Clays and Clay Minerals, Vol. 26, No. 5, pp. 318–326, 1978.

ION EXCHANGE AND INTERSALATION REACTIONS OF HECTORITE WITH TRIS-BIPYRIDYL METAL COMPLEXES*

SISTER MARY FRANCES TRAYNOR, F.S.E., M. M. MORTLAND, AND T. J. PINNAVAIA

Departments of Crop and Soil Science and Chemistry, Michigan State University
East Lansing, Michigan 48823

(*Received 3 October 1977*)

Abstract—The binding of tris-bipyridyl metal complexes of the type $M(bp)_3^{2+}$ ($M = Fe^{2+}, Cu^{2+}, Ru^{2+}$) to hectorite surfaces is shown to occur by two mechanisms: (1) replacement of Na^+ ions in the native mineral by cation exchange up to its cation exchange capacity and (2) intersalation of excess salt beyond the exchange capacity. In the cation exchange mechanism, the binding of metal complex is strongly favored over Na^+. The intersalation reactions are dependent on the nature of the counter-anion: SO_4^{2-}, $Br^- > ClO_4^-$, Cl^-. The homoionic $M(bp)_3^{2+}$-hectorites, which exhibit rational 18 Å X-ray reflections, have been characterized with regard to their BET surface areas, water adsorption isotherms, types of water present, selected reactions in the intercalated state, and orientation of the complex ions in the interlayer regions. Mixed $Fe(bp)_3^{2+}$, Na^+-hectorites have also been examined and the results suggest segregation of the two ions between interlayers or within interlayers. Solid state intersalated phases have been isolated with 18 Å and 29.5 Å spacings. In general, surface areas of the intersalated phases are low, but the 18 Å phase derived from $[Fe(bp)_3]SO_4$ adsorption shows a high surface area, which even exceeds the surface area of homoionic $Fe(bp)_3^{2+}$-hectorite.

Key Words—Bipyridyl, Exchange, Hectorite, Intersalation, Tris-bipyridyl.

INTRODUCTION

2,2'-Bipyridyl (bp) and the related α-diimine ligand ortho-phenanthroline (phen) are noted for their ability to form stable complexes with many transition metal ions. Tris complexes of the type $M(bp)_3^{n+}$ or $M(phen)_3^{n+}$ are of special interest when bound to the interlayer surfaces of smectite. Because of their cage-like shape, these species should be capable of propping apart the interlayers of the mineral by about 8 Å in absence of a coadsorbed solvent. Under such conditions, one expects the surface regions between the exchange ions to be available for the adsorption or surface-catalyzed reactions of various molecules.

Thus, Berkheiser and Mortland (1977) have recently demonstrated that $Fe(phen)_3^{2+}$ and $Cu(phen)_3^{2+}$ do in fact act as 8 Å molecular props in hectorite and that the homoionic exchange forms of the mineral have an N_2 surface area in the range 200–300 m²/g. This surface area is available for the adsorption of polar (H_2O) and larger nonpolar (benzene) molecules. In addition to finding some unusual redox properties of the mineral bound ions, they also found that $Fe(bp)_3^{2+}$- and $Cu(bp)_3^{2+}$-hectorites are capable of binding metal complex in excess of two times the cation exchange capacity of the mineral through intercalation of the bromide or sulfate salts.

Theilmann and McAtee (1975) have found that related *tris*-ethylenediamine complexes $Cr(en)_3^{3+}$, $Co(en)_3^{3+}$, and $Cu(en)_3^{2+}$ afford appreciable surface areas when they occupy the exchange sites of montmorillonite. The metal complex clays showed promise as chromatographic supports for separation of light hydrocarbons and nitrogen oxides. They also observed bonding of metal complex cation in excess of the exchange capacity of the mineral.

The purpose of the present study was to investigate the binding of tris-bipyridyl complexes of Fe^{2+}, Cu^{2+}, and Ru^{2+} in hectorite. The $Ru(bp)_3^{2+}$ complex was included in the study because it has been reported that monolayers of bipyridyl ruthenium cations in a hydrophobic environment are capable of catalyzing the photodecomposition of water (Sprintschnik et al., 1976). It was of interest, therefore, to determine if the same catalytic reaction could be observed with $Ru(bp)_3^{2+}$ monolayers in hectorite.

The results indicate that certain similarities exist between the intercalation chemistry of the bipyridyl and orthophenanthroline complexes under conditions where there is one equivalent of metal complex per equivalent of mineral. However, new, more dramatic intersalation reactions have been revealed in the metal bipyridyl complex experiments described in this report.

EXPERIMENTAL

Hectorite clay

Hectorite was obtained from the Baroid Division of National Lead Company as a centrifuged and spray-dried powder. Previously reported conductometric titration of a Cu(II)-hectorite gave a CEC of 70 meq/100 g. Chemical analysis of homoionic $Fe(bp)_3$-hectorite indicated a CEC of 80 meq/100 g.

2,2'-Bipyridyl complexes

2,2'-Bipyridyl was purchased as reagent grade from Aldrich Chemical Company and was used without fur-

---

* Journal Article No. 8450 Michigan Agricultural Experiment Station. This work was partially supported by National Science Foundation grant No. CHE76-80370-A01.

ther purification. In the preparation of all complexes a solution of the ligand was added to aqueous solutions of the metal salt. All salts were recrystallized from water and were stored over $CaCl_2$ or P_2O_5.

$[Fe(bp)_3](ClO_4)_2$ and $[Fe(by)_3](ClO_4)_3 \cdot 3H_2O$ were prepared according to the methods of Burstall and Nyholm (1952). The $Fe(bp)_3{}^{3+}$ salt was stored in vials wrapped with aluminum foil to prevent photoreduction. $[Fe(bp)_3]Cl_2 \cdot 5H_2O$ was prepared according to the method of Inskeep (1962), except that prior to being recrystallized from water the complex was washed with hot benzene to remove excess ligand. The bromide salt of $Fe(bp)_3{}^{2+}$ was prepared by adding excess KBr to a solution of the chloride salt until crystals formed. Hydrated $[Fe(bp)_3]SO_4$ was obtained by addition of excess amine to a solution of $FeSO_4 \cdot 7H_2O$, washing the dark red paste with hot benzene, and recrystallizing from water; chemical analysis gave 11.02% N; 7.78% Fe; 4.09% S.

$[Cu(bp)_3](ClO_4)_2$ was prepared after the method of Percy and Thornton (1971). The preparation of the Cu(I) complex, $[Cu(bp)_2](ClO_4)$, was adapted from the method of Schilt and Taylor (1959) for the synthesis of the phenanthroline complex.

$[Ru(bp)_3]Cl_2$ was prepared according to the method of Burstall (1936).

Metal complex exchange forms of hectorite

Homoionic $Fe(bp)_3{}^{2+}$-, $Ru(bp)_3{}^{2+}$- and $Cu(bp)_3{}^{2+}$-exchange forms of hectorite were prepared by adding in fourfold excess a solution of the metal complex as the Cl^- or $ClO_4{}^-$ salt to the Na^+ exchange form of the mineral. After the suspension had been allowed to equilibrate 24 hr at room temperature, the mineral was filtered and washed thoroughly with water until the filtrate was colorless.

Self-supporting, oriented film samples of homoionic $M(bp)_3{}^{2+}$-hectorite complexes were prepared by suspending for several days at slightly elevated temperature precast films of Ca^{2+}-hectorite in water solutions containing stoichiometric amounts of the complex salt. Complete exchange was indicated by the disappearance of color from the solution. The orientated Ca^{2+}-hectorite samples were obtained by allowing a 1% water suspension of the mineral to evaporate at room temperature on a flat polyethylene surface and then peeling the dried films away.

Orientated samples of $Cu(bp)_2{}^{2+}$-hectorite were obtained by first preparing $Cu(bp)_2{}^+$-hectorite by cation exchange between film samples of Ca^{2+}-hectorite and $[Cu(bp)_2]ClO_4$ in acetonitrite solution and then oxidizing the mineral-bound $Cu(bp)_2{}^+$ ion with a 0.1% aqueous solution of H_2O_2.

Ion exchange adsorption isotherms

Ion exchange isotherms were obtained for the adsorption of $Fe(bp)_3{}^{2+}$, $Cu(bp)_3{}^{2+}$, and $Ru(bp)_3{}^{2+}$ on Na(I)-hectorite by adding aliquots of metal complex solution to 0.05 g of Na^+-hectorite and bringing the suspension volume to 50.00 ml. The suspensions were allowed to equilibrate for 48 hr, and then the supernatant solution was analyzed spectrophotometrically for metal ion concentration. The amount of complex adsorbed by the mineral phase was determined by difference. Absorption maximums were obtained at 522 nm for $Fe(bp)_3{}^{2+}$, 297 nm for $Cu(bp)_3{}^{2+}$, and 449 nm for $Ru(bp)_3{}^{2+}$. Adsorption isotherms were reproducible as determined by checking selected points on the isotherms.

Water adsorption studies

Water adsorption isotherms were obtained 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 after 7 days of equilibration was compared to the 150°C dried material.

Self-supported film samples were used for the infrared studies of adsorbed water. The samples were allowed to equilibrate at 30% relative humidity (RH) for 24 hr before a spectrum was recorded. Spectral changes after heating the samples at 100, 200, and 250°C for 2 hr were also noted.

Redox experiments

Qualitative redox experiments were performed on the mineral bound $M(bp)_3{}^{2+}$ complexes, and the results were compared with those for the complexes in homogeneous solution. Changes in oxidation states were indicated when appropriate color changes in the complex ion were observed.

Surface area measurements

Hectorite samples containing zero to one equivalent of $M(bp)_3{}^{2+}$ per equivalent of mineral were prepared for surface area determination by treating Na^+-hectorite with the appropriate amount of metal complex as the $ClO_4{}^-$ or Cl^- salt in aqueous solution. The samples were washed with water and then freeze-dried.

A series of $Fe(bp)_3{}^{2+}$ hectorites containing intercalated $Fe(bp)_3{}^{2+}$ salts with $ClO_4{}^-$, Cl^-, Br^-, and $SO_4{}^{2-}$ anions were prepared by treating 0.05 g of Na^+-hectorite in 50 ml of water with a 5.7-fold excess of the desired metal complex salts. $Fe(bp)_3{}^{2+}$-hectorites containing intercalated $[Fe(bp)_3]SO_4$ were also prepared by treating the same quantity of sodium clay with a 2.3-, 10.2- or 29-fold excess of $[Fe(bp)_3]SO_4$ in 50 ml of water. These intercalated samples were centrifuged to remove as much supernatant liquid as possible before being air-dried.

Surface areas were determined with a Perkin-Elmer Shell Model 212-B sorptometer at liquid nitrogen temperature using N_2 as the adsorbate and He as the carrier

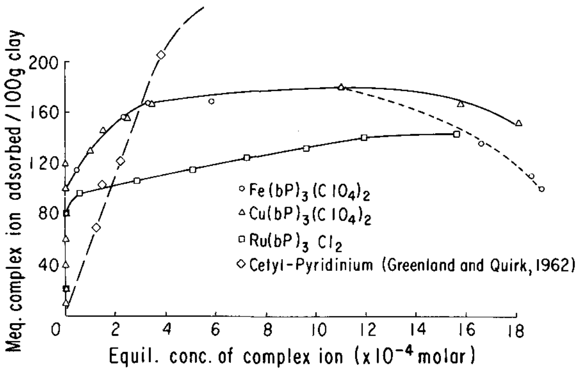

Fig. 1. Adsorption isotherms (20°) for $[Fe(bp)_3](ClO_4)_2$, $[Cu(bp)_3](ClO_4)_2$, and $[Ru(bp)_3]Cl_2$ on hectorite and for cetylpyridinium bromide on montmorillonite in aqueous suspension.

gas. All samples were degassed by heating at 160°C under flowing helium. The absorption data were plotted according to the BET equation. Approximately 40 mg of sample was used for each determination.

Berkheiser and Mortland (1977) compared the Langmuir, Hüttig, and BET equations for N_2 adsorption on $Fe(phen)_3^{2+}$-hectorite and found the BET equation to give the best fit. Because of the similarities between phenanthroline and bipyridyl complexes the adsorption data in the present work were plotted according to the BET equation.

X-ray powder diffraction measurements

A Philips X-ray diffractometer with Ni-filtered Cu-Kα radiation was used to measure 001 basal spacing. Powder samples of the metal complex hectorite were prepared by placing aqueous suspensions onto glass slides and drying them at room temperature, 100 or 150°C. In some cases self-supported films were used by placing the film on a glass slide. Diffractograms were usually recorded to three orders of (001) reflections.

Spectroscopic measurements

UV-VIS and ESR spectra were obtained for selected metal-complex hectorite samples. UV-VIS spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer using 1-cm quartz cells for liquid determinations and fused quartz disks 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 similarly 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 frequency 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%, 77% RH, 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

The adsorption isotherms in Figure 1 demonstrate that $Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$, and $Ru(bp)_3^{2+}$ all have a marked affinity for the surfaces of Na^+-hectorite in aqueous suspensions. Included in the figure for comparison is the isotherm reported by Greenland and Quirk (1962) for adsorption of cetylpyridinum bromide, $[n\text{-}C_{16}H_{33}NC_5H_5]Br$, on Na^+-montmorillonite. It can be seen that the amounts of metal complex adsorbed exceed the cation exchange capacity of the mineral. In order to maintain electrical neutrality, the complex ions bound in excess of the exchange capacity must be accompanied by intercalated counterions.

The isotherms for $Fe(bp)_3^{2+}$ and $Cu(bp)_3^{2+}$ (as ClO_4^- salts) show several interesting features. In the region between 0 and 80 meq of bound complex per 100 g of clay, the slope is vertical, indicating the exchange equilibrium $Na^+\text{-hectorite} + M(bp)_3^{2+} \rightleftharpoons M(bp)_3^{2+}\text{-hectorite} + Na^+$ lies 100% to the right. In the region between 80 and 160 meq/100 g, excess salt begins to penetrate the interlayer regions. X-ray diffractograms of dried samples with loadings of 80 and 160 meq/100 g both give 18 Å basal spacings, independent of drying temperature over the range 20–150°C. This spacing is consistent with the value (8 Å) expected for monolayers of complex ions oriented on the surface with their threefold axis perpendicular to the silicate sheets. Apparently, excess complex salt is readily accommodated in the surface regions between the coulombically bound monolayers of exchange cations.

Additional $[Fe(bp)_3](ClO_4)_2$ and $[Cu(bp)_3](ClO_4)_2$ is intersalated at total loadings corresponding to 160–180 meq/100 g. At these loadings it is likely that some interlayers expand beyond a monolayer, because the 18 Å diffraction peak of dry samples broadens asymmetrically toward lower Bragg angles, indicating the presence of interstratification with higher spacings.

Perhaps the most interesting feature of the $[Fe(bp)_3](ClO_4)_2$ and $[Cu(bp)_3](ClO_4)_2$ isotherms is the *desorption* of salt which occurs at concentrations beyond $\sim 1 \times 10^{-3}\,M$. X-ray data of dried samples prepared in this region of the isotherms show a return to more homogeneous interlayer distances with 001 spacings near 18 Å. It is possible that desorption occurs because ion pairing in solution at higher concentrations is favored over ion pairing in the intercalated state.

The shape of the adsorption isotherm for $[Ru(bp)_3]$

Cl_2 is similar to those for $[Fe(bp)_3](ClO_4)_2$ and $[Cu(bp)_3](ClO_4)_2$, except that no desorption of intercalated salt is observed up to solution concentration of 1.6×10^{-3} M. Also, the amount of complex capable of being intersalated beyond the CEC is less than for the iron and copper systems. It is possible that differences in solvation of the complex cations contribute to the differences in adsorption, despite their similar size and shape. Solvation effects may be implicated, for example, by the differences in the amounts of $[Fe(bp)_3](ClO_4)_2$ and $[Cu(bp)_3](ClO_4)_2$ retained on the clay at concentrations beyond 1×10^{-3} M. However, the major cause of the differences between the ruthenium and the iron and copper systems is most likely due to the fact that Cl^- is the counterion in the ruthenium system and that this ion behaves differently from ClO_4^- in electrostatic properties when imbedded in hydrated monolayers of complex cation.

Distinct 18 Å spacings are observed when samples containing up to 120 meq of $Ru(bp)_3^{2+}$ per 100 g are dried in the temperature range 20–150°C. At higher concentrations broad, interstratified peaks approaching a d value of 24 Å are present.

It is to be noted that the shape of the isotherms for the bipyridyl metal complexes is quite different from that for cetylpyridinium bromide on montmorillonite. Also, the isotherm for the cetylpyridinium salt is not reversible. This intersalated system, which exhibits 42 Å spacings, is stable to washing with water on benzene (Greenland and Quirk, 1962). In contrast, all of the intercalated bipyridyl complex salts bound in excess of the CEC can be removed by washing with water or methanol.

Anion effects on $Fe(bp)_3^{2+}$ adsorption

The differences in the $[Fe(bp)_3](ClO_4)_2$ and $[Ru(bp)_3]Cl_2$ isotherms shown in Figure 1 prompted an examination of anion effects on the intersalation of $Fe(bp)_3^{2+}$ salts. The results with ClO_4^-, Cl^-, Br^-, and SO_4^{2-} counterions are plotted in Figure 2.

As expected for cation exchange, the curves are independent of anion up to the cation exchange capacity of the mineral. However, the additional bonding of complex cation through intercalation of salt, is dramatically dependent on the nature of the anion. The greatest tendency for intersalation occurs for the SO_4^{2-} and Br^- salts. Unlike the ClO_4^- salt, which shows an adsorption maximum as discussed earlier, the binding of the SO_4^{2-} and Br^- salts is continuous with increasing complex concentration up to $\sim 6.3 \times 10^{-3}$ M. The Cl^- salt shows the least tendency toward intersalation, reaching a maximum of ~113 meq/100 g at very low concentrations and remaining at this value at all higher concentrations.

The qualitative order for intersalation of the SO_4^{2-}, Br^-, and Cl^- salts parallels the predicted tendency toward ion pairing based on electrostatic arguments. However, the peculiar behavior of the ClO_4^- salt which should show the least tendency toward ion pairing cannot be explained at this time. A more explicit explanation of the adsorption data will require future studies of the thermodynamic differences for ion pair formation in solution and in the intercalated state.

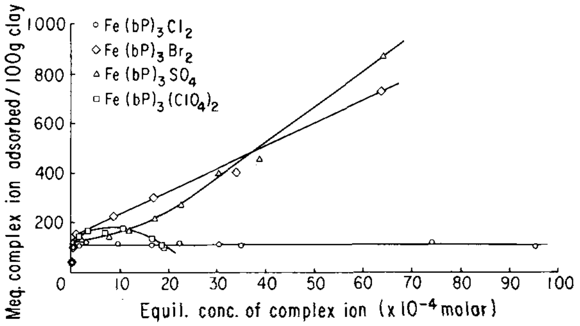

Fig. 2. Adsorption isotherms (20°) of $[Fe(bp)_3]Cl_2$, $[Fe(bp)_3]Br_2$, $[Fe(bp)_3](ClO_4)_2$, and $[Fe(bp)_3]SO_4$ on hectorite in aqueous suspension.

The X-ray basal spacing of the intersalated $Fe(bp)_3^{2+}$-hectorite systems are of some interest. At all loadings beyond the cation exchange capacity, the Cl^- and Br^- systems, like the ClO_4^- system discussed earlier, show monolayer spacings of 18 Å, independent of drying temperature over the range 20–150°C. Some tendency toward interstratification at high loadings is noted as a broadening of the diffraction line. Thus even though the $[Fe(bp)_3]Br_2$ can be intersalated to a much larger extent than the corresponding Cl^- salt, both systems form only monolayers of complex cation in the dry state. Presumably, an appreciable fraction of the free salt is expelled from the interlayers upon drying the $Fe(bp)_3$ Br_2 system at high loadings.

The $[Fe(bp)_3]SO_4$-hectorite system exhibits 18 Å diffraction peaks at loadings between 80 and 180 meq/100 g. At higher loadings there is evidence for interstratification and then at ca. 460 meq/100 g a highly ordered system is obtained which exhibits 10 orders of reflection for $d_{001} \simeq 29.5$ Å. This spacing persists up to loadings of 850 meq/100 g. The results show that well-ordered one or two monolayer systems of $Fe(bp)_3^{2+}$ can be obtained in the dry state when SO_4^{2-} is the counterion. Apparently the SO_4^{2-} ion is more effective in ordering two molecular layers of complex cation than is Br^-.

Water adsorption studies

Water adsorption isotherms for *homoionic* $Fe(bp)_3^{2+}$-, $Cu(bp)_3^{2+}$-, and $Ru(bp)_3^{2+}$-hectorites are shown in Figure 3. These samples contain only coulombically bound complex cations and are free of any intercalated anions. The curves approximate Brunauer's type III isotherms, indicating that adsorbate–

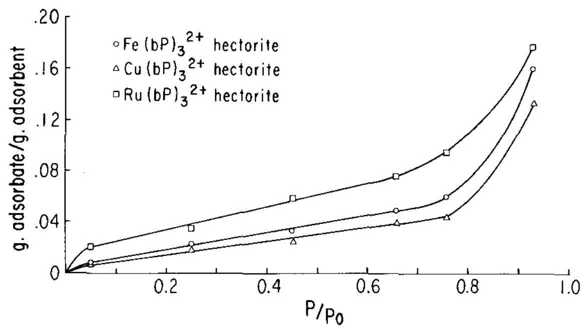

Fig. 3. Adsorption isotherms for H_2O on homoionic $M(bp)_3^{2+}$-hectorites at 20°C.

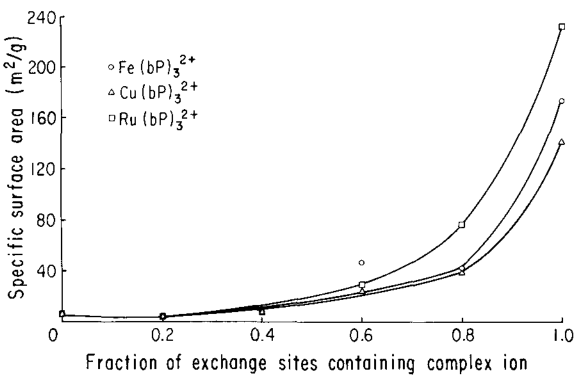

Fig. 4. Specific N_2 surface areas of hectorite fractionally saturated with $M(bp)_3^{2+}$. The surface area calculated according to the BET equation. The activation temperature was 160°C.

adsorbate interactions predominate over adsorbate–adsorbent interactions. Although the cations have the same charge and similar size, the $Ru(bp)_3^{2+}$-hectorite shows a somewhat greater capacity for water than the analogous iron(II) and copper(II) systems.

The OH stretching frequencies of adsorbed water were observed by allowing the homoionic hectorites to equilibrate at P/Po = 0.3 and then heating the samples at temperatures of 100, 200, and 250°C. Two types of water are distinguished. A band centered at 3400 cm^{-1} in all samples is assigned to water associated with the complex cations. A second band at 3575 cm^{-1} indicates the presence of water hydrogen bonded to the silicate oxygen (Farmer and Russell, 1967). The 3400 cm^{-1} band is retained up to 250° C for the $Ru(bp)_3^{2+}$ and $Fe(bp)_3^{2+}$ clays, but the band is lost at 250° C for $Cu(bp)_3^{2+}$-hectorite.

If a model of the metal-complex hectorite is considered in which the complex cations are separated by an average distance of 12 Å, there is ample space between cations for surface associated water. The water associated with the complex cation may be explained by a model suggested by Jensen et al. (1958). The metal complexes contain three bidentate ligands. The regions between ligands define three pockets, each capable of binding up to two water molecules. The loss of the 3400 cm^{-1} band from $Cu(bp)_3^{2+}$-hectorite at 250°C may be associated with the loss of a bipyridyl ligand at this temperature. ESR evidence for the thermal transformation of octahedral $Cu(bp)_3^{2+}$ to planar $Cu(bp)_2^{2+}$ on hectorite surfaces is discussed below.

Surface area determinations

Specific N_2 surface areas were determined for mixed $M(bp)_3^{2+}$, Na^+-hectorite systems. Curves showing the dependence of surface area on the fraction of exchange sites occupied by $M(bp)_3^{2+}$ complex ions are shown in Figure 4.

It is known that the charge distribution among different layers of hectorite is nonuniform (Lagaly and Weiss, 1975). Some interlayers have high charge density with closely spaced cations and others of low charge have more widely spaced cations. The negative deviations from a linear relationship between surface area and fraction of $M(bp)_3^{2+}$ ion on the exchange sites may originate from the nonuniform layer charge. The negative deviations from linearity could then be explained by the complex cations preferentially filling interlayers of highest charge density, resulting in low N_2 surface areas due to crowding of the large complex cations. Alternatively, both Na^+ and $M(bp)_3^{2+}$ ions may occupy the same interlayers, but the metal complexes could be segregated laterally in "islands" which are inaccessible to N_2 upon dehydration.

Independent evidence for the segregation of Na^+ and $M(bp)_3^{2+}$ interlayers with 12 Å and 18 Å basal spacing is supported by X-ray powder diffraction patterns of dry samples. Sharp rational diffraction peaks of 18 Å are observed only when the exchange sites are fully saturated with $M(bp)_3^{2+}$ ions. The smallest tendency toward interstratification for the mixed $M(bp)_3^{2+}$, Na^+-hectorites occurs with $Ru(bp)_3^{2+}$. For example, at a $M(bp)_3^{2+}$ to Na^+ meq ratio of 0.3:0.7, the ruthenium system exhibits a 17 Å reflection, whereas copper and iron give reflections of 13 Å and 14.7 Å, respectively. The $Ru(bp)_3^{2+}$ ion also gives the highest surface areas. The $Cu(bp)_3^{2+}$-hectorites show the lowest surface areas, perhaps due to loss of a bipyridyl ligand and partial collapse of the interlayers on heating at the activation temperature of 160° C (cf. section on ESR spectroscopy).

The observed N_2 surface areas of *homoionic* $Fe(bp)_3^{2+}$-, $Cu(bp)_3^{2+}$-, and $Ru(bp)_3^{2+}$-hectorites are 174, 141, and 233 m^2/g, respectively. If the cross-sectional area of a $M(bp)_3^{2+}$ ion in a plane perpendicular to its threefold axis is taken to be 130 $Å^2$, then the surface area occupied by the complex cations in contact with upper and lower silicate sheets is 548 m^2/g. The sum of the calculated and observed surface areas range from 689 m^2/g for $Cu(bp)_3^{2+}$-hectorite to 781 m^2/g for $Ru(bp)_3^{2+}$-hectorite. These values are near the theoretical surface area of the mineral.

A very interesting phenomenon was observed in measuring the surface areas of homoionic $M(bp)_3^{2+}$-hectorites. If the samples were prepared by adding one equivalent of metal complex chloride or perchlorate per equivalent of clay and the samples *not* washed, then very low surface areas in the range 12–37 m^2/g were obtained. Washing the samples caused the surface areas to increase to the values reported above. Apparently, although the cation exchange equilibrium strongly favors the complex cation, some of the NaCl or $NaClO_4$ formed in the exchange reaction is retained in the interlamellar voids and interferes with N_2 penetration and adsorption.

As noted in earlier discussions of the adsorption isotherms, all of the *intersalated* systems in the dry state give 18 Å monolayer spacings. At high loadings, all of the salts show an increased tendency toward interstratification, suggesting the presence of higher spacings; but the only salt which affords higher spacings of several rational orders is $[Fe(bp)_3]SO_4$, where at a loading of 460 meq/100 g the d_{001} is about 29.5 Å. It is not possible to provide a precise composition for the intersalated phases in the dry state, because the amount of free salt that is expelled from the interlayers upon drying is not easily determined. Nevertheless, it was of interest to examine the surface areas of some of the intersalated phases. The results are presented in Table 1.

Table 1. Effects of intersalated $M(bp)_3^{2+}$ salts on the N_2 surface area of hectorite.

Salt	Total $M(bp)_3^{2+}$ Loading[a] (meq/100 g)	d-Spacing[b] (Å)	Surface Area (m^2/g)
$[Cu(bp)_3](ClO_4)_2$	180	18.4	10
$[Ru(bp)_3]Cl_2$	158	17.6	10
$[Fe(bp)_3](ClO_4)_2$	180	18.8	12
$[Fe(bp)_3]Cl_2$	113	18	92
$[Fe(bp)_3]Br_2$	230	18	21
$[Fe(bp)_3]SO_4$	121	18.0	265
	170	18.0	252
	275	26.8 (17.6)[c]	13
	460	29.5	8

[a] The total loading includes coulombically bound $M(bp)_3^{2+}$ ions and $M(bp)_3^{2+}$ ions bound as excess intersalated salt in *aqueous* suspension.

[b] The d-spacing are for samples dried at room temperature.

[c] Value in parentheses are for the minor diffraction peak.

It is seen that the intersalated 18 Å phases, with the exception of those provided by $[Fe(bp)_3]SO_4$, exhibit surface areas that are appreciably lower than those provided by the homoionic $M(bp)_3^{2+}$ clays. Despite the presence of intercalated salt, the interstratified 18 Å phases obtained from $[Fe(bp)_3]$ SO_4 intersalation have a surface area (~260 m^2/g) which is even larger than that provided by homoionic $Fe(bp)_32+$-hectorite (174 m^2/g). It is possible that most of the $[Fe(bp)_3]SO_4$ intersalated in aqueous suspension is expelled from the interlayers upon drying, thus leaving an essentially homoionic system. This explanation, however, is unlikely in view of the fact that intersalation of $[Fe(bp)_3]SO_4$ in the dry state is unequivocally indicated by the existence of a highly ordered 29.5 Å phase in which two molecular layers of complex cation must be present. In contrast to the interstratified 18 Å phase derived from $[Fe(bp)_3]$ SO_4, the rational 29.5 Å phase shows a low surface area (~10m^2/g). It is possible that the higher spacings present in the interstratified 18 Å phase are different in composition or structure from those of the rational 29.5 Å phase and account for most of the observed surface area. Whatever the reason may be, high surface areas are obtained only when the intercalated counterion is SO_4^{2-}.

Reactions of intercalated $M(bp)_3^{2+}$ ions

Berkheiser and Mortland (1977) have previously shown that $Cu(phen)_3^{2+}$ is reduced by dithionite to $Cu(phen)_2^+$ on the interlayer surfaces of hectorite. They also showed that $Fe(phen)_3^{3+}$ on hectorite in the presence of water or other protonic solvents is reduced to $Fe(phen)_3^{2+}$, but that the reduction does not occur in the presence of aprotic solvents. This redox chemistry of $Cu(phen)_2^{2+}$ and $Fe(phen)_3^{3+}$ on the silicate surfaces is similar to that observed for the ions in aqueous solution, except that the reduction of $Fe(phen)_3^{3+}$ is much faster on the clay surfaces than in solution. Other differences from solution behavior were noted by the failure of $Fe(phen)_3^{2+}$ to be oxidized by Ce(IV) or PbO_2 in H_2SO_4 solution. Possible explanations for these differences have been discussed by Berkheiser and Mortland (1977).

In the present work, the redox properties of $Cu(bp)_3^{2+}$, $Fe(bp)_3^{3+}$, and $Fe(bp)_3^{2+}$ on hectorite closely parallel those of the analogous phenanthroline complexes. In addition, no oxidation by PbO_2 or Ce(IV) in H_2SO_4 solution was noted for $Ru(bp)_3^{2+}$ on hectorite, even though these oxidations do occur in solution.

One of the objectives of this work was to determine if monolayers of $Ru(bp)_3^{2+}$ on hectorite would catalyze the photochemical splitting of water to H_2 and O_2 as reported by Sprintschnik et al. (1976) for surfactant derivatives of $Ru(bp)_3^{2+}$ in a monolayer environment. No oxygen evolution was detected by a Clark electrode after irradiation of a 1 wt% suspension of homoionic $Ru(bp)_3^{2+}$-hectorite with a 100 W mercury lamp for 3 days. More recently, Sprintschnik et al. (1977), have reported that their original observation was caused by the presence of unknown impurities and that the observation could not be reproduced.

ESR spectra of $Cu(bp)_3^{2+}$- and $Cu(bp)_2^{2+}$-hectorites

In our earlier discussions we alluded to the possibility that $Cu(bp)_3^{2+}$ on the exchange sites of hectorite may

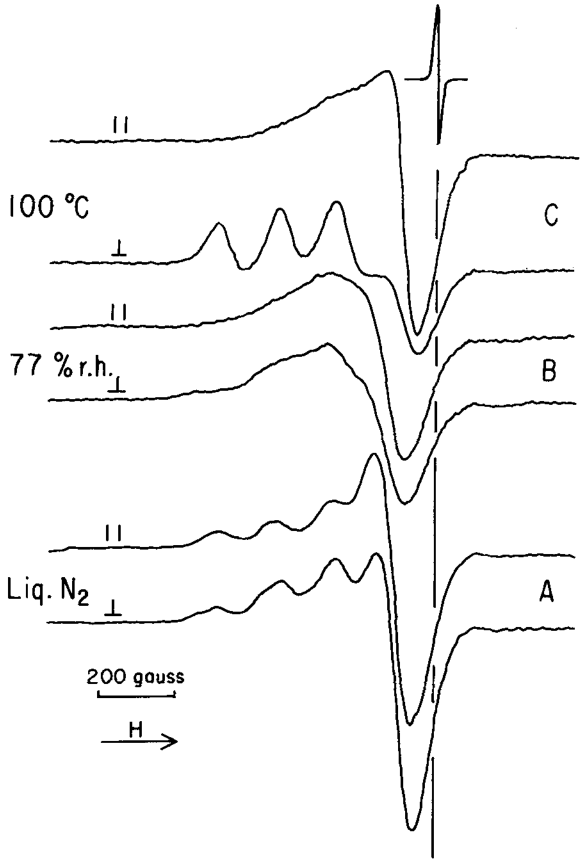

Fig. 5. ESR spectra of oriented thin films of $Cu(bp)_3^{2+}$-hectorite at (A) liquid nitrogen temperature, (B) 77% RH and 25°C and, (C) at 25°C after heating to 100°C. The free electron signal indicates g = 2.0028; films were oriented parallel (||) and perpendicular (⊥) to the magnetic field H.

lose a ligand when heated beyond 100°C. X-ray powder diffraction is of little value in determining this point as the d-spacings of the heated samples are little changed from that of the unheated sample (17.6 Å). However, ESR spectroscopy provides good evidence for the thermal loss of one bipyridyl ligand.

Figure 5 shows the ESR spectra of an oriented film sample of $Cu(bp)_3^{2+}$-hectorite at −196°C and at 25°C and 77% RH. The spectrum at −196°C is anisotropic ($g\parallel = 2.14$, $g\perp = 2.08$, $A = 0.0158\ cm^{-1}$) and independent of orientation in the magnetic field. The spectrum at 25°C and 77% RH is also anisotropic and orientation independent, except that some broadening is observed due to partial averaging of $g\parallel$ and $g\perp$ through tumbling and dynamic Jahn-Teller effects (Noack et al., 1971; Hathaway et al., 1974). The lack of orientation dependence indicates that the elongated axis of the Jahn-Teller distorted ion is oriented near 45° to the silicate sheets. Alternatively, the orientation of the ion may be viewed in terms of its pseudo threefold axis being oriented perpendicular to the silicate sheets. This result verifies the conclusions deduced earlier from d_{001} values on the orientation of the intercalated $M(bp)_3^{2+}$ ions. A similar orientation has been found for six-coordinate $Cu(H_2O)_6^{2+}$ (Clementz et al., 1973) and $Cu(en)_3^{2+}$ (Velghe et al., 1977) on layered silicate surfaces.

The ESR spectrum of $Cu(bp)_3^{2+}$-hectorite after being heated to 100°C (Figure 5C) is anisotropic at 25°C ($g\parallel = 2.24$, $g\perp = 2.07$, and $A = 0.0158\ cm^{-1}$). However, the spectrum is orientation dependent with $g\parallel$ being observed when H° is perpendicular to the silicate sheets and $g\perp$ being observed for H° parallel to the sheets. Essentially the same spectral parameters ($g\parallel = 2.24$, $g\perp = 2.07$, $A = 0.0170\ cm^{-1}$) and orientation dependence is observed for an authentic sample of $Cu(bp)_2^{2+}$-hectorite prepared by oxidation of $Cu(bp)_3^{1+}$ with H_2O_2. Thus there is little doubt that $Cu(bp)_3^{2+}$ undergoes thermal dissociation of a ligand on the surfaces of hectorite. A similar result has been found for $Cu(phen)_3^{2+}$-hectorite (Berkheiser and Mortland, 1977), except that dissociation of phenanthroline appeared to occur even at 25°C and 77% RH.

CONCLUSION

(1) The ion exchange equilibrium between Na^+ and $Fe(bp)_3^{2+}$, $Cu(bp)_3^{2+}$, or $Ru(bp)_3^{2+}$ cations on hectorite surfaces in aqueous suspensions lies completely in the direction of the complex cation. Binding of metal complex beyond the CEC of the mineral occurs through intersalation of metal complex salt. The fact that anions can be intercalated within the interlamellar regions of the clay after saturation of the exchange sites with complex cations suggests that the $M(bp)_3^{2+}$ ions are very effective in shielding the anions from the electrostatic charge of the silicate layers.

(2) The intersalation of $Fe(bp)_3^{2+}$ salts is highly dependent on the nature of the counter-anion. The extent of intersalation tends to increase with increasing tendency toward ion pairing (e.g., $SO_4^{2-} > Br^- > Cl^-$). The behavior of the ClO_4^- salt is anomalous, showing an absorption maximum and subsequent desorption of intersalated salt with increasing concentration of salt in solution. The relative stability of ion pairs in solution and in the intercalated state may regulate the extent of intersalation.

(3) The *homoionic* $M(bp)_3^{2+}$ exchange forms of the clay exhibit complex cations oriented with their threefold axis perpendicular to the silicate sheets. This orientation is verified by the orientation independence of the anisotropic ESR spectrum of $Cu(bp)_3^{2+}$-hectorite. The nitrogen surface areas are in accord with the theoretical surface area of the mineral. Anomalously low surface areas are obtained if the clays are not thoroughly washed following the exchange reaction, suggesting interference of nitrogen penetration by the exchange salt. The $M(bp)_3^{2+}$ clays are stable to heating at 250°C, except that $Cu(bp)_3^{2+}$ loses one bp ligand at 100°C. Surface area and X-ray diffraction measure-

ments of mixed $Fe(bp)_3^{2+}$, Na^+-hectorite systems show that the two ions are segregated between or within interlayers.

(4) Dehydration of $M(bp)_3^{2+}$-hectorites containing intercalated $M(bp)_3^{2+}$ salts affords solid intersalated phases with 18 Å spacings. At loadings corresponding to about 6 times the CEC of the mineral, $[Fe(bp)_3]SO_4$ gives a rational 29.5 Å intersalated phase containing two molecular layers of complex cation. Some free salt is expelled from the interlayers during the transition from the wet to the dry state. In all cases the nitrogen surface areas are low, except for the 18 Å phase derived from $[Fe(bp)_3]SO_4$ intersalation where the nitrogen surface area is even larger than the surface area obtained for homoionic $Fe(bp)_3^{2+}$-hectorite. The sulfate anion exhibits a greater ability to order the intersalated phases than does Br^-, Cl^-, or ClO_4^-.

(5) The redox behavior of $Fe(bp)_3^{2+}$ and $Ru(bp)_3^{2+}$ in the intercalated state differs from the solution state by failing to be oxidized with PbO_2 or Ce(IV) in H_2SO_4. Either the redox potentials are altered in the intercalated state or the reactions are kinetically slow. $Ru(bp)_3^{2+}$ monolayers in hectorite fail to catalyze the photodecomposition of water.

REFERENCES

Berkheiser, V. E. and Mortland, M. M. (1977) Hectorite complexes with Cu(II) and Fe(II)-1,10-phenanthroline chelates: *Clays & Clay Minerals* **25**, 105–112.

Burstall, F. H. (1936) Optical activity dependent on coordinated bivalent ruthenium: *J. Chem. Soc.*, 173.

Burstall, F. H. and Nyholm, R. S. (1952) Studies in co-ordination chemistry. Part XIII. Magnetic moments and bond types of transition-metal complexes: *J. Chem. Soc.*, 3570–3579.

Clementz, D. M., Pinnavaia, T. J. and Mortland, M. M. (1973) Stereochemistry of hydrated copper(II) ions on the interlamellar surfaces of layer silicates. An electron spin resonance study: *J. Phys. Chem.* 77(2), 196–200.

Farmer, V. C. and Russell, J. D. (1967) Infrared absorption spectrometry in clay studies: *Clays & Clay Minerals, Proc. 15th Nat. Conf.* pp. 121–142.

Greenland, D. J. and Quirk, J. P. (1962) Adsorption of 1-n-alkyl pyridinium bromides by montmorillonite: *Clays & Clay Minerals* **9**, 484–499.

Hathaway, B. J., Hodgson, P. G. and Power, P. C. (1974) Single-crystal electronic and electron spin resonance spectra of three tris-chelate copper(II) complexes: *J. Inorg. Chem.* **13**(8), 2009–2013.

Inskeep, R. G. (1962) Infrared spectra of metal complex ions below 600 cm^{-1}—I. The spectra of the tris complexes of 1,10 phenanthroline and 2,2′-bipyridine with the transition metals iron(II) through zinc(II): *J. Inorg. Nucl. Chem.* **24**, 763–776.

Jensen, A., Basolo, F. and Neuman, H. M. (1958) Mechanism of racemization of complex ions. IV. Effect of added large ions upon the rates of dissociation and racemization of *tris*-(1,10-phenanthroline) iron(II) ion: *J. Am. Chem. Soc.* **80**, 2354–2358.

Lagaly, G. and Weiss, A. (1975) The layer charge of smectite layer silicates: *Proc. Int. Clay Conf.* 157–159.

Noack, M., Kokoszka, G. F. and Gordon, G. (1971) Dynamic Jahn-Teller effects and magnetic anisotropies in aqueous solutions and water-ethanol glasses of copper(II) solvates and complexes with 2,2′-dipyridine: *J. Chem. Phys.* **54**(3), 1342–1350.

Percy, G. C. and Thorton, D. A. (1971) Crystal field aspects of vibrational spectra IV. The effect of *d*-orbital splitting on the infrared spectra of transition metal (II) complexes of *cis*-chelating bidentate ligands: *J. Mol. Struct.* **10**, 39–48.

Schilt, A. A. and Taylor, R. C. (1959) Infrared spectra of 1,10-phenanthroline metal complexes in the rock salt region below 2000 cm^{-1}: *J. Inorg. Nucl. Chem.* **9**, 211–221.

Sprintschnik, G., Sprintschnik, H. W., Kirsch, P. P. and Whitten, D. G. (1976) Photochemical cleavage of water: A system for solar energy conversion using monolayer-bound transition metal complexes: *J. Am. Chem. Soc.* **98**, 2337–2338.

Sprintschnik, G., Sprintschnik, H. W., Kirsch, P. P. and Whitten, D. G. (1977) Preparation and photochemical reactivity of surfactant ruthenium(II) complexes in monolayer assemblies and at water–solid interfaces: *J. Am. Chem. Soc.* **99**, 4947–4954.

Thielman, V. J., and McAtee, Jr., J. L. (1975) The relationship between structural properties of metal-tris ethylenediamine montmorillonite and their behavior as gas chromatographic packing materials: *Clays & Clay Minerals* **23**, 173–180.

Velghe, F., Schoonheydt, R. A., Uytterhoeven, J. B., Peigneur, P. and Lunsford, J. H. (1977) Spectroscopic characterization and thermal stability of copper(II) ethylenediamine complexes on solid surfaces. 2. montmorillonite: *J. Phys. Chem.* **81**, 1187–1194.

Резюме- Показано,что связывание трех-бипиридилового металлического комплекса типа $M(bp)_3^{2+}$ ($M=Fe^{2+}$,Cu^{2+},Ru^{2+})с поверхностями гекторита происходит двумя путями: 1)замещением ионов Na^+ в естественном минерале в результате катионного обмена до его возможного предела 2)внедрением избыточной соли за возможный предел обмена. При катионном обмене связывание металлического комплекса значительно сильнее,чем Na^+.Реакции внедрения соли зависят от природы противо-аниона:SO_4^{2-},Br^->ClO_4^-,Cl^-. Гомоионные $M(bp)_3^{2+}$-гекториты, которым присущи рациональные отражения рентгеновских лучей 18Å,характеризуются в соответствии с их поверхностными зонами,определенными методом BET,изотермами адсорбции воды,типами присутствующей воды,избранными реакциями в интеркалированном состоянии,ориентацией сложных ионов в промежутках между слоями. Были исследованы также смешанные $Fe(bp)_3^{2+}$,Na^+-гекториты и установлено,что кулонное связывание сложного катиона предпочитается в промежутках между слоями с наибольшей плотностью заряда. Были изолированы интерсолированные фазы в твердом состоянии с промежутками 18Å и 29.5Å. В целом,поверхностные зоны интерсалированных фаз являются низкими,но фаза 18Å,полученная в результате адсорбции $[Fe(bp)_3]SO_4$,показывает более значительную поверхностную зону по сравнению с поверхностной зоной гомоионного $Fe(bp)_3^{2+}$-гекторита.

Kurzreferat- Die Bindung von tris-bipyridyl Metallkomplexen vom Typ $M(bp)_3^{2+}$ ($M= Fe^{2+}, Cu^{2+}, Ru^{2+}$) an Hektoritoberflächen befolgt zwei Mechanismen: (1) Auswechslung von Na^+ Kationen im natürlichen Mineral durch Kationenaustausch bis zu seiner Kationenaustauschkapazität und (2) Intersalation von überschüßigem Salz über die Austauschkapazität hinaus. In dem Kationenaustauschmechanismus wird die Bindung von Metallkomplexen dem Natrium vorgezogen. Die Intersalationsreaktionen hängen von der Natur der Anionen ab: SO_4^{2-}, $Br^- >$ ClO_4^-, Cl^-.Die homoionischen $M(bp)_3^{2+}$ Hektoriten, die rationale 18 Å Röntgenreflektionen besitzen, wurden durch ihre BET-Flächen, Wasseradsorptionsisothermen, Arten von Wasser anwesend und durch ausgewählte Reaktionen im eingelagerten Zustand und Orientierung von komplexen Ionen in den Zwischenschichtgebieten, charakterisiert. Gemischte $Fe(bp)_3^{2+}$ Na- Hektoriten wurden auch untersucht und die Resultate zeigen,daß coulombische Bindung von komplexen Kationen in Zwischenschichten mit der höchsten Ladungsdichte bevorzugt ist. Feste,intersalierte Phasen mit 18 Å und 29,5 Å Abständen sind isoliert worden. Im allgemeinen sind die Flächen der intersalierten Phasen klein aber die 18 Å Phase, die von der $[Fe(bp)_3]\ SO_4$ Adsorption herstammt, zeigt eine Fläche, die über die Fläche von homoionischem $Fe(bp)_3^{2+}$ - Hektorit hinausgeht.

Résumé-La liaison de complexes métalliques de tris-bipyridyl du type $M(bp)_3^{2+}$ ($M=Fe^{2+}, Cu^{2+}, Ru^{2+}$) à des surfaces d'hectorite se passe par l' intermédiaire de 2 mécanismes: (1) remplacement par échange de cations des ions Na^+ d'un minéral jusqu'à sa capacité d'échange de cations et (2) intersalation du sel en excès au-delà de la capacité d'échange de cations.Dans le mécanisme d'échange de cations,la liaison du complexe métallique se passe préferentiellement aux dépens de Na^+.Les réactions d'intersalation dépendent de la nature du contre-anion:$SO_4^{2-}, Br^- > ClO_4^-$, Cl^-.Les hectorites homoioniques $M(bp)_3^{2+}$,qui montrent des réflexions rationelles de rayons-X de 18 Å,ont été caractérisées quant à leurs aires de surface BET,les isothermes d'adsorption,les types d'eau présents,les réactions sélectionées dans l'état intercalé,et l'orientation des ions complexes dans les régions interfeuillet.Des hectorites mélangées $Fe(bp)_3^{2+}$; Na^+ ont aussi été examinées et les résultats suggèrent la ségrégation des 2 ions entre les couches interfeuillet ou au sein même des couches interfeullet.Des phases intersalées à l'état solide ont été isolées avec des périodicités de 18 Å à 29.5 Å.En général,les aires de surface des phases interslées sont petites,mais la phase 18 Å dérivée de l'adsorption $[Fe(bp)_3]SO_4$ montre une large aire de surface,plus grande même que celle de l'hectorite homoionique:$Fe(bp)_3^{2+}$.