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EFFECTS OF TRIS(2,2'-BIPYRIDYL) Fe(II),
Cu(II) and Ru(II) COMPLEX CATIONS AND
SALTS AND PROPERTIES OF SMECTITE

presented by

Sister Mary Frances Traynor, F.S.E.

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Max M. Mortland
Major professor

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EFFECTS OF TRIS(2,2'-BIPYRIDYL) Fe(II), Cu(II) AND Ru(II) COMPLEX CATIONS AND SALTS AND PROPERTIES OF SMECTITE

By

Sister Mary Frances Traynor, F.S.E.

A DISSERTATION

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ABSTRACT

EFFECTS OF TRIS(2,2' - BIPYRIDYL) Fe(II), Cu(II) AND Ru(II) COMPLEX CATIONS AND SALTS ON PROPERTIES OF SMECTITE

By

Sister Mary Frances Traynor, F.S.E.

Properties of complexes of a trioctahedral smectite (hectorite) with 2,2'-bipyridyl (bp) chelates of iron(II), copper(II) and ruthenium(II) were determined by a variety of chemical and physical measurements. The complex cations showed high selectivity for the hectorite surface; these clay complexes gave high surface areas. Excess salt was found to interfere with nitrogen penetration and adsorption. The *tris*-bipyridyl Cu(II) complex was found to lose a ligand, effecting a change in orientation in the interlayer.

X-ray diffractograms, surface area measurements and adsorption isotherms showed an apparent "anion effect" when Fe(II) complex salts were added in high concentrations. Each of the anions gave distinctly different isotherms, and at some levels of adsorption, different X-ray basal spacings. Evidence is presented for complex ion-pair formation, precipitation and the formation of

highly ordered, porous structures within the interlayers which resulted when the counter-ion of $Fe(bp)_3^{2+}$ was changed.

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INTRODUCTION

Clay minerals, being ubiquitous constituents of the natural environment, are known to interact with numerous organic compounds to form complexes of varying stabilities and properties. Clay-organic complexes are utilized on a large scale in lubricants, pollution control systems, paints, paper, medicine, cosmetics, etc. The interaction between soil clay minerals and applied fertilizers, pesticides and herbicides is also an important area of investigation. Chelate complexes of exchange ions in smectite are of interest in environmental studies as well as industrial applications. Clay minerals may be important sinks for the deactivation of metal ion or chelated metal ion pollutants. Properties of chelated metal ion clay complexes may be different from those minerals containing only hydrated ionic species. Many of the potential uses or applications of clay-organic interactions to the natural environment or to industry can be determined only after the properties of well-defined systems, using pure clays and known organic complexes, have been studied.

Properties of the layered silicates change when different ions or chelated ions are adsorbed. Adsorption of ions or chelated metal ions by smectites may create changes in the chemical and physical properties of the clay. Adsorption of gases, surface area measurements, X-ray basal spacings and oxidation-reduction potentials may be altered by exchange of complex metal ions onto the silicate surfaces.

The properties of Na(I)-hectorite exchanged with Fe(II), Cu(II) or Ru(II) chelated with 2,2'-bipyridyl, a weak diimine base, have been investigated. Changes in surface area measurements, X-ray basal spacings and oxidation-reduction properties were some of the parameters investigated. Through use of electron spin resonance spectroscopy, the structural and dynamical properties of the Cu(II) system were evaluated. The character of the surface environment can be investigated by using the Cu(II) ion as a probe. Properties of smectite may also be altered when metal complex cations and their anions are adsorbed by the clay after the cation exchange sites are fully satisfied by complex cations. Also, a difference in the nature of the anions in the interlayer may effect changes in the clay system. Surface area measurements may be affected due to precipitation and crowding of the complex salts, or highly ordered porous structures may exist giving rise to high surface areas and large basal spacings.

LITERATURE REVIEW

Clay-Organic Interactions

The smectite clay minerals have been shown to undergo cation exchange not only for positive inorganic ions, but also for large organic cations. As early as 1939, a number of organic salts of montmorillonite were prepared and their characteristic interplanar spacings measured (Gieseking, 1939), and the (001) values used as a method for determining molecular structure (Hendricks, 1941). Large organic ions are held more firmly by the clay than are inorganic positive ions. Forces of attraction between the cation and the silicate layers are not only coulombic forces between ions but also van der Waals attractions of the molecules to the surface. Values of d(001) depend upon the structure of the organic cation and the manner in which it is adsorbed on the silicate surface (Hendricks, 1941). Since these early investigations, there have been numerous studies and reviews of clay-organic reactions and complexes.

The importance of the nature of the clay mineral in organic complex formation has been pointed out by Brindley (1970) in a review of clay-organic complexes. Although complex formation between clays and organic substances has been known since antiquity, Theng's text (1974) is the first to deal comprehensively with the science of clay-organic reactions. He considers interactions with uncharged polar organic compounds as well as positively charged organic species. Organic reactions catalyzed by clay minerals and the interaction with organic compounds of biological importance are becoming of increasing importance in this field of study. Clay-organic reactions up to 1965 have been reviewed by Greenland (1965). More recent developments, particularly a review of important binding mechanisms involved in clay-organic complexes, have been reviewed by Mortland (1970). Solomon (1968) and Doner and Mortland (1969) have described complexes and interactions between organic molecules and transition metal ions, due to π-bonding, at clay surfaces. Few references have been found describing interactions of chelated transition metal complexes on smectites. Effects of complexes of Cu(II) and Fe(II) chelated with 1,10-phenanthroline adsorbed on hectorite have been investigated by Berkheiser and Mortland (1977). The importance and significance of such reactions is on the frontiers of clay-organic research and holds great promise in such diverse fields as agronomy and energy production technology.

2,2'-Bipyridyl Ligand

The 1,10-phenanthroline and 2,2'-bipyridyl ligands have long been used as complexing agents by analytical chemists. The α-diimine ligands have played a major role in the development of coordination chemistry, notably in connection with their analytical, structural, kinetic and thermodynamic properties as well as their biological and optical activity (Mason, 1968). A study with various organic materials has shown that a complex is formed between the 2,2'-bipyridyl molecule and montmorillonite. The complex is specific to montmorillonite and replaces water molecules in inter-sheet positions in the clay structure (Chester and Elderfield, 1971).

Complexes of these ligands with transition metal ions are noted for their high formation constants in aqueous solution, and in some cases for their high molar absorptivity, making them useful indicators in oxidimetry. Although similar in many respects, the kinetics and thermodynamics, as well as other properties, of transition metals chelated with these ligands would make an interesting comparison. Indeed, a great deal of the literature discusses and compares complexes of the two ligands. 2,2'-bipyridyl is known to form highly stable metal chelates, the most thoroughly studied being the iron(II) complex. Of more recent interest are the Cu(II) and Ru(II) complexes. These metal-bipyridyl complexes have been known for many years (Blau, 1898), but no reports have been found concerning the interaction of these complexes with clay minerals.

In order to understand the interactions of metal chelated complexes with clay minerals, it is of utmost importance that the chemical properties of the unadsorbed species first be understood.

Electron-Transfer and Oxidation-Reduction Investigations

The search for new fuels, new sources of energy, and new methods for solar energy conversion is currently one of the most active areas of applied research. A frequently suggested route for solar energy conversion involves the photochemical conversion of readily available stable starting materials to high energy products. One of the most efficient processes for conversion of light energy into chemical energy has been shown to be photo-induced electron transfer. There is indication that the excited state of $Ru(bp)_3^{2+}$ has potential use in sensitization studies involving absorption bands in the visible or near-UV region (Demas and Adamson, 1973). The tris(2,2'-bipyridyl)Ru(II)Cl_2, a strongly luminescent complex, has attracted a great deal of attention in view of its powers in sensitization both of electron (Gafney and Adamson, 1972; Demas and Anderson, 1973; Bock, et al., 1974; Navon and Sutin, 1974 and Creutz and Sutin, 1976) and energy transfer processes (vanHouten and Watts, 1975 and Natarajan and Endicott, 1973).

Various metal derivatives of 2,2'-bipyridyl and related compounds have been proposed and demonstrated to be advantageous as high potential reversible indicators in oxidation-reduction titrations. Schilt (1963) has studied the influence of acid concentration on the formal potentials of the tris(2,2'-bipyridyl) complexes of Fe and Ru. As the concentration of acid is increased there is a decreasing trend in potential. The decreases in formal potentials are such that very extensive and stable ion-pair formation between the complex cations and acid anions appears to be indicated. Dissociation of Fe(II) and Fe(III) species was found to be appreciable in acid solution. Solution stability is favorable for the Ru complex but $Fe(bp)_3SO_4$ dissociates in concentrated solutions of strong acids (Schilt, 1963 and Miller and Prince, 1966).

Burgess and Prince (1965) have studied the kinetics of the reactions of tris(2,2'-bipyridyl)iron(II) and have shown that the equilibrium $Fe(bp)_2^{2+} + bp \rightleftarrows Fe(bp)_3^{2+}$ is attained relatively slowly. They found kinetics of ligand replacement in sodium hydroxide solution to be similar for iron tris-complexes of 2,2'-bipyridyl and 1,10-phenanthroline, whereas in acid solution they were very different. The difference in behavior lies in the large effect of acid concentration on the rate of bipyridyl complexation and the small effect on the 1,10-phenanthroline analog. Protonated intermediates have been suggested to explain the acid dependence in the bipyridyl case where the 2,2'-bipyridyl ligand is more flexible.

It has been suggested that the oxidation of $Ru(bp)_3^{2+}$ is affected by the overall free-energy change (George and Irvine, 1954). Irvine (1959) studied the kinetics of the oxidation of $Fe(bp)_3^{2+}$ and $Ru(bp)_3^{2+}$ in an attempt to establish unequivocally the importance of the standard free-energy change in determining the rate of a redox reaction. His results show that there is a direct relation between the rate and the standard free energy of a redox reaction. He also unexpectedly found the oxidation of the $Ru(bp)_3^{2+}$ ion to be catalyzed by sunlight. The formation of $Fe(bp)_3^{2+}$ is highly exothermic ($H= -24.3$kcal./mole) whereas the formation of $Fe(bp)_3^{3+}$ is due almost entirely to a large favorable entropy change (George, Hanania and Irvine, 1959). The small entropy differences for the Fe and Ru bipyridyl complexes suggest that the large organic molecule effectively shields the central metal atom, so that changes in its charge hardly affect surrounding water molecules in the second coordination shell.

In a study of the oxidation-reduction potentials of some copper complexes, James and Williams (1961) found that for a given pK_a the bipyridyl couple has a much lower potential than does the corresponding 1,10-phenanthroline. Due to the weaker π-acceptor character of bipyridyl, it stabilizes the cupric relative to cuprous more than does the phenanthroline.

Infrared Spectroscopy Studies

One of the most powerful tools for studying organic molecules and clay organic complexes is infrared spectroscopy. Through observations of changes in the stretching and bending modes of molecules, molecular configurations, coordination and bonding mechanisms can be deduced.

The infrared spectra of 2,2'-bipyridyl has been obtained and band assignments made by Strukl and Walter (1971). They determined that the nitrogen atoms are trans to one another and the molecule possesses C_{2h} symmetry. The absorption bands of bipyridyl and the $Cu(bp)_3^{2+}$ and $Fe(bp)_3^{2+}$ molecules between 200 and 1600 cm^{-1} have been assigned (Inskeep, 1962), and agree with assignments for bipyridyl, $Fe(bp)_3^{2+}$ and $Fe(bp)_3^{3+}$ between 600 and 1600 cm^{-1} reported by Schilt and Taylor (1959).

Infrared spectra have been used to propose configurations of bipyridyl-Cu(II) complexes. C_2 symmetry and cis configuration of the bipyridyl ligands in $Cu(bp)_2^{2+}$ has been suggested due to the splitting of the 770 cm^{-1} band (Hathaway, et al., 1969). The $Cu(bp)_2^{2+}$ cation cannot involve a strictly square-coplanar stereochemistry for steric reasons. The most reasonable possibility is that both bipyridyl ligands are twisted out of the plane of the copper(II) ion in opposite directions. Although the molecular structure is not clear, this would give evidence of pseudo-tetrahedral configuration (Hathaway, et al., 1969), which is in agreement with findings of Percy and Thornton (1972). In studies using $Cu(bp)_2(ClO_4)_2$, perchlorate was not found to enter the coordination sphere, probably due to steric reasons. Inskeep (1962) indicated that the splitting of the 600 cm^{-1} band of $Cu(bp)_3^{2+}$ into a triplet gave evidence for tetragonal distortion and Jahn-Teller stabilization of the d^9 Cu(II) system. Splitting of the stretching band v(M-N) of $Cu(bp)_3^{2+}$ in the region below 400 cm^{-1} was likewise construed as evidence for tetragonal distortion (Percy and Thornton, 1971 and 1972). However, stability constants suggest that distortion of the regular octahedral configuration is either absent or small. It is believed that the bonding of the Fe complex differed from the bonding of the copper complex, as the v(M-N) band for Fe(II) was 423 cm^{-1} while Cu(II) occurred at 297 cm^{-1}. This indicates that the degree of π-bonding is greater for the Fe complexes. However, the overall stability due to π-bond formation for these Fe complexes is diminished by the energy required to pair the two electrons necessary to form these low-spin complexes.

The infrared absorption bands of hectorite, a trioctahedral mineral, are convenient to use in studies of water since their lattice OH bands are sharp, weak and lie at higher frequencies than the water bands. In studies with tetramethylammonium ion on hectorite, Farmer and Russell (1967) found the band at 3630 cm^{-1} to be due to weak hydrogen bonds to oxygens of the silicate lattice and the lower frequency band at 3425 cm^{-1} due to water-water hydrogen bonding. They found that the 3425 cm^{-1} absorption band increased in intensity in K-hectorite indicating that water directly coordinated to the cation forms H-bonds with surrounding water molecules rather than with the silicate lattice. Charge associated with substitution in the octahedral layer can be expected to be more diffusely spread over the surface oxygens than the more localized charge associated with tetrahedral substitution. This results in weaker hydrogen bonding to surface oxygens in octahedrally substituted smectites than in tetrahedrally substituted ones (Farmer and Russell, 1967). Burchett and Meloan (1972) investigated hydrogen bonding between water and the nitrogens of tris-phenanthroline Fe(II) and tris-bathophenanthroline Ru(II). They concluded that the metal of the chelate might be the site of attachment instead of the nitrogen of the ligand since no orbitals would be available for bonding water. Through use of I.R. spectroscopy, they concluded that a peak observed at 985 cm^{-1} for $Fe(bp)_3^{2+}$ which was not present in the ligand spectrum was due to water bonded to metal of the chelate. It is feasible that the water could bond to the metal because the six d electrons of Fe(II) and Ru(II) are not located in the faces of the octahedral chelate, therefore, the electrons on the oxygen of water could be donated to the metal. Additionally, if back-bonding is occurring in the M-N bond of the chelate, this would reduce the electron density around the metal making it even more susceptible to accepting electrons from the water.

Electron Spin Resonance Spectroscopy Studies

Structural and dynamical parameters of paramagnetic ions on smectite surfaces can be evaluated through use of electron spin resonance (ESR) spectroscopy. The stereochemical orientation and hydration state of various Cu complexes in the interlamellar region of layer silicates has been determined by means of this powerful tool (Clementz, et al., 1973 and Berkheiser and Mortland, 1975 and 1977). The environment of the cation in the interlayer can be investigated by determining the type of resonance produced in the ESR spectrum. There are no known ESR investigations of tris-bipyridyl Cu(II) on the surface of smectite clays, however there have been many investigations of this complex in other solid matrices and solutions.

Hexacoordinated copper (II) ions in solids are known to be octahedrally coordinated and exhibit a Jahn-Teller distortion due to interaction between the d^9 electronic system and the ligand field. Allen, et al. (1964) have found that at sufficiently high temperatures, the $Cu(bp)_3^{2+}$ system resonates among three equivalent tetragonal distortions along the three, fourfold axes of the octahedron. The result of this resonance is an effective octahedron which will give rise to an isotropic g-value (only one value for the g and A spin-Hamiltonian parameters). The averaging of the magnetic anisotropy at higher temperatures is often referred to as "dynamic Jahn-Teller effect." If the temperature is lowered sufficiently, the complexes are frozen into one of the distortions and an anisotropic g-value is expected (Allen, et al., 1964). The behavior of $Cu(bp)_3^{2+}$ in solution has also been interpreted in terms of dynamic Jahn-Teller effects. It was originally thought that the anisotropy of g and A was due to the random reorientations of the complexes in the liquid. However, the behavior of $Cu(bp)_3^{2+}$ exhibits the same anomalous behavior as $Cu(OH_2)_6^{2+}$ probably due to the homogeneous nature of their respective coordination spheres, and anisotropy is due to dynamic

Jahn-Teller effects (Noack, et al., 1971). They assume that fast reorientations of the axis of distortion occur only when all orientations are equivalent. This can only be true for homogeneous hexacoordinated Cu(II) complexes but not for inhomogeneous hexacoordinated complexes such as $Cu(bp)(OH_2)_4^{2+}$. The line widths of $Cu(bp)_3^{2+}$ were found to be dependent upon temperature and bulk viscosity.

The findings of Hathaway, et al. (1974) question earlier suggestions that the $Cu(bp)_3^{2+}$ cations will always involve a D_3 symmetry and undergo dynamic Jahn-Teller distortion. The latter will only arise when the cation is present in high symmetry crystal lattices, such as trigonal or hexagonal, in which the Cu(II) ion may occupy a special position of D_3 symmetry. When $Cu(bp)_3^{2+}$ is present in lower symmetry crystals the more usual static elongated rhombic octahedral sterochemistry will be present and no genuine dynamic Jahn-Teller effect will operate.

METHODS AND PROCEDURES

Preparation of Hectorite Clay

The hectorite used was #B1-26 obtained from the Baroid Division of National Lead Company as a centrifuged and spray-dried powder. Exchangeable Na(I) in the raw material was 84.2 meq/100 g. Cu(II) saturation and conductometric titration of Cu(II) with NaOH gave a CEC of 70 meq/100 g. The sodium-saturated hectorite was freeze-dried and stored in brown glass bottles. The whole cell formula for this hectorite is:

$$M^+_{0.42}(Mg_{5.42}Li_{0.68}Al_{0.02})\ (Si_{8.0})\ O_{20}\ (F,OH)_4$$

Preparation of 2,2'-Bipyridyl Complexes

The bipyridyl ligand was purchased as reagent grade compound from Aldrich Chemical Company and used without further purification. Tris(2,2'-bipyridyl) ferrous perchlorate, $Fe(bp)_3(ClO_4)_2$, and $Fe(bp)_3(ClO_4)_3 \cdot 3H_2O$ were prepared according to methods of Burstall and Nyholm (1952). The dark, blue-green ferric complex was wrapped in aluminum foil to prevent photoreduction. Tris(2,2'-bipyridyl)ferrous chloride pentahydrate, $Fe(bp)_3Cl_2 \cdot 5H_2O$, prepared according to Inskeep (1962), with the exception of being extracted with hot benzene, was stored over anhydrous $CaCl_2$. Tris-(2,2'-bipyridyl)ferrous sulfate heptahydrate, $Fe(bp)_3SO_4 \cdot 7H_2O$, was prepared by adding an excess of the amine to a solution of $FeSO_4 \cdot 7H_2O$ and heated for one hour. The solution was evaporated to a low volume and the dark red paste extracted several times with hot benzene. The remaining material was dissolved in water and crystallized from solution, washing with water. Crystals were collected in a büchner funnel and dried over P_2O_5. Tris(2,2'-bipyridyl)ferrous bromide, $Fe(bp)_3Br_2$, was prepared by adding an excess of the amine dissolved in methanol to a solution of $FeCl_2 \cdot 4H_2O$. The solution was heated and an excess of KBr added until crystals formed. The crystals were washed several times with cold water and stored over P_2O_5. Tris(2,2'-bipyridyl) cupric perchlorate, $Cu(bp)_3(ClO_4)_2$, was prepared after the method of Percy and Thornton (1971) and stored as the bright blue powder. The preparation of $Cu(bp)_2(ClO_4)$ was modified from the method of Schilt and Taylor (1959) for the phenanthroline complex. The brownish-purple precipitate was stored over $CaCl_2$. The $Ru(bp)_3Cl_2$ was prepared according to procedures of Burstall (1936).

Preparation of Metal-Complex Exchange Forms of Hectorite

Homoionic (Fe, Cu, Ru bipyridyl complex ions) samples of the <2μ fraction of the hectorite were prepared by adding the metal complex in excess of four times the exchange capacity to the Na(I) clay. After 24 hours the clay was washed thoroughly with water until all color in the wash disappeared. The metal-complex exchange forms of hectorite were freeze-dried and the red, blue and orange clays were stored in brown bottles. The Ru complex clay was wrapped in aluminum foil to prevent photodecomposition. For experiments that required self-supported films, the metal-bipyridyl complex was added as a water-solution to films of Ca-hectorite. In order to accelerate the exchange, the closed weighing bottle was placed on top of a 100 °C oven for several days until the exchange was complete and disappearance of the colored complexes from solution resulted. An acetonitrile solution of the Cu(I) complex and Ca-hectorite were used to obtain $Cu(bp)_2^{1+}$- hectorite. The bluish-purple film was then washed with water and placed in 0.1 percent H_2O_2. It reacted immediately and became green, oxidizing to $Cu(bp)_2^{2+}$- hectorite.

Ion Exchange-Adsorption Isotherm Studies

Ion exchange isotherms were developed for the adsorption of $Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$ and $Ru(bp)_3^{2+}$ on Na(I)-hectorite by adding the appropriate amount of metal complex aqueous standard solution to a known weight (0.05 g) of Na-hectorite and bringing the suspension volume to 50.00 ml. The suspensions were allowed to exchange for 48 hours, centrifuged and the supernatant analyzed for the concentration of metal complex by UV-VIS spectrophotometry. Absorption maximums were obtained at 522 mμ for $Fe(bp)_3^{2+}$, 297 mμ for $Cu(bp)_3^{2+}$ and 449 mμ for $Ru(bp)_3^{2+}$. Adsorption isotherms were repeatable to within experimental error as determined by checking selected points on the isotherms.

Water Adsorption Isotherms and Water Studies Using I.R.

Water adsorption isotherms were developed by placing fully saturated $Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$ and $Ru(bp)_3^{2+}$-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 after seven days of equilibration. Self-supported films of the Fe, Cu and Ru complex hectorites, prepared by adding one or two symmetries of metal complex standard solution to Na(I)-hectorite, were placed in an atmosphere of 30 percent relative humidity (obtained by use of a saturated solution of CrO_3) for 24 hours. Samples were held in a brass cell with vacuum stopcock and NaCl windows. Infrared spectra were obtained on a Beckman IR-7 spectrophotometer. Subsequently each sample was heated at 100°C, 200°C, and 250°C for two hours and an infrared spectrum obtained after each heat treatment.

Oxidation-Reduction Experiments

Qualitative experiments were performed on the Fe, Cu and Ru complex clays and the salts of each metal. Reagent grade chemicals were used as received from the supplier in all cases. Change in oxidation status was assumed to occur when appropriate color changes were observed.

Surface Area Measurements

Samples of Na-hectorite were partially exchanged with $Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$ and $Ru(bp)_3^{2+}$ from zero to one equivalent fractions and were freeze-dried. Other samples were prepared where 5.71 symmetries of $Fe(bp)_3^{2+}$ of the ClO_4^-, Cl^-, Br^- and SO_4^{2-} salts were added to Na-hectorite and the surface areas of the freeze-dried, dehydrated materials were determined. Other symmetries (2.29, 10.24 and 28.57) of the Fe complex (SO_4^{2-}) were prepared and surface areas obtained. All samples were degassed by heating at 160°C under flowing He gas. Surface areas were determined with a Perkin-Elmer Shell Model 212 B Sorptometer at liquid nitrogen temperatures using N_2 as the adsorption gas and He as the carrier gas. Data was plotted according to the BET equation. Approximately 40 mg of adsorbent were used for each determination.

X-Ray Diffraction Measurements

A Philips X-ray diffractometer using Ni-filtered Cu-Kα radiation was used for all diffractograms. Samples of the metal complex hectorite were prepared by placing the aqueous suspensions onto glass slides and drying to room temperature, 100°C and 150°C. In some cases self-supported films were used by placing the film on a glass slide. Diffractograms were recorded to three orders of (001) reflections.

Spectral Measurements

IR, UV-VIS and ESR spectra were taken of selected metal-complex hectorite samples. UV-VIS spectra in the region of 200 to 600 mμ were recorded on a Beckman DK-2A ratio recording spectrophotometer using 1 cm quartz cells for liquid determinations and fused quartz discs for thin clay films. A dilute suspension of the metal complex clay was deposited on a quartz disk, air-dried and coated with a thin layer of mineral oil to reduce scattering. A film of Na-hectorite prepared and treated similarily was placed in the reference beam to compensate for absorption by the clay mineral.

Infrared spectra in the region of 4000 to 600 cm^{-1} were obtained on a Beckman IR-7 spectrophotometer. Self-supported films were used for the metal-complex hectorite samples and KBr pellets were prepared for the pure compounds.

Electron paramagnetic resonance spectra (ESR) were recorded at X-band on a Varian E-4 ESR spectrometer using quartz tubes containing thin films of the metal complex clay. Samples were placed in chambers of 0 percent, 77 percent r.h. or heated to 100°C for one week before measurements were made. Standard pitch served as a standard for which $g = 2.0028$.

RESULTS AND DISCUSSION

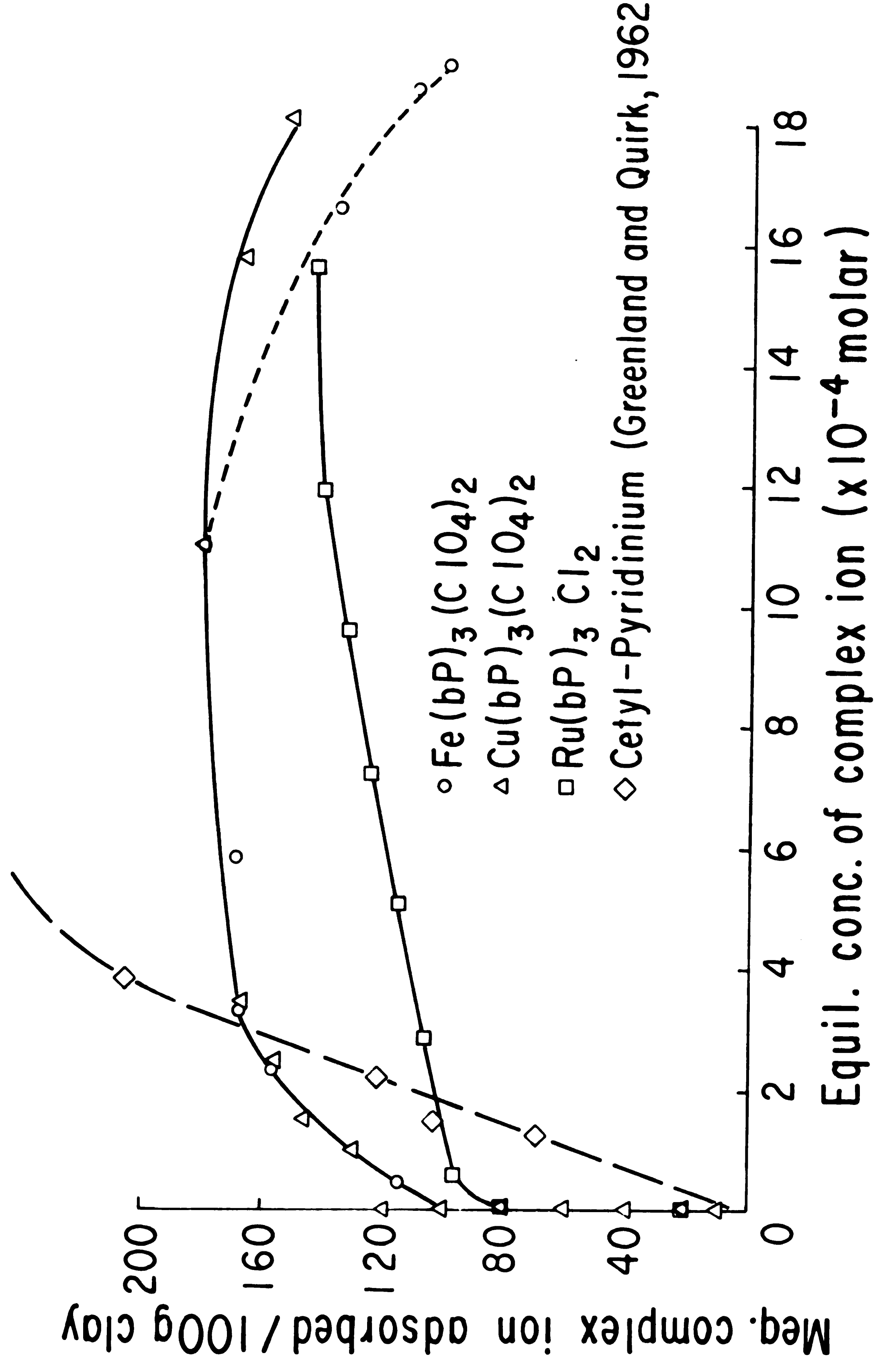
Adsorption Isotherms

$Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$ and $Ru(bp)_3^{2+}$ all exhibit a marked affinity for the silicate surface, in aqueous solution, when exchanged onto Na(I)-hectorite (Figure 1). This is perhaps due to 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 clay surface.

The Fe and Cu bipyridyl complexes were adsorbed in excess of two times the cation exchange capacity of the clay, while the Ru complex was adsorbed to twice the CEC. It is presumed that this excess is adsorbed as the complex salt in the same manner as described by Berkheiser and Mortland (1977) for phenanthroline complexes. Greenland and Quirk (1962) have also found long chain 1-n-alkyl pyridinium bromides to be adsorbed in this manner by Na(I)-smectite. The bipyridyl complexes show a more distinct selectivity for the clay than do the cetyl-pyridinium bromides. This is most likely due to the divalent character of the bipyridyl complexes.

Adsorption isotherm data for the Fe and Cu bipyridyl complexes show the presence of four distinct

Figure 1.--Adsorption isotherms of $Fe(bp)_3(ClO_4)_2$, $Cu(bp)_3(ClO_4)_2$ and $Ru(bp)_3Cl_2$ on hectorite and cetyl-pyridinium bromide on smectite.


○ Fe (bP)$_3$ (C lO$_4$)$_2$
△ Cu(bP)$_3$(C lO$_4$)$_2$
□ Ru(bP)$_3$ Cl$_2$
◇ Cetyl-Pyridinium (Greenland and Quirk, 1962)
Equil. conc. of complex ion (x 10^{-4} molar)
0
2
4
6
8
10
12
14
16
18
Meq. complex ion adsorbed / 100g clay
40
80
120
160
200

regions: (I) From 0 to 70 meq/100 g the interlayers are being filled with complex ion by ion exchange, (II) from 70 to approximately 160 meq/100 g, voids present between the exchanged complex ions in the interlayer are being filled with the complex salt, (III) the slope decreases almost reaching a plateau from 160 to 180 meq/100 g, and (IV) the slope becomes negative.

These data correlate well with X-ray diffraction data given in the following section. In region I the layers were being filled with the metal complex through ion exchange and gave rise to an 18 Å basal spacing at 70 meq/100 g. As the slope decreased in region II, voids present between clay-complexed molecules were being filled with Fe or Cu complex salt. In this region X-ray diffractograms gave rational 18 Å basal spacings until the clay had adsorbed approximately 160 meq/100 g. This indicates that while the metal complexes are filling voids between clay-complexed molecules, they are not affecting the interlayer spacing. This is in agreement with phenanthroline data of Berkheiser and Mortland (1977) where they found no change in the basal spacing of the air-dried complexes which contained more than one symmetry of metal phenanthroline. The van der Waals interaction between exchanged metal complexes and excess complex molecules may be an important driving force in promoting complex molecules to enter voids. In region III the slope decreased to a greater degree almost reaching a plateau. Since all exchange sites and voids were occupied, the complex molecules which continued to be adsorbed, expanded some of the silicate sheets still further as shown by the increase in d spacings in Tables 1 and 2. As the clay was exposed to higher concentrations of metal complex, the 18 Å reflections indicate considerable interstratification. It was anticipated that with even higher added concentrations a discrete 26 Å peak denoting a complete double layer, consisting of exchanged complex cations and molecules of their salts, would be formed. Such was not the case. As the concentration of added metal complex was increased, the slope became negative (region IV). X-ray data show a return to relatively homogeneous systems near 18 Å. The Fe system gave the best evidence for this type of behavior. It is not clear at this time why decreased adsorption occurred when high concentrations of metal complex were added. It may be possible that an ion-ion interaction was taking place which at very high concentrations favored the solution rather than the clay.

The adsorption isotherm of $Ru(bp)_3^{2+}$ is similar to the first three regions of the Fe and Cu complex isotherms (Figure 1), although total adsorption was less. Fewer molecules of $Ru(bp)_3Cl_2$ were necessary to fill voids than was found in the Fe or Cu system. Distinct 18 Å spacings were present to 120 meq/100 g clay, in contrast to 160

Table 1.--X-ray basal spacings, d(001), of Na(I)-hectorite exchanged at various levels with $Cu(bp)_3(ClO_4)_2$ and $Ru(bp)_3Cl_2$.

$Cu(bp)_3^{2+}$				$Ru(bp)_3^{2+}$			
S*	Air dry	100°C	150°C	S*	Air dry	100°C	150°C
0.0	11.5	10.0	10.0	0.0	11.5	10.0	10.0
0.29	13.2	13.0	12.6	0.29	17.0	16.4	17.3
0.57	13.4	13.2	13.4	0.57	17.0	17.6	17.6
0.86	16.0	15.2	14.7	0.86	17.3	17.6	17.6
1.14	17.6^{s}	17.6^{s}	17.3^{s}	1.14	18.0^{s}	18.0^{s}	18.0^{s}
1.43	17.6^{s}	17.6^{s}	17.3^{s}	1.43	18.0^{s}	18.4^{s}	18.4^{s}
1.71	18.8^{s}	18.4^{s}	18.0^{s}	1.71	18.0^{s}	18.4^{s}	18.4^{s}
2.00	18.4^{s}	18.4^{s}	18.0^{s}	2.00	18.0^{s}	18.8^{s}	18.4^{s}
2.29	18.0^{s}	18.4^{s}	18.0^{s}	2.29	18.0	18.4^{s}	18.4^{s}
2.57	18.8^{s}	18.4^{s}	18.4^{s}	2.57	18.4	18.4	18.4
2.86	18.4	18.4^{s}	18.4^{s}	2.86	18.4	18.4	18.8
4.29	18.4	18.0^{s}	18.0^{s}	4.29	18.4	18.4	18.4
5.71	18.4	18.8	18.4	5.71	24.5(17.0)	22.1(17.6)	22.1(18.8)
8.57	22.1(17.3)^{a}	18.4	18.4				
11.43	18.0	18.8	18.4	11.43	25.2(17.3)	26.0(17.3)	22.6(17.6)
17.14	18.8	18.0	18.4				
22.86	18.4	18.0	18.4				
28.57	18.4	18.4	18.4				

*S denotes symmetries of metal complex ion added to clay.

[s] denotes a sharp, rational peak.

[a] number in ( ) indicates the more intense peak.

Table 2.--X-ray basal spacings, d(001), of Na(I)-hectorite exchanged at various levels with $Fe(bp)_3(ClO_4)_2$ and $Fe(bp)_3SO_4$.

- - - - - - $Fe(bp)_3(ClO_4)_2$ - - - - - - - -				- - - - - - - $Fe(bp)_3SO_4$ - - - - - -		
S*	Air Dry	100°C	150°C	S*	Air dry	100°C
0.0	11.5	10.0	10.0	0.0	11.5	10.0
0.29	14.5	13.6	13.4	0.29	14.7	14.7
0.86	17.0	17.0	16.7	0.86	17.0	17.0
1.43	17.6[s]	17.6[s]	17.6[s]	1.43	17.6[s]	
1.71	18.0[s]	18.0[s]	18.0[s]	1.71	17.6[s]	
2.29	18.4[s]	18.0[s]	18.0[s]	2.29	18.0[s]	
4.29	18.4	18.0	18.8	4.29	18.0	
5.71	18.8	18.0	18.8	5.71	18.0	
8.00	(25.2)[a]16.7	(23.8)16.7	21.0	8.00	18.0	18.4
10.29	(26.0) 16.4	(25.2)16.4	21.0	10.29	(26.8)17.6	25.2(18.0)
11.43	17.6	17.6	18.4			
22.86	17.3	18.0	18.8	22.86	(27.6)16.1	(25.2)17.0
28.57	16.7	17.6	18.4	28.57	(27.6)15.5	(27.6)15.2
				58.14	(27.6)16.4	(27.6)16.4
				85.71	22.1	
				114.28	17.6	

[*] S denotes symmetries of metal complex ion added to clay.

[s] denotes a sharp, rational peak.

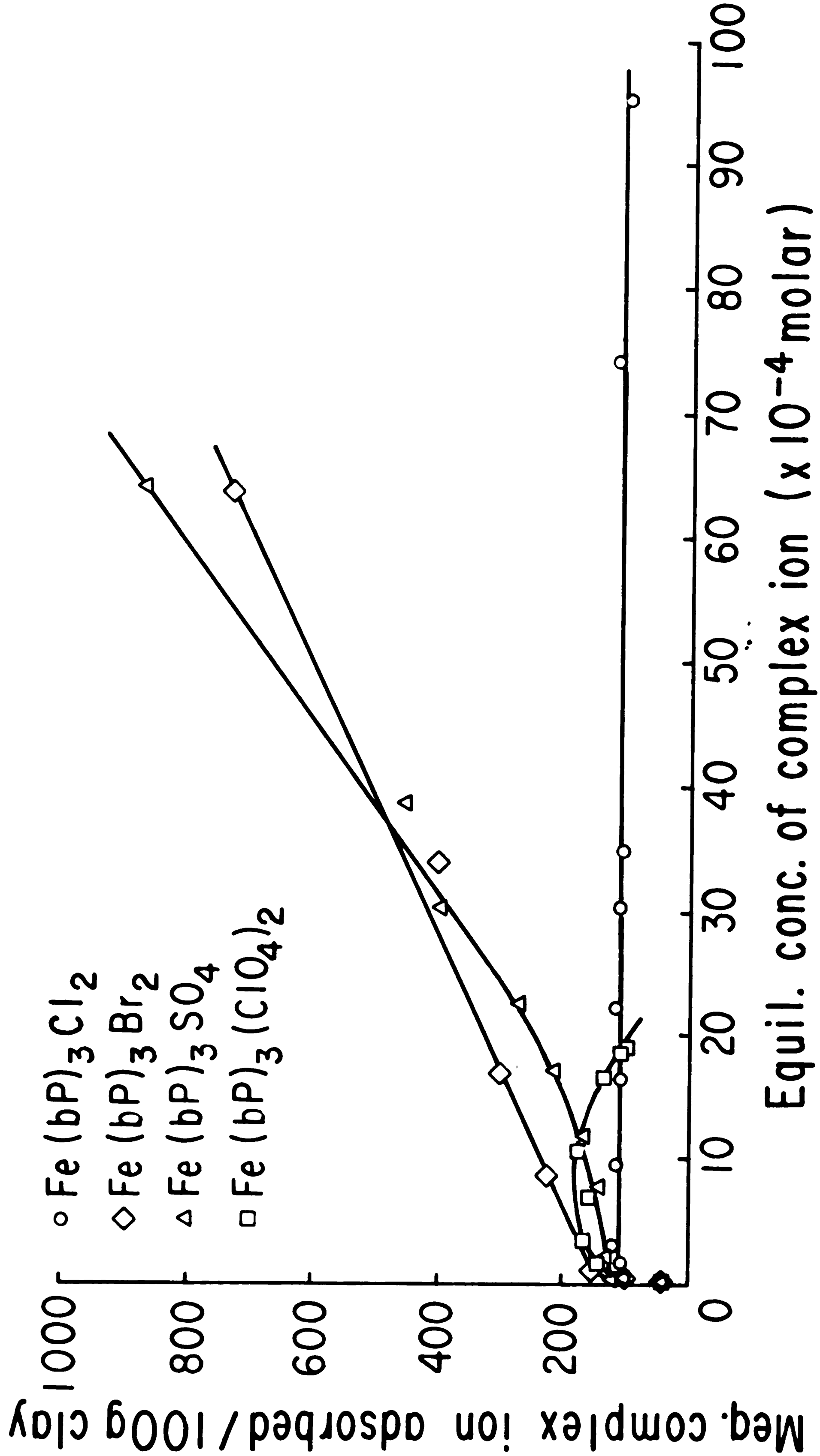
a number in ( ) indicates the more intense peak.

meq/100 g clay for Fe and Cu. At higher concentrations interstratified peaks approaching a spacing of 24 Å were present. It appears that the tris-bipyridyl Ru complex contains more waters of hydration (supported by the IR data) and hence occupies more space, thus allowing for fewer molecules to occupy voids. Since the counter-ion is also present in the interlayer a difference in anion may contribute to this effect.

Unlike the cetyl-pyridinium clay of Greenland and Quirk (1962) which exhibited a 42 Å basal spacing and was stable against washing with water or benzene, the bipyridyl clay complexes were not found to be stable. When the hectorite adsorbed complexes in excess of the exchange capacity, almost all of the non-coulombically bound complex was removed by washing with water or methanol. This difference may be due to a higher level of van der Waals interaction between the cetyl-pyridinium complex than between organic ions in the $M(bp)_3^{2+}$ complex. Additionally, the $M(bp)_3^{2+}$ adsorption isotherms were reproducible within experimental error in contrast to the reported cetyl-pyridinium adsorption data. The erratic behavior of those systems may be due to hydrolysis of the cetyl-pyridinium complexes (Greenland and Quirk, 1962). The $M(bp)_3^{2+}$ complexes were stable over the course of the investigation with no observable change in the molar absorptivity of the complexes in solution. In addition, no diffraction peaks were observed for the free salt.

Since the $Fe(bp)_3(ClO_4)_2$ treated clays gave the most striking results in the adsorption isotherm investigations, the Fe(II) complex was studied in greater detail. Two major points of interest which arose from the adsorption of $Fe(bp)_3(ClO_4)_2$ onto Na(I)-hectorite were (1) the cause of decreased adsorption at high concentrations and, (2) the appearance of large basal spacings. In an attempt to ellucidate further information concerning these points, the counter-ion was changed and similar adsorption isotherm studies and X-ray diffraction analyses were performed. If indeed an ion-ion interaction was occurring and creating a system where the ion-pair preferred the clay surface at low concentrations and the equilibrium solution at high concentrations, by using a good ion-pairer, such as Cl^-, one would expect to see greater interaction. Therefore, a similar adsorption study was conducted using $Fe(bp)_3Cl_2$ as the adsorbate; results are shown in Figure 2. An adsorption maxima was obtained rapidly and sharply at 114 meq/100 g of clay. This is approximately 1.6 times the cation exchange capacity; less than observed in the perchlorate study. As in the former system, excess $Fe(bp)_3Cl_2$ is believed to be filling voids within the clay complex. No evidence of higher basal spacings was observed. Beyond the cation exchange capacity all

Figure 2.--Adsorption isotherms of $Fe(bp)_3Cl_2$, $Fe(bp)_3Br_2$, $Fe(bp)_3(ClO_4)_2$ and $Fe(bp)_3SO_4$ on hectorite.



○ Fe (bP)$_3$ Cl$_2$
◇ Fe (bP)$_3$ Br$_2$
△ Fe (bP)$_3$ SO$_4$
□ Fe (bP)$_3$ (ClO$_4$)$_2$
Meq. complex ion adsorbed / 100g clay
1000
800
600
400
200
0
10
20
30
40
50
60
70
80
90
100
Equil. conc. of complex ion (x 10^{-4} molar)

basal spacings were 18 Å. There was no evidence of ion-pair formation. These distinctly different isotherms indicate that there must be an effect due to the counter-ion. Hence, Fe(II) complexes with Br^- and SO_4^{2-} anions were synthesized and used in further adsorption isotherm investigations. Figure 2 shows that the isotherm for $Fe(bp)_3Br_2$ adsorption is strikingly different from the Cl^- or ClO_4^- systems. High levels of adsorption occurred, up to 730 meq/100 g, when 28.57 symmetries of metal complex was added to Na(I)-hectorite. Adsorption was linear and all points gave 18 Å spacings with the exception of the higher ones which were broad and interstratified. Since X-ray data do not indicate that the excess material was present in the interlayers (except at the highest loading) and due to the linear relationship of adsorption with the equilibrium solution, it is likely that the molecular complex salt was precipitated on the edges of the clay mineral. Another possibility is that large diffuse layers of $Fe(bp)_3Br_2$ were present in the interlayers but upon drying were squeezed out. The presence of salt diffraction peaks on the X-ray diffractograms would support both hypotheses, and, in fact were present at high concentrations.

$Fe(bp)_3SO_4$ was also adsorbed at very high concentrations. The isotherm more closely resembles that for Br^- than any of the others. In contrast to the Br^-

system, the X-ray basal spacings for the SO_4^{2-} system correlate extremely well with the isotherm data. The lower region of the isotherm follows that described for the ClO_4^- system. In the presence of high concentrations of the $Fe(bp)_3SO_4$ solution, the $Fe(bp)_3^{2+}$- hectorite showed continual adsorption of the molecular complex. With additions greater than 2.29 symmetries the basal spacings at 18 Å showed increasing interstratification and decreased intensity accompanied by the appearance of a peak at 27.6 Å (Table 2). Therefore, it appears that the molecular $Fe(bp)_3SO_4$ is located in the interlayer and as a result has further spread the silicate sheets.

X-Ray Diffraction Studies

Suspensions of Na(I)-hectorite containing fractional or multiple symmetries of $Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$ or $Ru(bp)_3^{2+}$ were allowed to dry into thin films on glass slides. Basal spacings of the Fe, Cu and Ru complex clays were determined at three levels of hydration and are shown in Tables 1 and 2. At levels of adsorption below one symmetry, diffractograms of the metal complex clays indicated random interstratification of 12 Å and 18 Å layers. This is indicative of nonhomogeneous systems in which some layers contain the metal complex and others do not. Increasing metal complex concentration resulted in progression toward a higher proportion of 18 Å layers and less interstratification. Rational 18 Å spacings were obtained at one symmetry and persisted to 2.57 symmetries. Increasing interstratification resulted when the clay was exposed to higher concentrations of metal complex. With the addition of 8.57 symmetries of $Cu(bp)_3(ClO_4)_2$, two separate peaks occurred, both reflecting random interstratification. Upon dehydration, one very broad peak centered at 18 Å resulted. With even higher loading the 18 Å peaks still indicated interstratification but no distinct higher spacings were obtained.

Diffractograms of the $Ru(bp)_3^{2+}$- hectorite indicate that nonrational diffraction peaks of 17 Å were obtained at lower symmetries than what was found in the iron or copper system. This indicates that the complex cations are more uniformly distributed between the clay layers giving a greater proportion of 18 Å spacings. Distinct 18 Å spacings were obtained between one and two symmetries. As the clay was exposed to higher concentrations (up to 5.71 symmetries) of $Ru(bp)_3^{2+}$, greater interstratification occurred. Although highly interstratified, the peak around 22 Å obtained at this level of addition, persisted when heated to 150°C. A greater proportion of the clay layers were expanded by the Ru complex with addition of 11.43 symmetries of metal complex. These high basal spacings were obtained with lower levels of Ru complex addition than what was necessary for similar basal spacings with the copper complex. This indicates that the Ru complex was distributed more uniformly in the interlayer than was found in the copper system. It was not possible to obtain a distinct, rational d(001) spacing with higher metal complex concentrations for either system.

Beyond the exchange capacity of the clay, excess metal complex cations must be present with their counterions, ClO_4^- or Cl^-. X-ray results are in agreement with molecular dimensions of the tris-bipyridyl complexes. Space-filled models of the complexes show that the cations are approximately 8 Å thick and should give 18 Å spacings. As expected from the geometry of the large complex cations, the basal spacings changed very little upon dehydration.

X-ray basal spacings for Na(I)-hectorite exchanged with $Fe(bp)_3^{2+}$ are found in Table 2. Results indicate behavior very similar to the Cu and Ru systems. A diffraction peak of 25 Å occurred when the clay was exposed to metal complex concentrations eight times the exchange capacity. The peak at 16 Å may be due to diffraction effects resulting from interstratification of the d(001) 18 Å and some higher spacing. Similar spacings were obtained with addition of 10.29 symmetries of $Fe(bp)_3$-$(ClO_4)_2$ to the clay. In an attempt to isolate a single, distinct spacing of the more expanded material, higher concentrations of metal complex were added. These higher levels of added complex gave only single interstratified 18 Å spacings. These data are in agreement with the adsorption isotherms. The region which approached a plateau (region III) on the adsorption isotherms is where higher spacings were found. As the slope of the isotherm decreased (region IV), interstratified 18 Å spacings began to persist. In order to determine if the anion was contributing to this adsorption phenomenon and giving these basal spacings, $Fe(bp)_3^{2+}$ with counter-ions Cl^-, Br^- and SO_4^{2-} were added to the clay in a wide range of concentrations.

X-ray diffractogram data for the Cl^- system showed rational 18 Å spacings for all levels of $Fe(bp)_3Cl_2$ added. This is consistent with adsorption isotherm data which indicated no multilayer metal complex adsorption. Similarly, the Br^- system showed clear, rational 18 Å spacings up to additions of ten symmetries. Addition of 15 and 28 times the exchange capacity resulted in 18 Å peaks which were interstratified. These results are not consistent with adsorption isotherm data which show a continuous increase in complex ion adsorption. Data for the SO_4^{2-} system, found in Table 2, resembles the ClO_4^- system at the lower symmetries. As metal complex concentration was increased beyond the exchange capacity, broadening of the 18 Å spacing took place until two peaks occurred at 10.29 symmetries. As concentrations increased, the 27 Å peak intensity increased and the 18 Å decreased. The most distinct 27 Å peak was obtained with the addition of 28.57 symmetries, and is shown in Figure 3. This persisted when heated to 100°C. Ten orders of reflection were obtained and have been assigned the following: d(001) 27.6 Å, d(002) 15.2 Å, d(003) 9.7 Å, d(005) 5.9 Å, d(008) 3.7 Å, and d(0010) 3.0 Å. The higher orders of reflection indicate the true d(001) to be 29.7 Å. Similar spacings were obtained when 58.14 symmetries were added. However, more interstratification was present. Very high additions, up to 114.3 symmetries resulted in an interstratified system.

Water Adsorption Isotherms

Water adsorption isotherms are shown in Figure 4 for $Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$ and $Ru(bp)_3^{2+}$- hectorite at one symmetry levels. The isotherms approach Type III in Brunauer's classification (Brunauer, 1945). Such curves indicate that adsorbate-adsorbate interactions predominate over adsorbate-adsorbent interactions (Barrer and McLeod, 1955). The $Ru(bp)_3^{2+}$- hectorite isotherm begins to approach an S-shaped curve indicative of Type II in Brunauer's classification where adsorbate-adsorbent interactions are predominant. The amount of water adsorbed by $Ru(bp)_3^{2+}$- hectorite at P/P_O less than 0.66 is about the same as that adsorbed by tetramethylammonium saturated

Figure 3.--X-ray diffractogram of $Fe(bp)_3^{2+}$- hectorite prepared by addition of 28.57 symmetries of $Fe(bp)_3SO_4$ to Na(I)-hectorite.

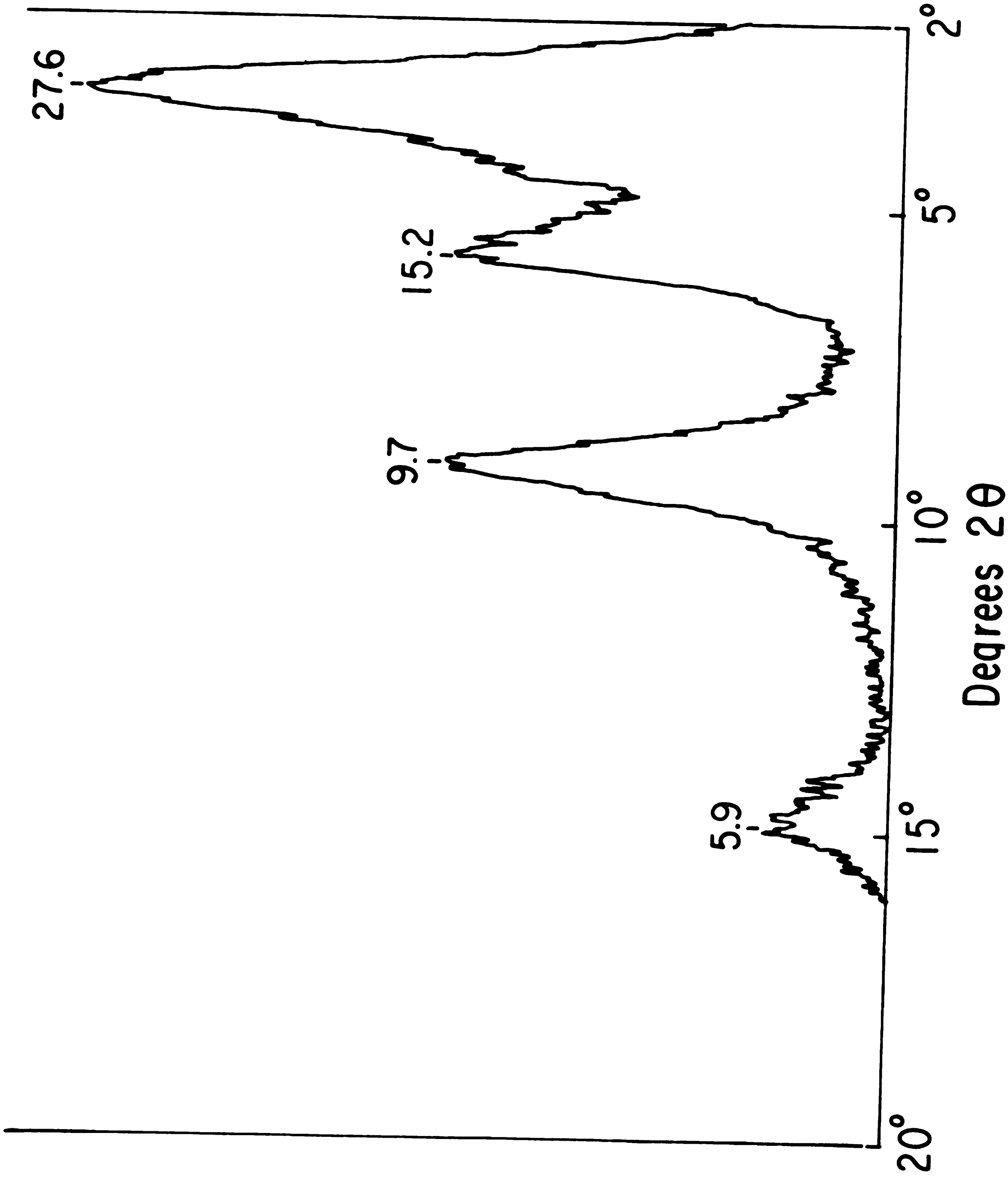
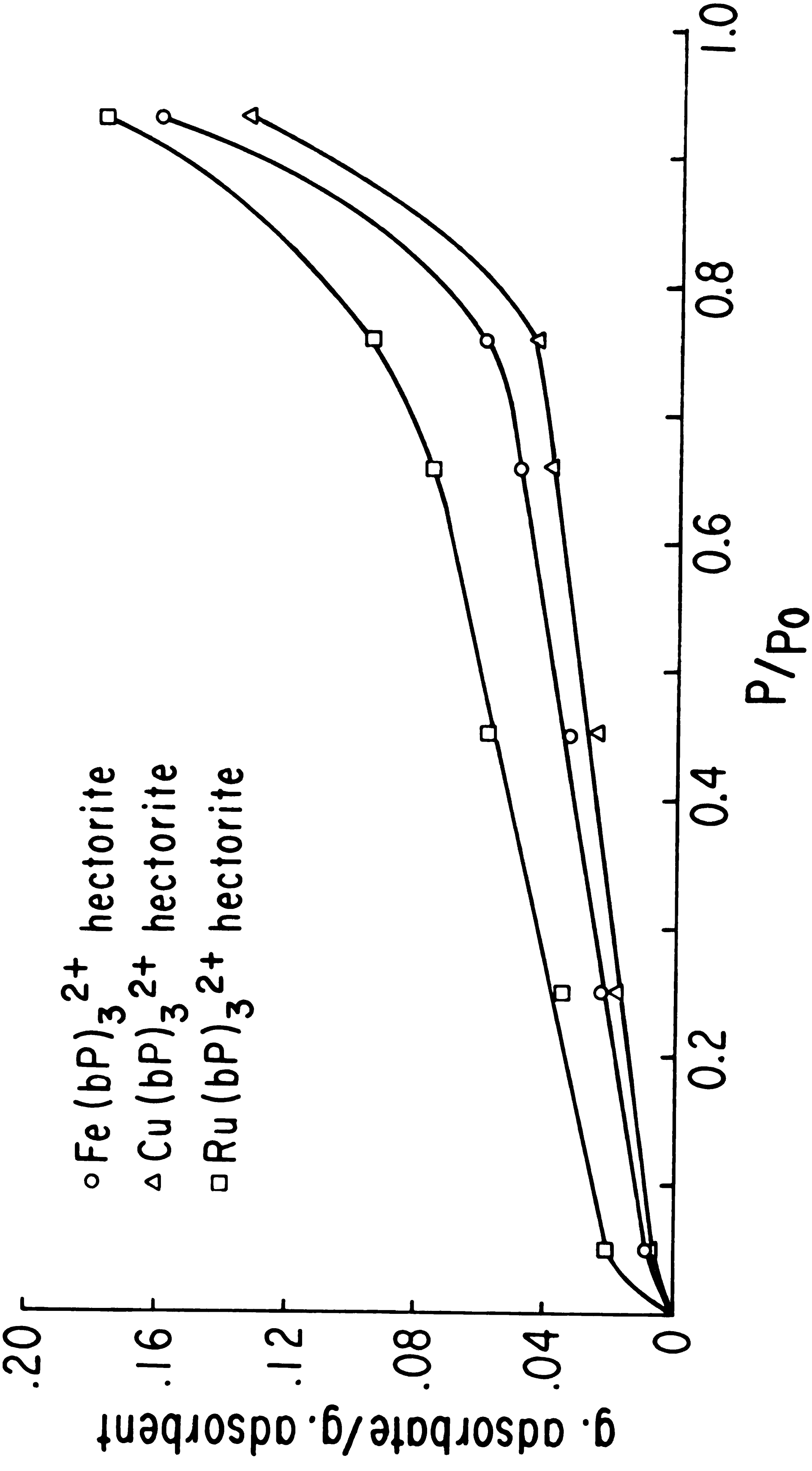

27.6
15.2
9.7
5.9
2°
5°
10°
15°
20°
Degrees 2θ

Figure 4.--Adsorption isotherms of H_2O on $M(bp)_3^{2+}$- hectorite at 20°C.


○ $Fe(bP)_3^{2+}$ hectorite
△ $Cu(bP)_3^{2+}$ hectorite
□ $Ru(bP)_3^{2+}$ hectorite
g. adsorbate/g. adsorbent
0
.04
.08
.12
.16
.20
P/Po
0.2
0.4
0.6
0.8
1.0

smectite (Gast and Mortland, 1971). Beyond $P/P_o = 0.66$ approximately one and one half times as much water is adsorbed by the $Ru(bp)_3^{2+}$- hectorite as by the tetramethylammonium smectite and presumably exists as physically bound water in the interstices between the cations. The $Ru(bp)_3^{2+}$- hectorite isotherm closely resembles the Fe and Cu phenanthroline isotherms reported by Berkheiser and Mortland (1977). However, at $P/P_o = 0.93$ the $Fe(phen)_3^{2+}$ and $Cu(phen)_3^{2+}$- hectorite adsorbed 26 percent and 30 percent water, respectively in comparison to 18 percent adsorbed by $Ru(bp)_3^{2+}$- hectorite. The $Fe(bp)_3^{2+}$ and $Cu(bp)_3^{2+}$- hectorite isotherms resemble the Fe and Cu phenanthroline curves of Berkheiser and Mortland at higher P/P_o. Water adsorbed by Fe and $Cu(bp)_3^{2+}$- hectorite is approximately one-half that adsorbed by Fe and Cu phenanthroline hectorite.

Infrared Water Studies

An infrared study of the water adsorption properties of the metal complex hectorites was conducted to further ellucidate adsorption mechanisms of the clay-water systems. The O-H stretching vibrations of water were observed by IR spectroscopy at 30 percent relative humidity followed by dehydration at temperatures of 100°C, 200°C and 250°C. The absorption bands indicate that there are two different kinds of water present in the metal complex hectorites. The band centered at 3400 cm^{-1} indicates water associated with the metal cation complex and hydrogen-bonded to other water molecules in the second coordination sphere (Farmer and Russell, 1967). The higher frequency band at 3575 cm^{-1} is attributed to water weakly hydrogen-bonded to silicate oxygens (Farmer and Russell, 1967). The spectra for the three metal complex clays with one symmetry of metal complex are shown in Figure 5. It is observed that as the metal complex hectorites are heated the O-H band at 3575 cm^{-1} becomes more distinct. This would indicate that as the system becomes dehydrated, the water associated with the metal cation complex is gone and hence a decrease in the intensity of the absorption band. A small amount of water remains bonded to the silicate oxygens at 3575 cm^{-1}. Water associated with the copper complex is less tightly held than water associated with the Ru complex, as noted by observing the disappearance of the band upon heating to 250°C. The $Ru(bp)_3^{2+}$- hectorite still contained appreciable water upon heating to 250°C. The greater affinity of the $Ru(bp)_3^{2+}$- hectorite for water is also supported by the water adsorption isotherm.

Figure 6 shows the effect upon the O-H stretching bands by the addition of one symmetry beyond the exchange capacity (two symmetries) to the metal-complex hectorites. When Na-hectorite is treated with two symmetries of metal

Figure 5.--Infrared spectra of Fe(bp)$_3^{2+}$, Cu(bp)$_3^{2+}$ and Ru(bp)$_3^{2+}$-hectorite (70 meq/100 g) from 3800 cm^{-1} to 3000 cm^{-1} at (A) 30% r.h., (B) 100°C, (C) 200°C and (D) 250°C.

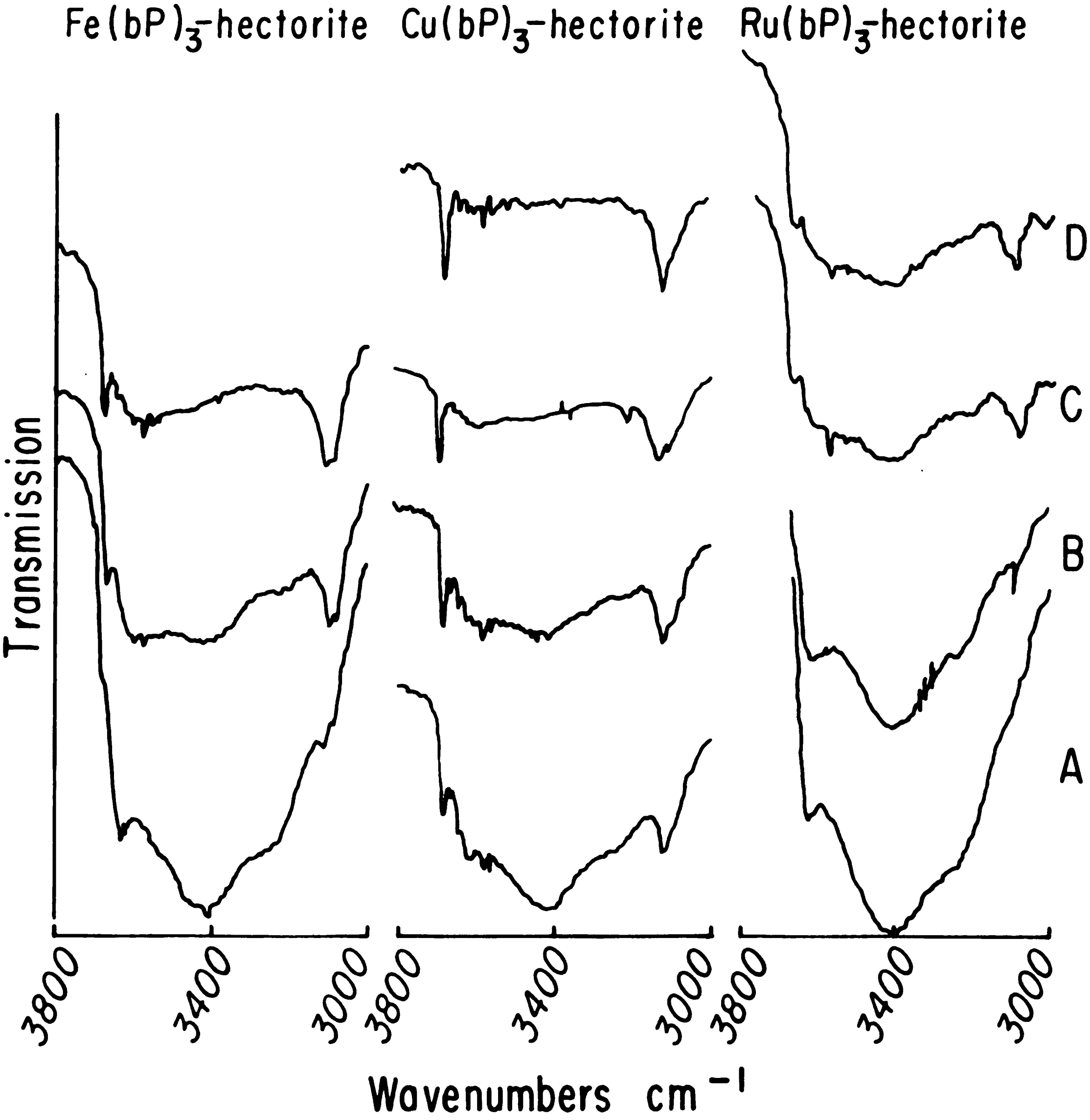
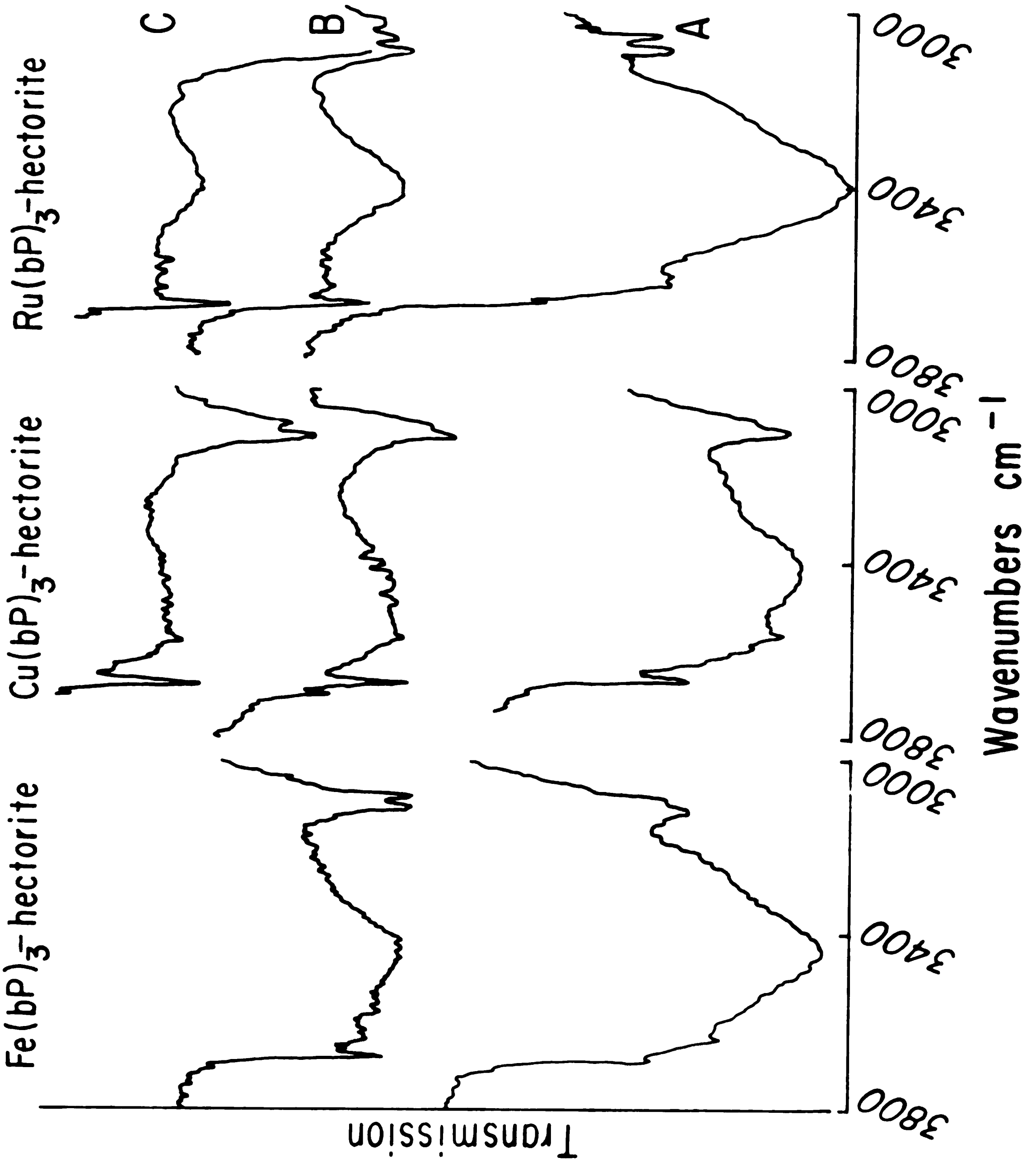

Fe(bP)$_3$-hectorite
Cu(bP)$_3$-hectorite
Ru(bP)$_3$-hectorite
Transmission
D
C
B
A
3800
3400
3000
3800
3400
3000
3800
3400
3000
Wavenumbers cm^{-1}

Figure 6.--Infrared spectra of $Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$ and $Ru(bp)_3^{2+}$-hectorite (two symmetry additions) from 3800 cm^{-1} to 3000 cm^{-1} at (A) 30% r.h., (B) 100°C and (C) 200°C.


Fe(bP)$_3$-hectorite
Cu(bP)$_3$-hectorite
Ru(bP)$_3$-hectorite
C
B
A
Transmission
3800
3400
3000
3800
3400
3000
3800
3400
3000
Wavenumbers cm^{-1}

complex, it appears that less water is associated with it than in the metal complex clays prepared with one symmetry. The excess $M(bp)_3X_2$ are most likely occupying voids and not allowing as many water molecules to enter. The $Ru(bp)_3^{2+}$- hectorite also shows evidence that water is more tightly associated with it than with the Fe and Cu analogs.

If a model of the metal complex hectorite is considered in which the complex cations are separated by a distance of 12 Å, the adsorbed water could be bound to the silicate surface or associated with the metal complex. The metal complex is not spherical in shape but the three perpendicular bipyridyl ligands jut out from the center, leaving empty space between. If, in a manner suggested by Jensen, Basolo and Neuman (1958), two water molecules resided in each pocket, six water molecules would be allowed to coordinate to the complex cation. Remaining water molecules would likely be bound to the silicate sheet and would exist as interstitial water at high P/P_o.

Nitrogen Adsorption and Surface Area Determinations

Specific surface areas of the $Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$ and $Ru(bp)_3^{2+}$- hectorite systems were obtained at fractional and multiple symmetries (based on a CEC of 70 meq/100 g) of the complex cation added to Na(I)-hectorite. Berkheiser and Mortland (1977) compared the Langmuir, Hüttig and BET equations for N_2 adsorption on tris-phenanthroline-Fe(II)-hectorite and found the BET equation to give more realistic surface areas. Due to the similarity of the reactions of tris-phenanthroline Fe(II) and tris-bipyridyl-Fe(II) complexes with hectorite, the data for these investigations was plotted according to the BET equation. Additionally, X-ray basal spacings and complex salt adsorption isotherm data gave evidence of adsorption beyond the cation exchange capacity. Since the $M(bp)_3^{2+}$ cation separates the silicate sheets by approximately 8 Å, additional adsorption could occur in areas between complex cations on the exchange sites. The BET equation may be represented by the following:

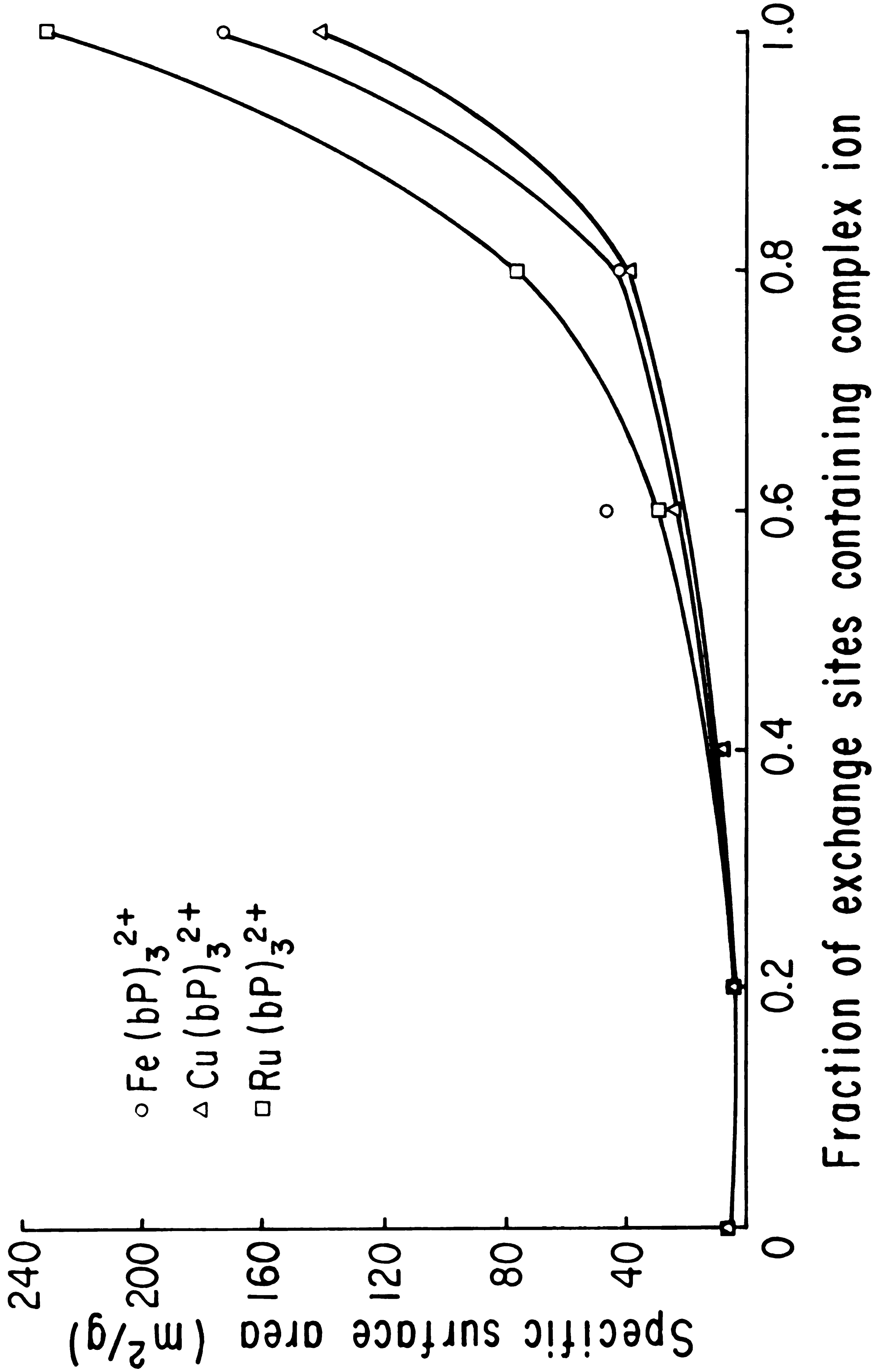
$$\frac{x}{v_{ads}}(1-x) + \frac{1}{cv_m} + \frac{(c-1)x}{cv_m},$$

where $x=p/p_o$, v_{ads}=volume of gas adsorbed at pressure p and v_m=the volume adsorbed at the monolayer point, c=a constant. The BET equation assumes that the heat of adsorption of the first monolayer may have a special value but the heat of adsorption of each succeeding layer equals the heat of vaporization of the liquid adsorbate. The equation also assumes that the Langmuir equation applies to each layer of a multilayer film. Hence, the Langmuir model which was appropriate for monolayer adsorption on the contracted tetramethylammonium saturated smectites described by Clementz and Mortland (1974), would not be expected to give an accurate measure of the surface areas of these systems.

Figure 7 shows the change in surface area as the clay is increasingly saturated with $M(bp)_3^{2+}$ cations to one symmetry. These data along with the X-ray basal spacings suggest that certain layers tend to become $M(bp)_3^{2+}$ saturated before appreciable quantities of complex cations enter other interlayers. The figure shows a negative deviation from a linear relationship between specific surface area and the fraction of exchange sites containing the $M(bp)_3^{2+}$ cation. This behavior suggests that layers with high charge density were filled with the complex cations before layers of low charge density. This would result in a reduction of N_2 adsorption in those regions due to crowding of the large complex cations. On the other hand, a positive deviation from a linear plot would indicate that the $M(bp)_3^{2+}$ cations were regularly distributed in the interlayers, thus permitting nitrogen adsorption in layers not completely saturated with complex cation. Lagaly and Weiss (1975) have observed charge heterogeneity in smectites and vermiculites; the degree of inhomogeneous charge distribution was not determined in this study.

Because of similarity in the structures and charges of the Fe(II), Cu(II) and Ru(II) complexes, the

Figure 7.--Specific surface areas of hectorite fractionally saturated with $M(bp)_3^{2+}$ calculated according to the BET equation.


○ $Fe\,(bP)_3^{2+}$
△ $Cu\,(bP)_3^{2+}$
□ $Ru\,(bP)_3^{2+}$
Specific surface area (m^2/g)
240
200
160
120
80
40
0
0.2
0.4
0.6
0.8
1.0
Fraction of exchange sites containing complex ion

curves would be expected to closely resemble one another, and this appears to be the case. The lower surface areas of the $Cu(bp)_3^{2+}$- hectorites than the Fe(II) and Ru(II) analogs may be attributed to a loss of bipyridyl ligands, causing a partial collapse of some interlayers. ESR spectra indicate that upon heating the tris complex to 100°C, the Cu(II) atom loses a ligand and becomes a bis complex. Since the complex clays were degassed at 160°C, this is a reasonable explanation. The relative instability of the tris-bipyridyl Cu(II) complex compared with Ni(II) has been explained by James and Williams (1961) to be due to the absence of Jahn-Teller distortion in the tris-bipyridyl Cu(II) complex. Percy and Thornton (1971), among others, (Noack, et al., 1971 and Hathaway, et al., 1974) indicate that distortion of the complex may take place but the associated Jahn-Teller stabilization is insufficient to reverse the frequency order of Ni>Cu predicted by crystal field theory. The greater stability of the tris-bipyridyl Fe(II) complex may arise from the π-electron interaction between the metal and ligands causing a lowering of the energy of the ground configuration (Hanazaki and Nagakura, 1969). For strong crystal field ligands, the maximum crystal field stabilization energy (CFSE) is for the d^6 electronic Fe(II) system with a subsequent linear decrease of the CFSE to zero from Co(II) through Zn(II) except for the possibility of the

Jahn-Teller stabilized d^9 system of Cu(II) (Inskeep, 1962). Of the metal ions which are stabilized by bipyridyl ligands those of iron and ruthenium are most stable (Schilt, 1969). The tris-bipyridyl Ru(II)-hectorite generally exhibited higher surface areas for all points. The basal spacings for the three complexes on the clay at one symmetry were 18 Å.

The calculated and observed surface areas of $M(bp)_3^{2+}$- hectorite are summarized in Table 3. The cross-sectional area of the $M(bp)_3^{2+}$ cation was calculated from a space-filled molecular model which was approximately spherical and was taken to be 130 $Å^2$. Adsorption of N_2 on the surface of bipyridyl ligands would cause measured surface areas to be high since the areas of the adsorbent includes both surface of the complex cation plus the mineral surface.

As a result of the apparent "anion effect" observed in the adsorption isotherm studies and high basal spacings obtained through X-ray diffraction analysis, particularly with sulfate as the counter-ion, the surface areas of $Fe(bp)_3^{2+}$- hectorite were studied in greater detail. The effect of changing the counter-ion is shown in Table 4 for clays prepared with concentrations of metal complex 5.71 times the exchange capacity of the clay. The monovalent anions gave low surface areas, while the divalent, SO_4^{2-} anion exhibited a surface area three to

Table 3.--Calculated and observed surface areas of $M(bp)_3^{2+}$ - hectorite (one symmetry) according to the BET equation.

Calculated area occupied by $M(bp)_3^{2+}$ cations including both silicate surfaces of interlayer		548 m^2/g
Observed nitrogen surface areas		
(a)	$Fe(bp)_3^{2+}$- hectorite	174 m^2/g
(b)	$Cu(bp)_3^{2+}$- hectorite	141 m^2/g
(c)	$Ru(bp)_3^{2+}$- hectorite	233 m^2/g
Total surface areas		
(a)	$Fe(bp)_3^{2+}$- hectorite + nitrogen surface area	722 m^2/g
(b)	$Cu(bp)_3^{2+}$- hectorite + nitrogen surface area	689 m^2/g
(c)	$Ru(bp)_3^{2+}$- hectorite + nitrogen surface area	781 m^2/g

21 times greater than the other three. According to adsorption isotherm data, the Br^- and SO_4^{2-} systems both adsorbed high amounts of metal complex, 231 and 170 meq/100 g, respectively at the addition level of 5.71 symmetries. Hence the great differences in surface area were unexpected.

Multiple symmetries of $Fe(bp)_3SO_4$ were added to Na(I)-hectorite and surface areas of the resulting complex clays were determined and are reported in Table 4. Very high surface areas were obtained at 2.27 and 5.71 symmetries, while higher symmetries gave extremely low surface areas. All clays were analyzed as freeze-dried

Table 4.--Effects of counter-ion and high concentrations of $Fe(bp)_3X$ (where X = Cl_2, Br_2, $(ClO_4)_2$ or SO_4) on nitrogen surface areas of $Fe(bp)_3^{2+}$-hectorite.

Effects of Counter-Ion on Surface Area

5.71 symmetries* of metal complex added to Na(I)-hectorite	meq. adsorbed /100 g	Observed surface areas
$Fe(bp)_3Br_2$	231	21 m^2/g
$Fe(bp)_3Cl_2$	113	92 m^2/g
$Fe(bp)_3(ClO_4)_2$	180	12 m^2/g
$Fe(bp)_3SO_4$	170	252 m^2/g

Effects of High Concentrations of $Fe(bp)_3SO_4$

Symmetries of $Fe(bp)_3SO_4$ added to Na(I)-hectorite	Observed surface areas
2.29	265 m^2/g
5.71	252 m^2/g
10.29	13 m^2/g
28.57	8 m^2/g
pure salt	5 m^2/g

*4 meq./g clay/50 ml.

powders after centrifugation with no washing. Repeated washing removed all but 80 meq/100 g of the $Fe(bp)_3^{2+}$ and resulted in rational basal spacings of 18 Å. This indicates that the excess metal complex is non-coulombically bound and is probably physically adsorbed. Crowding of the large complex cations and presence of high concentrations of salt which interferred with nitrogen adsorption on the surfaces may be partially responsible for the clays with low surface areas.

This phenomenon, which has been attributed to excess salt interferring with nitrogen adsorption, is substantiated by data obtained when Fe, Cu and Ru bipyridyl hectorites, prepared at one symmetry were analyzed after washing and with no washing (Table 5). It is clear that the surface area is greatly reduced when excess salts are not removed. In this case, NaCl or $NaClO_4$ are most likely precipitated on edges and interfere with nitrogen penetration and adsorption. This effect was also observed for the three metal complex clays prepared with 5.71 symmetries of metal complex and left unwashed (Table 6).

X-ray data, in conjunction with adsorption isotherm and surface area measurements of the sulfate system, give evidence for a large porous structure within the interlayer, which has the effect of separating the silicate sheets by approximately 20 Å and providing large surfaces for nitrogen adsorption. There are several possible structures which could give rise to such observations. In order to maintain electrical neutrality, additions of complex molecules above one symmetry which were adsorbed by the clay, would necessitate the counterion as well as the complex cation entering the interlayers.

Table 5.--Effects of washing on nitrogen surface areas of $M(bp)_3^{2+}$- hectorite (where M = Fe, Cu or Ru).

1 symmetry of metal complex added to Na(I)- hectorite	Observed surface areas
$Fe(bp)_3(ClO_4)_2$	
washed	174 m^2/g
unwashed	37 m^2/g
$Cu(bp)_3(ClO_4)_2$	
washed	141 m^2/g
unwashed	17 m^2/g
$Ru(bp)_3Cl_2$	
washed	233 m^2/g
unwashed	12 m^2/g

Table 6.--Surface areas of hectorite after addition of 5.71 symmetries of metal complex.

Complex salt	Observed surface areas
$Fe(bp)_3(ClO_4)_2$	12 m^2/g
$Cu(bp)_3(ClO_4)_2$	10 m^2/g
$Ru(bp)_3Cl_2$	10 m^2/g

Thus, the sulfate anion may reside between the two $Fe(bp)_3^{2+}$ cations, neutralizing a single charge on each, with the silicate surface also neutralizing a single charge on each complex cation. If each $Fe(bp)_3^{2+}$ cation were approximately 8 Å in diameter and the SO_4^{2-} anion 2 to 3 Å, a total spread of the silicate sheets by this 19 Å structure would give approximately a 29 Å d(001) value. The $Fe(bp)_3SO_4$ complex is known to be unstable in acid solution (Schilt, 1963 and Burgess and Prince, 1965). Mortland and Raman (1968) have studied the effect of exchangeable cations on surface acidity and its relationship to hydration. No reference was found as to a similar effect due to exchangeable metal complex cations. However, if metal complex cations effected greater surface acidity, dissociation of the $Fe(bp)_3SO_4$ complex may occur, with the resultant loss of a bipyridyl ligand. The SO_4^{2-} anion could then serve as a bridge between the two $Fe(bp)_2^{2+}$ cations with charge being neutralized by the silicate surface. Lastly, the SO_4^{2-} anion may exist between the $Fe(bp)_3^{2+}$ cations by residing in the pockets or faces of the cations thus creating a well-ordered arrangement in the interlayer. This would be similar to a description given by Jensen, Basolo and Neuman (1958) for the sulfonate ion residing in the pockets formed by ligands of tris-phenanthroline Fe(II).

Oxidation-Reduction Reactions

A qualitative study of the oxidation-reduction properties of iron, copper and ruthenium complexes and these complexes on hectorite (one symmetry) was conducted. Change in oxidation status was assumed to occur when the following color changes were observed:

Fe(II) ⟶ Fe(III), red ⟶ blue-green

Cu(II) ⟶ Cu(I), blue ⟶ brownish-purple

Ru(II) ⟶ Ru(III), orange ⟶ green

Table 7 summarizes the reactions. The $Fe(bp)_3^{3+}$ cation was found to be extremely unstable in solution (except in strong acids) and on the clay surface. In all solvents used, the Fe(III) complex reduced to the Fe(II) complex within minutes. No correlation was found between solvents causing this reduction and solvent ionization potentials or dipole moments. In contrast to this, Fe(III) phenanthroline has been found to be stable as the salt and adsorbed on the clay in solvents such as acetonitrile, acetone and benzene (Berkheiser and Mortland, 1977). The Fe(II) complex salt could be oxidized to $Fe(bp)_3^{3+}$ by use of PbO_2 or Ce(IV) in 0.1 $\underline{N}$ H_2SO_4. However, neither of these oxidizing agents with oxidation half-cell potentials near 1.7 volts were able to oxidize the $Fe(bp)_3^{2+}$ when adsorbed on the clay. By use of concentrated nitric acid, both the metal complex salt and the metal complex adsorbed

Table 7.--Summary of oxidation-reduction reactions with Fe, Cu and Ru bipyridyl complexes on hectorite and in the complex ion salts.

Metal ion in bipyridyl complex	Solvents or reagents added	Reaction Observed	
		Clay Complex	ClO_4^- salt
Fe(II)	PbO_2 in $0.1\underline{N}$ H_2SO_4	NR*	Ox
	Ce(IV) in $0.1\underline{N}$ H_2SO_4	NR	Ox
	H_2O_2	NR	NR
	Conc. HNO_3	Ox	Ox
Fe(III)	H_2O	Rn	Rn
	Methanol	Rn	Rn
	Ethanol	Rn	Rn
	Acetone	Rn	Rn
	Acetonitrile	Rn	Rn
	Benzene	Rn	Rn
	Cyclohexene	Rn	Rn
	1-hexene	Rn	Rn
	nitromethane	Rn	Rn
Cu(II)	Dithionite in $0.1\underline{N}$ H_2SO_4	Rn	Rn
	Hydrazine	Rn	Rn
	Hydroquinone in $0.1\underline{N}$ NaOH	NR	NR
	H_2O	NR	NR
Cu(I)	Quinone in $0.1\underline{N}$ H_2SO_4	Ox	Ox
	Ce(IV) in $0.1\underline{N}$ H_2SO_4	Ox	Ox
	PbO_2 in $0.1\underline{N}$ H_2SO_4	Ox	Ox
	H_2O_2	Ox	Ox
Ru(II)**	PbO_2 in $0.1\underline{N}$ H_2SO_4	NR	Ox
	Ce(lV) in $0.1\underline{N}$ H_2SO_4	NR	Ox
	Quinone in $0.1\underline{N}$ H_2SO_4	NR	NR
	H_2O_2	NR	NR
	Conc. HNO_3	Ox	Ox

[*] NR = no reaction, Ox = oxidation of metal ion, Rn = reduction of metal ion.

[**] Cl^- salts were used in these reactions.

on the clay were able to be oxidized. However, damage to the silicate structure probably occurred by use of the strong acid.

The oxidation potential of the $Fe(bp)_3^{2+}/Fe(bp)_3^{3+}$ couple observed in M sulfuric or hydrochloric acid by Hume and Kolthoff (1943) was 1.06 volts. Schilt (1963) and Hume and Kolthoff (1943) observed that the redox potential decreased as acid concentration increased and attributed this to ionization of the oxidized form. Therefore, it seems reasonable to assume that at higher pH's the redox potential would increase thus making it more difficult to oxidize the metal complexes. It may be that interaction with the silicate surface causes destabilization of the oxidized species compared to the reduced form similar to that observed by James and Williams (1961). If the electron-donating ability of the nitrogen atom is decreased, destabilization of the Fe(III) complex should result (Ford-Smith and Sutin, 1961). Increases in the redox potential of Fe and Cu complexes with substituted phenanthroline ligands were thought to be due to steric hindrance between ligands on the metal ion and to greater basicity of the chelates. Hanazaki and Nagakura (1969) have studied the electronic structure of $Fe(bp)_3^{2+}$ and have stated that the remarkable stability of the complex ion is due to great stabilization of the ground state through interaction between the metal and ligands.

Tris-bipyridyl Cu(II) loses a ligand upon reduction to Cu(I). This has been substantiated by both visual observations of color change from blue of the tris complex to dark purple-brown of the $Cu(bp)_2^{1+}$ species, and by change in absorption observed with UV spectroscopy. The species produced by the reduction and the synthesized complex of $Cu(bp)_2^{1+}$ both absorb light at 430 mμ, whereas $Cu(bp)_3^{2+}$ absorbs at 297 mμ. Also, the addition of $Cu(bp)_2^{1+}$ to Na(I)-hectorite gave identical spectral results as when $Cu(bp)_3^{2+}$-hectorite was reduced. Similar reactions have been observed for Cu(I) and Cu(II) phenanthroline on hectorite (Berkheiser and Mortland, 1977). UV-VIS absorption spectra were obtained for the tris-bipyridyl Fe(II), Cu(II) and Ru(II) cations adsorbed on the clay and compared to absorption of the complex metal cations in solution. The perchlorate salts of Cu and Fe were used and the chloride salt of the Ru complex. A shift of 5 to 9 mμ was found for each. The copper clay complex absorbed light at 304 mμ, while in solution it absorbed at 297 mμ. The iron complex hectorite absorbed at 515 mμ in comparison to 522 mμ in solution, and the Ru complex clay absorbed at 456 mμ in comparison to 449 mμ in solution.

The $Ru(bp)_3^{2+}$ complexes were oxidized to the green $Ru(bp)_3^{3+}$ with PbO_2 and Ce(IV) in 0.1 N H_2SO_4. When adsorbed on the clay, the complex was not able to be oxidized by these oxidants. The standard oxidation potential for the $Ru(bp)_3^{2+}/Ru(bp)_3^{3+}$ couple is 1.23 volts (Gafney and Adamson, 1972). Evidently the clay raises this potential, or, the back reaction is so rapid that the oxidized form is not visibly seen. Schilt (1969) has found that both Ru(III) and Fe(III) complexes undergo spontaneous reduction when their solutions are made alkaline. Blau (1898) found that sunlight causes a slower but similar effect.

ESR Spectroscopy

Tris complexes of copper(II)-bipyridyl on the clay surface should show orientation independent spectra characteristic of other tetragonally distorted octahedral Cu(II) complexes whose axes are tilted at about a 45° angle with respect to the clay sheets (Clementz, et al., 1973). In contrast to this, the bis copper(II) complexes on the clay should exhibit orientation dependence where the Cu(II)-ligand plane is parallel to the silicate sheets (Berkheiser and Mortland, 1975 and Berkheiser and Mortland, 1977). Therefore, in order to determine the stereochemistry of the $Cu(bp)_3^{2+}$ complex on hectorite, ESR spectra of Cu(II) in $Cu(bp)_3^{2+}$ and $Cu(bp)_2^{2+}$ were compared. Self-supported films of $Cu(bp)_3^{2+}$- hectorite were prepared by adding one symmetry of the tris complex to Ca(II)-hectorite in water. The $Cu(bp)_2^{2+}$- hectorite was formed by the addition of a half symmetry of $Cu(bp)_2^{1+}$ to Ca(II)- hectorite in acetonitrile and subsequently oxidized to $Cu(bp)_2^{2+}$ with 0.1 percent H_2O_2. ESR spectra of the tris complexes at various levels of hydration are shown in Figure 8. At 77 percent r.h. and at liquid nitrogen temperatures the spectra are isotropic. As in other investigations (Noack, et al., 1971 and Hathaway, et al., 1974), the Jahn-Teller distortion dynamics are probably rapid enough to average the g and A tensors to produce an isotropic spectrum (spectra A and B). As the metal complex clay is heated, (C), the spectra becomes anisotropic and orientation dependent. This is most likely due to loss of bipyridyl ligands from the coordination spheres of the Cu(II) ions, to form a bis complex whose axis is perpendicular to the clay sheets. The tris-bipyridyl Cu(II) complex appears to be more stable than the analogous phenanthroline complex (Berkheiser and Mortland, 1977). They found evidence for loss of phenanthroline ligands at 45 percent r.h. This difference may be due to the greater flexibility of the bipyridyl than the phenanthroline ligand, resulting in greater stabilization due to Jahn-Teller distortion (Percy and Thornton, 1971 and Allen, et al., 1964). The isotropic g value

Figure 8.--ESR spectra of oriented thin films of Cu(II) in $Cu(bp)_3^{2+}$- hectorite at (A) liquid nitrogen temperature, (B) 77% r.h. and, (C) 100°C. The free electron signal indicates g=2.0028; films were oriented parallel (||) and perpendicular (⊥) to the magnetic field H.

given in Table 8 correlates well with the value of 2.114 reported for the nitrate salt by Allen, et al. (1964). At liquid nitrogen temperatures he gave values of $g_{\perp} = 2.046$ and $g_{||} = 2.268$.

The bis complex, at 0 percent r.h. and 77 percent r.h. and upon heating to 100°C gave well-oriented anisotropic spectra, an example of which appears in Figure 9, with basal spacings of 12.8 Å. The g-values taken from these spectra (Table 8) indicate that Cu(II) is coordinated predominately by bipyridyl rather than water since g-values of hydrated Cu(II) are near 2.30 (Clementz, et al., 1973 and Noack, et al., 1971). The g and A values are very similar to those reported for the bis-phenanthroline Cu(II) complex (Berkheiser and Mortland, 1977). Due to the low basal spacings of the bipyridyl complexes, the species probably exists as $Cu(bp)_2^{2+}$ rather than $Cu(bp)_2$-$(H_2O)_2^{2+}$, with Cu(II) coordinated to the bipyridyl ligands in the xy plane and to surface oxygens of the silicate lattice along the z-axis.

Although hyperfine splitting due to interaction with the Cu(II) nucleus occurred, no superhyperfine lines due to coupling of the unpaired electron to nuclei of the ligands was observed. This splitting was observed by Allen, et al. (1964) for the nitrate analog on polycrystalline samples and by Berkheiser and Mortland (1977) for the phenanthroline Cu(II) complex adsorbed onto

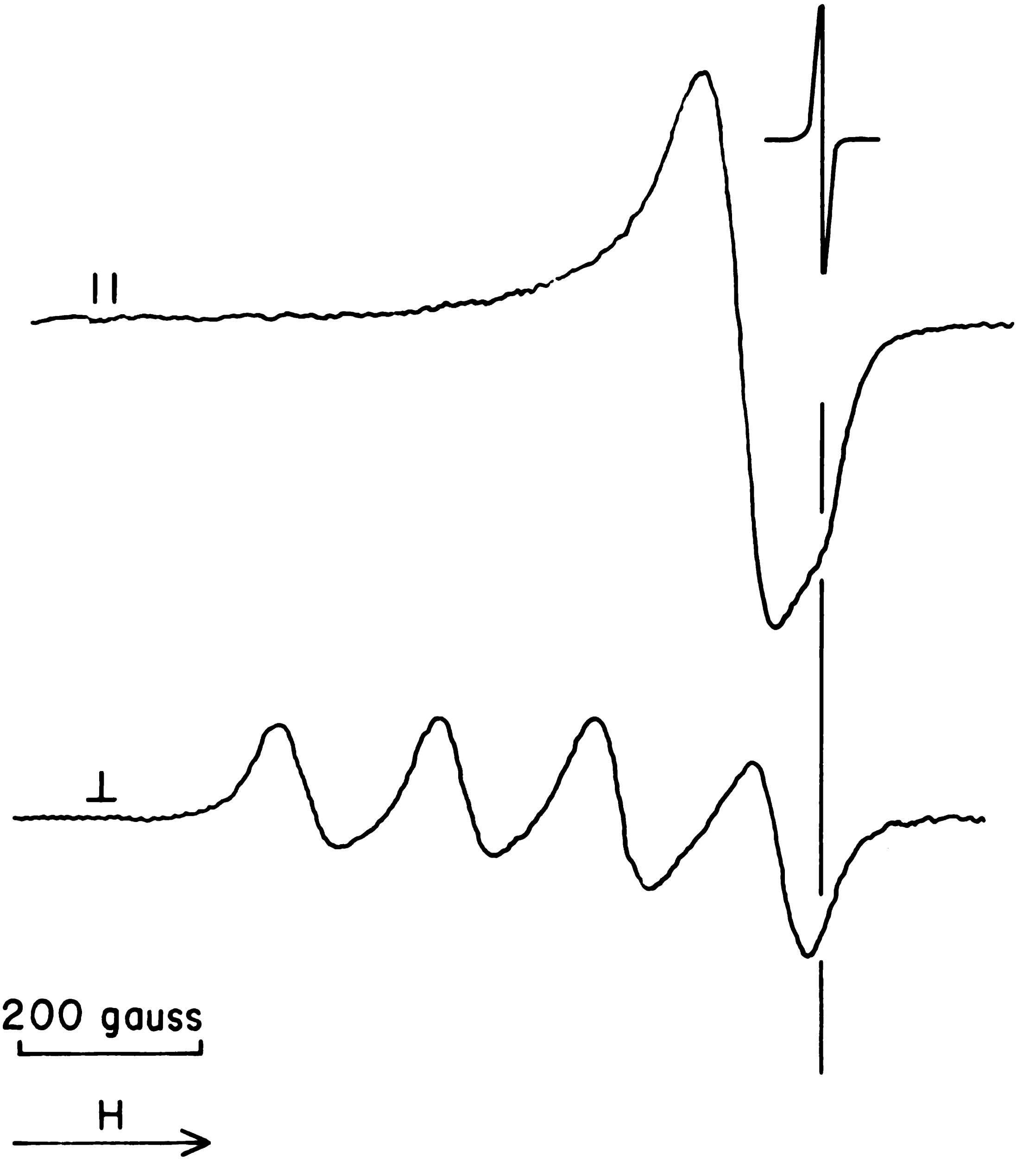
Table 8.--ESR parameters for $Cu(bp)_3^{2+}$ and $Cu(bp)_2^{2+}$- hectorite complexes.

Treatment	$g_{\|\|}$ (±0.005)	$g_{\perp}$ (±0.005)	g_{iso} (±0.005)	A $cm^{-1} x10^4$ (±2)
$Cu(bp)_3^{2+}$, liq. N_2	2.14	2.08	---	158
$Cu(bp)_3^{2+}$, 77% r.h.	---	---	2.10	a
$Cu(bp)_3^{2+}$, 100°C.	2.235	2.070	---	158
$Cu(bp)_2^{2+}$, ox.*, 77% r.h.	2.244	2.062	---	170
$Cu(bp)_2^{2+}$, ox., 100°C.	2.244	2.065	---	168
$Cu(bp)_2^{2+}$, ox., 0% r.h.	2.244	2.062	---	168

[a] denotes parameters which were not resolve.

*refers to $Cu(bp)_2^{1+}$ oxidized to $Cu(bp)_2^{2+}$ on the clay.

Figure 9.--ESR spectra of oriented thin films of 0.5 symmetries of Cu(II) in Cu(bp)$_2^{2+}$- hectorite at 77% r.h. The free electron signal indicates g=2.0028; films were oriented parallel (||) and perpendicular (⊥) to the magnetic field H.


II
⊥
200 gauss
H

smectite. In $Cu(bp)_2^{2+}$ and the $Cu(bp)_3^{2+}$ cation at 100°C, where the complex is in contact with the clay surface, spin-lattice relaxation mechanisms may cause broadening of the nitrogen hyperfine lines so they do not appear. In the tris complex at 77 percent r.h. the broadening is probably due to rapid molecular tumbling.

SUMMARY AND CONCLUSIONS

The adsorption of Fe(II), Cu(II) and Ru(II) bipyridyl complexes onto hectorite clay has given some results which were anticipated and are in agreement with data reported for a similar complex molecule, 1,10-phenanthroline. There are also several areas of investigation which differ.

1. The complex cations $Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$ and $Ru(bp)_3^{2+}$ show a marked affinity for exchange onto the surface of Na(I)-hectorite. Adsorption isotherm and X-ray diffractogram data show that the complex molecules are adsorbed beyond the cation exchange capacity of the clay, giving rational (001) spacings when adsorption is up to or exceeding twice the CEC. Previous investigations have shown that molecules of organic salts may be adsorbed in excess of the cation exchange capacity in an undissociated form, primarily due to van der Waals interactions (Grim, et al., 1947, Hendricks, 1941 and Bradley and Grim, 1947). More recently, 1-(n-alkyl)pyridinium bromides have been shown to be adsorbed to two and three times the CEC (Greenland and Quirk, 1962), and Fe and Cu phenanthroline complexes to twice the CEC (Berkheiser and Mortland, 1977).

2. Water adsorption of the metal complex clays, prepared at one symmetry, showed adsorbate-adsorbate interactions to be predominant. $Ru(bp)_3^{2+}$- hectorite consistently adsorbed more water than the Fe or Cu bipyridyl clays, but less water than reported for the Fe and Cu phenanthroline clays by Berkheiser and Mortland (1977). As metal complex salt was adsorbed after saturation of the exchange sites (up to two symmetries) with the complex cation, water adsorption was found to decrease as observed with infrared spectroscopy. The excess metal complex salt is probably occupying voids between exchanged metal complex cations and not allowing as many water molecules to enter. Grim (1968) also noted that the water adsorbing properties of montmorillonite are reduced as the basal surfaces of the mineral are covered with organic ions.

3. Qualitative observations of the oxidation-reduction properties of Fe(II) and Ru(II) bipyridyl showed that both metal complex salts were oxidized in acid aqueous solution, but when the complex cations were adsorbed on the clay, no oxidation occurred indicating the oxidation-reduction couple was raised. An alternative would be that the back reaction was so rapid, the oxidized complex was not visible. The Fe(III) bipyridyl complex salt was unstable in all solvents used, while the Fe(III) phenanthroline was reported by Berkheiser and Mortland (1977) to be stable as the salt and adsorbed on the clay,

in acetone, acetonitrile, and benzene. As reported for copper phenanthroline (Berkheiser and Mortland, 1977), the oxidation-reduction properties of Cu(I) and Cu(II) bipyridyl adsorbed on hectorite did not appear to change.

4. Surface areas of the metal complex clays at one symmetry approached 800 m^2/g, when considering area measured by nitrogen adsorption and area occupied by the complex cation. Nitrogen adsorption was found to decrease greatly when the clays were unwashed and contained excess salts. This indicates that the salt is interferring with nitrogen penetration and adsorption.

5. ESR data show the $Cu(bp)_3^{2+}$ complex to be isotropic and reside in the interlayer tilted at about a 45° angle to the clay sheets. Loss of a ligand occurred when the metal complex clay was heated, resulting in the formation of a *bis* complex whose axis was perpendicular to the clay sheets with an anisotropic spectrum, as well as being orientation dependent. Tris-phenanthroline Cu(II)-hectorite reacted in a similar manner (Berkheiser and Mortland, 1977), with loss of ligands occurring at 45 percent r.h. This indicates that phenanthroline ligands are lost more easily than bipyridyl from the Cu(II) atom. Due to greater flexibility of the bipyridyl ligands, more distortion resulting in greater Jahn-Teller stabilization may cause tris-bipyridyl Cu(II) to be more stable.

Of greatest interest and potential significance has been data obtained when high concentrations of tris-bipyridyl Fe(II) salts were added to Na(I)-hectorite. Adsorption isotherms, X-ray diffractograms and surface area measurements show an apparent "anion effect." Each of the anions, Cl^-, Br^-, ClO_4^- and SO_4^{2-}, gave distinctly different isotherms, and at some levels of adsorption, different X-ray basal spacings.

Ion-pair formation may have occurred in the perchlorate system with a resultant shift in equilibria such that the $Fe[(bp)_3ClO_4]^+$ preferred the clay surface at low concentrations and the equilibrium solution at high concentrations. X-ray basal spacings have been shown to change as metal complex additions were increased, and appear to be correlated with certain regions of the isotherm. Ion-pair formation of complex ions in solution can be detected by changes in the UV-VIS spectrum (Dickens, Basolo and Neuman, 1957). The spectrum of $Fe(bp)_3(ClO_4)_2$ in solution was compared to that of $Fe(bp)_3^{2+}$- hectorite and a shift of 7 mμ was found. Data presented by Dickens, Basolo and Neuman (1957) for tris-phenanthroline Fe(II) and Fe(III) indicate that it is unlikely that the Fe(II) complex would form ion-pairs, whereas the Fe(III) was found to undergo ion-pair formation. There is no conclusive evidence at this time for ion-pair formation in the $Fe(bp)_3(ClO_4)_2$ complex.

The Cl^- isotherm showed no evidence of ion-pair formation. An adsorption maximum was obtained rapidly and basal spacings above one symmetry were all 18 Å.

The Br^- system also gave rational 18 Å basal spacings, but adsorption isotherms showed that excess $Fe(bp)_3Br_2$ was adsorbed when high concentrations of metal complex were added to Na(I)-hectorite. Two hypotheses consistent with these findings are: (1) the molecular complex salt was precipitated on the edges of the clay mineral, or (2) large diffuse layers of $Fe(bp)_3Br_2$ were present in the interlayer but upon drying were squeezed to the edges. The presence of salt peaks on the X-ray diffractograms could support both hypotheses. Additionally, the surface areas of the clay with high symmetry additions gave low surface areas indicating the presence of salt interferring with nitrogen penetration and adsorption.

Tris-bipyridyl-ferrous sulfate, $Fe(bp)_3SO_4$, was also adsorbed in excess of the exchange capacity at high concentrations and resembles the Br^- isotherm. However, X-ray basal spacings changed with increasing metal complex addition, giving evidence that excess $Fe(bp)_3SO_4$ was present in the interlayer effecting a greater spread of the silicate sheets. When 28.57 symmetries of metal complex were added, ten orders of reflection were obtained, the higher orders indicating the (001) spacing to be about

29.7 Å. Very high surface areas were obtained at 2.29 and 5.71 symmetries of added metal complex. A low surface area for the clay treated with 28.57 symmetries is attributed to excess salt interferring with nitrogen penetration and adsorption as found with the Br^- system. The finding of high surface areas, in conjunction with large basal spacings and high adsorption, give indication for a structure within the interlayer which is very open and porous. There are at least three possible structures which may exist in the interlayer and exhibit these properties. First, the SO_4^{2-} anion may reside between the two $Fe(bp)_3^{2+}$ cations, neutralizing a single charge on each, with the silicate surface also neutralizing a single charge on each complex cation. This structure would be consistent with the basal spacing of 29.7 Å if each tris-bipyridyl Fe(II) complex were approximately 8 Å in diameter and the SO_4^{2-} anion 2-3 Å. Secondly, the SO_4^{2-} anion may serve as a bridge between two complex cations with the resultant loss of a ligand from each. Charge would be neutralized by the silicate surface. Thirdly, the SO_4^{2-} anion may reside in one of the pockets or faces of it's counter-ion, $Fe(bp)_3^{2+}$, in much the same way as Jensen, Basolo and Neuman (1958) found for the sulfonate ion. It would be expected that lower basal spacings would be found for these latter two structures. More extensive research is necessary in order to establish the stereochemistry of the structure and determine its properties.

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LITERATURE CITED

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