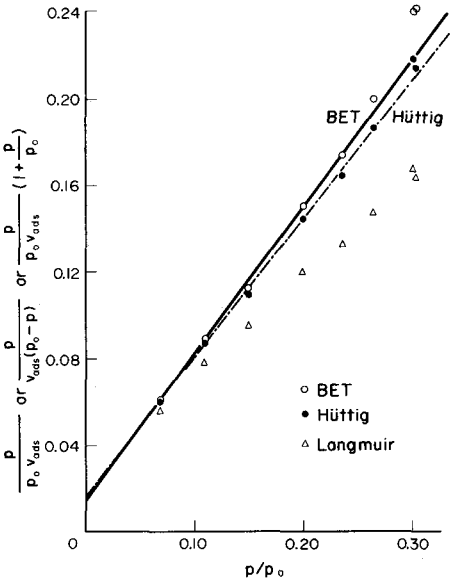


Figure 2. Data for adsorption of N_2 on $Fe(phen)_3^{2+}$ hectorite plotted according to BET, Langmuir, and Huttig equations.

cations, the basal spacings changed very little upon heating.

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 of the complex ion to Na(I)-hectorite. After heating for 18 hr at 160°C under flowing He gas, adsorption isotherms were obtained. Figure 2 shows data from N_2 adsorption isotherms plotted according to BET, Langmuir and Huttig 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 the volume adsorbed at the monolayer point, and b is a constant. 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 are as before, and c is a constant. Huttig'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 ~8 Å, allows for multilayer adsorption in areas unoccupied by the complex ions. In these systems, it seems that the BET and Huttig models provide a more satisfactory picture of the

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

Calculated area occupied by $Fe(phen)_3^{2+}$ 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

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 and 304 m^2/g, respectively for Langmuir, BET and Huttig 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 3 shows the increase in surface area with increasing saturation of the clay with $M(phen)_3^{2+}$. 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 $M(phen)_3^{2+}$ saturated before appreciable quantities of complex cations enter other parts of the interlayers. If the $M(phen)_3^{2+}$ 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 $M(phen)_3^{2+}$ (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 indepen-

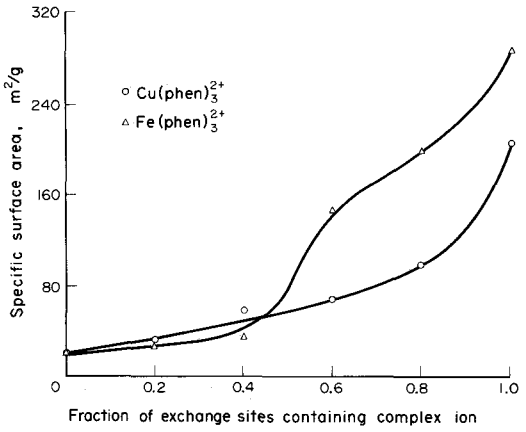


Figure 3. Specific surface areas of hectorite fractionally saturated with $M(phen)_3^{2+}$ calculated from the BET equation.

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dently 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 $Cu(phen)_3^{2+}$ 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 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).

Adsorption of water and benzene

Water and benzene adsorption isotherms are shown in Figure 4. 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 $Fe(phen)_3^{2+}$ and $Cu(phen)_3^{2+}$ hectorites as in the tetramethylammonium bentonite and presumably exists as physically bound H_2O in the interstices between the cations.

Water adsorption by $Fe(phen)_3^{2+}$ hectorite was studied in more detail since this complex gave the highest specific surface and the metal complex is more structurally stable than the Cu(II) complex. The O–H stretching regions of water were observed by i.r. 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 Å, and 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 *et al.* (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.

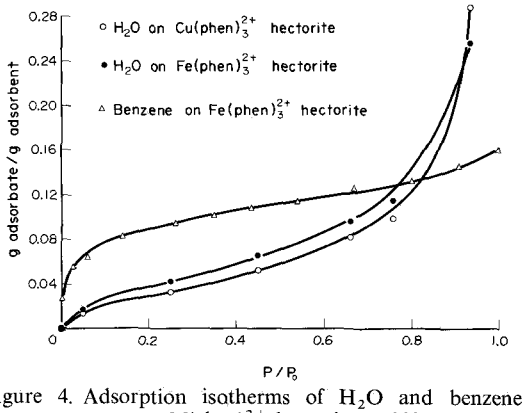


Figure 4. Adsorption isotherms of H_2O and benzene vapors on $M(phen)_3^{2+}$ hectorite at 20°C.

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) analogue.

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 $p/p_0 = 0.3$ there are 3.7 benzene molecules for every $Fe(phen)_3^{2+}$ cation on the average. No pleochroism was observed in the i.r. spectra of oriented thin films containing adsorbed benzene at $p/p_0 = 0.5$ (4.3 molecules benzene per cation). Benzene could adsorb on 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 and was taken to be 130 $Å^2$ (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 $Å^2$ and 27.8 $Å^2$, 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

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cause measured surface areas to be high since the area of the adsorbent includes both surface of the complex 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 N H_2SO_4 with oxidation half-cell potentials near 1.7 V 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 V 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 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 $Fe(phen)_3^{3+}$ on hectorite and include the alcohols, olefins and methyl ethyl ketone. No correlation was found between solvents causing reduction of $Fe(phen)_3^{3+}$ 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 $Cu(phen)_2^{1+}$ 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 $Cu(phen)_2^{1+}$ (Hall *et al.*, 1963). Also the addition of $Cu(phen)_2^{1+}$ to Na(I) hectorite gave identical spectral results.

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.

ESR spectroscopy

In order to determine the stereochemistry of the $Cu(phen)_3^{2+}$ complex on hectorite, ESR spectra of Cu(II) in $Cu(phen)_3^{2+}$ and $Cu(phen)_2^{2+}$ 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 $Cu(phen)_3^{2+}$ hectorite complex were prepared by the addition of one symmetry of the tris complex to Na(I) hectorite in 95% EtOH. The $Cu(phen)_2^{2+}$ hectorite complex was formed by addition of a half symmetry of $Cu(phen)_2^{1+}$ to Na(I) hectorite in acetonitrile, and subsequently oxidized to the $Cu(phen)_2^{2+}$ species with O_2. ESR spectra of these oxidized complexes are shown in Figure 5 at various levels of hydration. The increasing anisotropy of the spectra as dehydration increases (spectra A–D) is likely due to increasing loss of phen ligands from the coordination spheres of the Cu(II) ions. Under wet conditions, the X-ray basal spacing is 17.5 Å which may allow space for the $Cu(phen)_2^{2+}$ 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 $Cu(phen)_3^{2+}$ 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 *et al.*, 1964).

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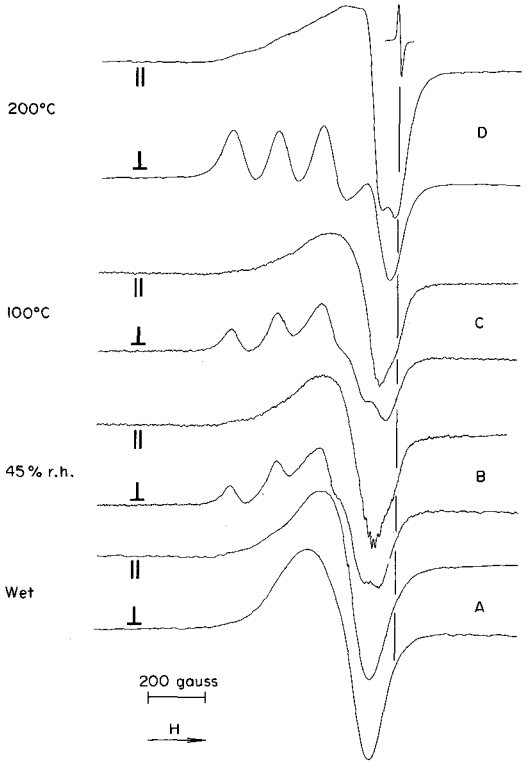


Figure 5. ESR spectra of oriented thin films of Cu(II) in $Cu(phen)_3^{2+}$ hectorite at different levels of hydration. The free electron signal indicates $g = 2.0028$; films were oriented parallel (∥) and perpendicular (⊥) to the magnetic field H.

At 45% relative humidity, the Cu(II) ion in both $Cu(phen)_3^{2+}$ and $Cu(phen)_2^{2+}$ hectorite becomes more 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 *et al.*, 1964; Hathaway *et al.*, 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 $Cu(phen)_2(H_2O)_2^{2+}$ species since on the average there are 8–10 H_2O molecules per Cu(II) ion. The interlayer spacing of 7 Å would accommodate 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 $Cu(phen)_2(H_2O)_2^{2+}$ species, and the complexes become more well 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 powder diffraction data where a higher degree of 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 $Cu(phen)_3^{2+}$ and $Fe(phen)_3^{2+}$ show marked affinity for exchange on to 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 $Ni(phen)_3^{2+}$ on $Fe(phen)_3^{2+}$ hectorite to behave in the same manner as observed for the adsorption of excess $Fe(phen)_3^{2+}$ beyond the exchange capacity. These van

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

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

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

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der Waals forces may also comprise an important driving force which causes a complete interlayer to be saturated before adsorption occurs in succeeding interlayers. The magnitude of the adsorption forces is great enough for the complex cations on exchange sites to almost completely resist exchange by TPA^+ and Mg(II).

(2) Adsorption of gases on to dehydrated $M(phen)_3^{2+}$ hectorite complexes probably occurs as multilayers on areas unoccupied by the complex ion. The high surface areas (up to $280\,m^2/g$) and X-ray powder 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 $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ couple showed that the smectite caused an increase in the potential in water and some alcohols above that in pure solvent.

(4) ESR data show that $Cu(phen)_3^{2+}$ 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 Cu(II) analogue compared to $Fe(phen)_3^{2+}$ hectorite.

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