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COMPLEXES OF DIETHYLENETRIAMINE (DIEN) AND TETRAETHYLENEPENTAMINE (TETREN) WITH Cu (II) AND Ni (II) ON HECTORITE

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Abstract—The nature of the complexes in aqueous solutions of Cu(II) and Ni(II) with diethylenetriamine (dien) and tetraethylenepentamine tetren) is pH-dependent. At M(II):dien = 2 and M(II):tetren = 1, the main complexes are $[M(dien\ H)_2(H_2O)_2]^{4+}$ and $[M(tetren\ H)(H_2O)_2]^{3+}$. In excess ligand (pH = 10.30), the majority species are $[M(dien)_2]^{2+}$ and $[M(tetren)(H_2O)]^{2+}$, and considerable amounts of monoprotonated amines are adsorbed. The surface of hectorite prefers the tetragonally distorted complexes in all cases studied. The complexes readily lose their axially coordinated water molecules to form planar complexes on the interlamellar surface. The planar Ni(II)-complexes are diamagnetic, showing that the surface is a very weak axial ligand. The divalent complexes $[M(dien)_2]^{2+}$ and $[M(tetren)(H_2O]^{2+}$ can also be partially transformed to the corresponding planar forms on the surface, especially in the case of $[Cu(dien)_2]^{2+}$. The driving forces are thought to be the acid nature of the clay-adsorbed water and the gain in crystal field stabilization energy of the transition metal ions.

Key Words—Amines, Complexes, Hectorite, Spectroscopy, Thermal Stability, Transition Metals.

INTRODUCTION

Montmorillonite-type clays have extremely high selectivity for complexes of transition metal ions with polyamines (Peigneur *et al.*, 1979). These complexes on the surface can be characterized in terms of thermodynamic stability constants (Maes *et al.*, 1977). For $[Cu(en)_2]^{2+}$ (en = ethylenediamine) the overall stability constant is three orders of magnitude larger than in aqueous solution (Maes *et al.*, 1978). This is partially due to an enthalpy term as the crystal field stabilization energy (CFSE) of $[Cu(en)_2]^{2+}$ on the surface is 12–20 kJ/mole above that in aqueous solution (Velghe *et al.*, 1977b). However, no major change in the Cu–N bonding characteristics was found (Schoonheydt, 1978). Also, $[Ni(en)_2]^{2+}$ is preferentially exchanged on the surface of these clays with respect to the tris- and the mono-complex (Schoonheydt *et al.*, 1979). Moreover, the bis-complex is diamagnetic, and the surface is an extremely weak ligand. With ligands such as dien and tetren the situation is more complicated. There is a strong competition between protonation and complexation of these ligands as well as complexation of partially protonated ligands (Sillén and Martell, 1964; Jonassen *et al.*, 1957). In view of the practical applications of these ligands in the removal of traces of transition metal ions from waste waters (Cremers *et al.*, 1979), a spectroscopic study has been undertaken to clarify the nature of the surface species.

EXPERIMENTAL

Materials

Natural hectorite from Hector, California, was purchased from Ward's Natural Science Establishment Inc., Rochester, New York. The <0.5-μm fraction was separated in the Na^+ form, freeze-dried, and stored. The cation-exchange capacity (CEC) for Na^+ was 0.55 meq/g, measured by the isotopic dilution technique.

Stock solutions of $[Cu(dien)_2]^{2+}$, $[Ni(dien)_2]^{2+}$, $[Cu(tetren)]^{2+}$, and $[Ni(tetren)]^{2+}$ where prepared by mixing the appropriate quantities of transition metal ion and ligand solutions. Prior to exchange the pH of the solutions was brought to ~10.35 with excess ligand. For maximum exchange 100 ml of 1% by weight clay suspension was put in dialysis tubings and equilibrated against 400 ml solution containing 1 meq of the transition metal ion complex in an end-over-end shaker at room temperature for four days. During exchange the pH was kept constant at 10.35 by addition of ligand. Partial exchange was achieved in the same way, but with 0.4 meq of the transition metal ion in the exchange solution. After exchange the samples were washed three times with ligand solutions of the same pH as the exchange solutions, freeze-dried, and stored.

In a second series of preparations the same aliquots of hectorite suspensions were exchanged in solutions with M(II):dien and M(II):tetren ratios (M(II) = Cu(II), Ni (II)) of 2 and 1 respectively. No special care was taken to control the pH during exchange. After completion of the exchange reaction the samples were washed three times with distilled water, freeze-dried, and stored. Exchangeable cation analyses of all samples are shown in Table 1. Quantitative analyses of the dien- and tetren-contents of the samples by the Kjeldahl method were not made. In Table 1, the samples denoted with a prime are those of the second series of preparations.

Procedures and techniques

Reflectance spectroscopy. The samples were placed in reflectance cells of the type described by Velghe *et al.*

Table 1. Exchangeable cation content of the hectorites.

Sample[1]	Na^+ (meq/g; dry)[2]	Ni^{2+} or Cu^{2+} (meq/g; dry)[2]
$Cu(dien)_2H1$	0.041	0.324
$Cu(dien)_2H1'$	0.24	0.440
$Cu(dien)_2H2$	0.12	0.573
$Cu(dien)_2H2'$	0.14	0.730
$Ni(dien)_2H1$	0.06	0.398
$Ni(dien)_2H1'$	0.38	0.460
$Ni(dien)_2H2$	0.035	0.741
$Ni(dien)_2H2'$	0.09	0.780
Cu(tetren)H1	0.049	0.259
Cu(tetren)H1'	0.17	0.490
Cu(tetren)H2	0.037	0.600
Cu(tetren)H2'	0.29	0.700
Ni(tetren)H1	0.032	0.360
Ni(tetren)H1'	0.22	0.480
Ni(tetren)H2	0.163	0.544
Ni(tetren)H2'	0.12	0.710

[1] H1 = hectorite exchanged with 0.4 meq transition metal/g clay. H2 = hectorite exchanged with 1 meq transition metal/g clay. ' = second series of preparations.

[2] The dry weight was determined by removal of water at 383°K until constant weight.

(1977a). The spectra were recorded in the range 2000–210 nm on a Cary 17 instrument equipped with a type I reflectance unit. The standards used were MgO (IR and visible regions) and $Mg(OH)_2$ (UV region). The spectra were digitalized and plotted as $F(R_\infty)$ against wavenumber (cm^{-1}) after computer-assisted substraction of the baseline (recorded with two standards). In that way spectra were obtained of the freeze-dried samples after evacuation at 373°K for one or two days to remove the adsorbed water. These spectra were supplemented by (1) transmission spectra of the complex solutions in the range 800–200 nm, (2) spectra of the freeze-dried samples recorded with Na^+-hectorite as the reference in the range 700–220 nm, and (3) by spectra of the clay suspensions directly after partial exchange prior to centrifugation and washing.

Electron paramagnetic resonance (EPR). EPR spectra of Cu^{2+}-loaded, air-dried, oriented films of hectorite were recorded between 2000 and 4000 Oe at liquid nitrogen temperature on Varian E-4 or E-9 instruments, equipped with a rectangular cavity. The standards were DPPH (g = 2.0037) or a Varian pitch (g = 2.0028). Spectra at liquid nitrogen temperature were also recorded of 0.001–0.005 M exchange solutions diluted in 0.1 M NaCl to avoid spin pairing.

Infrared spectroscopy (IR). IR spectra were recorded on a Beckman IR12 double beam instrument in the regions 1200–1800 cm^{-1} and 2800–3800 cm^{-1}. For these experiments KBr pellets with ~8% by weight complex-loaded clay were prepared and the spectra recorded in the bouble beam mode against pure KBr pellets.

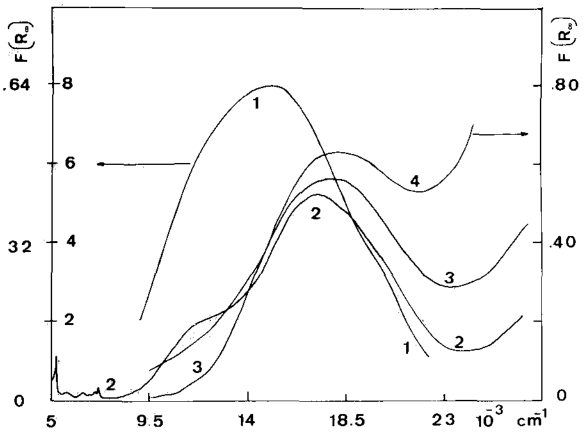

Figure 1. The reflectance spectra in the NIR-visible region of $[Cu(dien)_2]^{2+}$ ion exchanged on hectorite. (1) $Cu(dien)_2H2$ suspension; (2) $Cu(dien)_2H2$ freeze-dried; (3) $Cu(dien)_2H2'$ freeze-dried; (4) $Cu(dien)_2H2$ evacuated at 373°K.

Thermal stability and d_{001} spacings. The decomposition of the complex-loaded hectorites was followed in an automatic Mettler balance under N_2 flow with a heating rate of 4°/min in the temperature range 295°–873°K.

The 001 reflection was recorded on a Scintag-Seifert PAD II apparatus and fitted using a Lorentz curve. The 2θ values corresponding to the fitted maximum of the 001 peak were used for the determination of the average spacing between the clay platelets.

RESULTS

Table 1 shows that the exchange conditions significantly influence the surface composition of the clay. Excess ligand molecules in solution are partially protonated and compete with the complexes for exchange. Thus, at pH = 10.30 the amounts of Ni(II), Cu(II), and Na^+ on the surface are systematically smaller than after the second type of preparation. The final surface composition depends on the amount of protonated ligands and transition metal ion complexes and on the selectivity of the surface for each of the cationic species in solution.

All the reflectance spectra have common features in the near infrared region due to a combination band of water and overtones of CH–, NH–, and OH–vibrations. The CH– and NH–bands are respectively in the region 5600–6000 cm^{-1} and at 6500 cm^{-1}. The lattice OH–band is a very sharp band at 7200 cm^{-1}. The water bands at 5250 cm^{-1} and 7000 cm^{-1} are particularly useful in that they allow a direct and sensitive control of the dehydration. It was found that water was completely removed in vacuo by heating at 373°K for one day. The other bands in the spectra are of three types: d–d transitions of Cu(II) and Ni(II); ligand-to-metal charge transfer bands (LMCT) of the surface-immobilized complexes, and clay-lattice absorption bands. The last

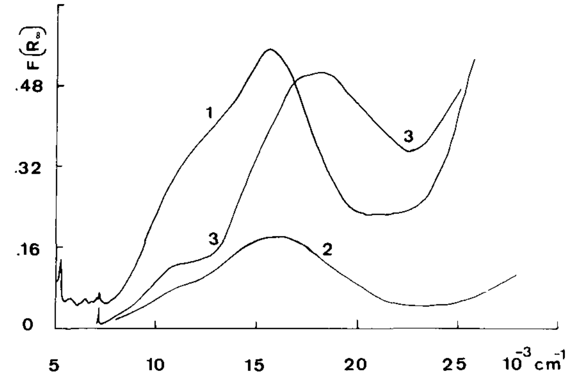

Figure 2. The reflectance spectra of $[Cu(tetren)]^{2+}$ on hectorite in the NIR-visible region. (1) Cu(tetren)H2, freeze-dried; (2) Cu(tetren)H2′, freeze-dried; (3) Cu(tetren)H2′, evacuated at 414°K.

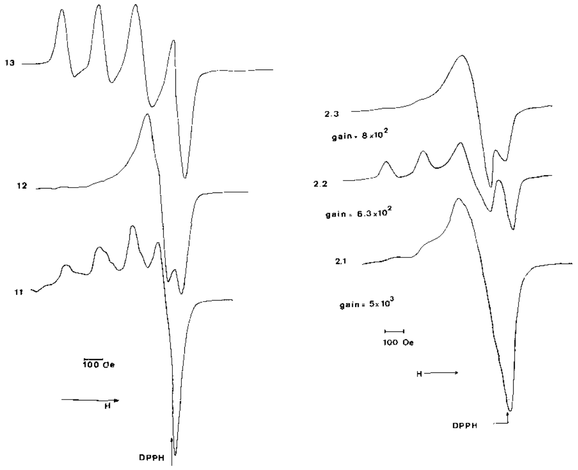

Figure 4. EPR spectra of $[Cu(dien)_2]^{2+}$. 1.1 = 10^{-3} M $Cu(dien)_2(NO_3)_2$ in 0.1 M $NaNO_3$; no excess ligand. 1.2 = $Cu(dien)_2H$, 10% of the CEC exchanged without pH control. c-axes of the platelets parallel to the magnetic field. 1.3 = same as 1.2. c-axes of the platelets perpendicular to the magnetic field. 2.1 = 5 × 10^{-3} M $Cu(dien)_2(NO_3)_2$ in 0.1 M $NaNO_3$ at pH 10.30. 2.2 = $Cu(dien)_2H2$ with c-axis parallel to the magnetic field. 2.3 = $Cu(dien)_2H2$ with c-axis perpendicular to magnetic field. (Samples at liquid N_2 temperature.)

two types considerably overlap in the UV region. Spectra were therefore recorded in the UV with Na^+-hectorite as a reference.

Reflectance spectroscopy and EPR of Cu(dien)$_2$- and Cu(tetren)-hectorites

Figures 1 and 2 show representative reflectance spectra of $Cu(dien)_2$-hectorites and Cu(tetren)-hectorites, respectively. The suspension spectra of $Cu(dien)_2H1$ and $Cu(dien)_2H2$ are very similar to that of the corresponding aqueous solution with an asymmetric band at 15,700 ± 300 cm^{-1} and an additional shoulder around 19,000 cm^{-1} (Figure 1). The latter increases at the expense of the former upon removal of water by freeze-drying and evacuation at 373°K. The result is a broad band with maxima at 17,500 cm^{-1} and 18,600 cm^{-1} for $Cu(dien)_2H2$ and $Cu(dien)_2H1$, respectively. When the samples were prepared without pH control, only one broad band was found after freeze-drying at 17,700 cm^{-1}, slightly asymmetric towards lower frequencies. This band shifted to 18,500 cm^{-1} after complete elimination of water, irrespective of the ion-exchange level.

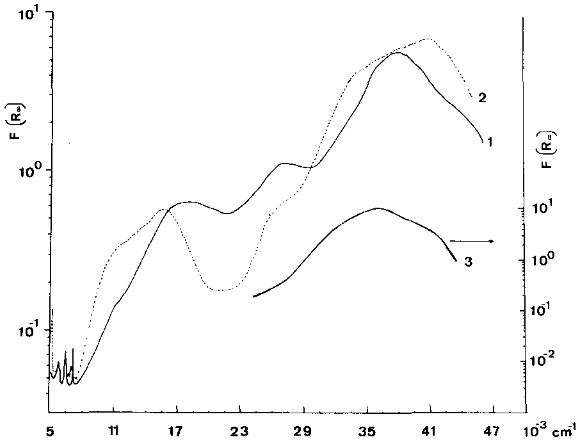

Figure 3. Reflectance spectra of Cu^{2+}-loaded hectorites. (1) $Cu(dien)_2H2$, evacuated at 373°K; (2) Cu(tetren)H2, freeze-dried; (3) $Cu(dien)_2H2$, freeze-dried.

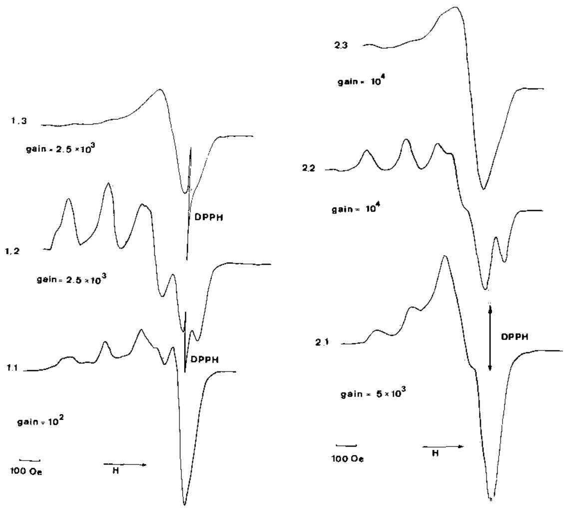

Figure 5. EPR spectra of $[Cu(tetren)]^{2+}$ at liquid nitrogen temperature. 1.1 = 10^{-3} M $Cu(tetren)(NO_3)_2$ in 0.1 M $NaNO_3$; no excess ligand. 1.2 = Cu(tetren)H, 10% of the CEC exchanged without pH control; c-axis parallel to magnetic field. 1.3 = as under 1.2; c-axis perpendicular to magnetic field. 2.1 = 5 × 10^{-3} M $Cu(tetren)(NO_3)_2$ in 0.1 M $NaNO_3$ at pH 10.30. 2.2 = Cu(tetren)H2; c-axis parallel to magnetic field. 2.3 = Cu(tetren)H2; c-axis perpendicular to magnetic field.

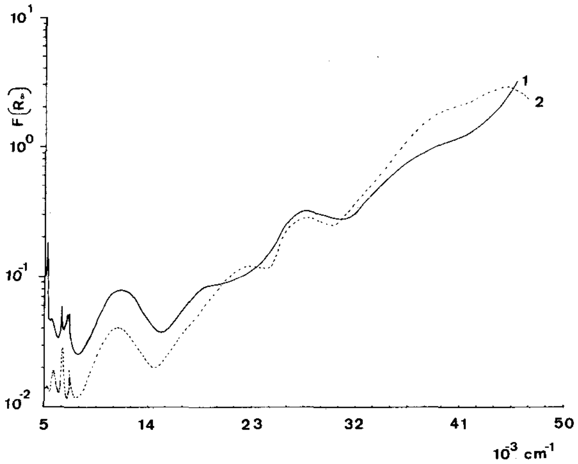

Figure 6. Reflectance spectra of Ni(dien)$_2$H2. (1) freeze-dried; (2) evacuated at 373°K.

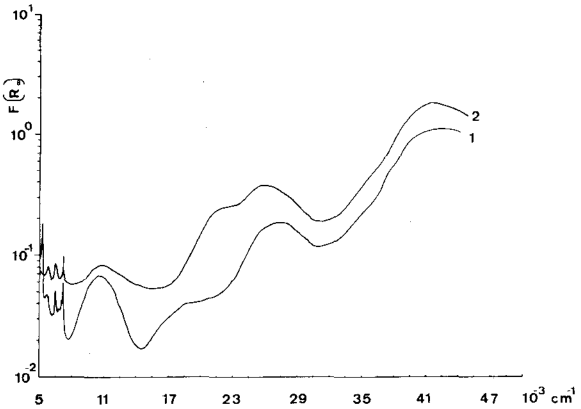

Figure 7. Reflectance spectra of Ni(tetren)H2. (1) freeze-dried; (2) evacuated at 373°K.

Figure 2 shows how the spectra of [Cu(tetren)]$^{2+}$ are influenced by the preparation procedure. Cu(tetren)H1, Cu(tetren)H2, and Cu(tetren)H2′ have their main d–d band maximum around 15,800 cm^{-1} with a 11,000 cm^{-1} shoulder, while the band maximum of Cu(tetren)H1′ is at 17,050 cm^{-1}. Elimination of water at 373°K does not induce hypsochromic band shifts for Cu(tetren)H1,2. For Cu(tetren)H1′, the band maximum is at 18,800 cm^{-1}; for Cu(tetren)H2′, at 17,125 cm^{-1}. Figure 3 shows the reflectance spectra with a logarithmic ordinate to emphasize the UV region. In the Cu(dien)$_2$H1 suspension the LMCT band is at 37,000 cm^{-1}, 2200 cm^{-1} below its position in aqueous solution. With removal of water it resolves into two components around 36,000 cm^{-1} and 40,700 cm^{-1}. The LMCT band of Cu(tetren)H2 and Cu(tetren)H1 is a broad band system between 34,000 and 41,000 cm^{-1}; it is at 37,700 cm^{-1} in solution. The band at 27,300 cm^{-1} is present in the spectra of all samples and intensifies on heating. It is therefore considered to be due to lattice absorption.

The EPR spectra of the solutions are compared to those of the hectorites in Figures 4 and 5. The spectra of the solutions are pH-dependent. Without excess ligand (spectra 1.1) axially symmetric species predominate with $g_{\parallel}$ = 2.195. There is admixture of other signals, but they were difficult to resolve. At pH = 10.30, an isotropic signal with g_{iso} = 2.070 dominates the Cu(dien)$_2$ spectrum with a small admixture of the axially symmetric species (spectrum 2.1 in Figure 4). The latter remains the dominant species for [Cu(tetren)]$^{2+}$ at pH = 10.30 but an isotropic signal with g_{iso} = 2.094 is superposed on it (spectrum 2.1 in Figure 5). The g-values and the corresponding resolved hyperfine splitting constants are summarized in Table 2. The EPR spectra of the Cu(dien)$_2$- and Cu(tetren)-loaded clays show the axially symmetric species with $g_{\parallel}$ in the range 2.18–2.20, whatever the exchange conditions and whatever the ligand. The spectra of the oriented clay platelets in Figures 4 and 5 show some admixture of parallel and perpendicular regions due to the imperfect alignment of the clay platelets. It is noteworthy too that

Table 2. Electron paramagnetic resonance parameters for [Cu(dien)$_2$]$^{2+}$ and [Cu(tetren)]$^{2+}$ in solution and on hectorite.

Sample	Preparation	$g_{\parallel}$ ± 0.01	$A_{\parallel}^{Cu}$ ± 0.0005 (cm^{-1})	$g_{\perp}$ ± 0.01
Cu(dien)$_2$-solution	no pH adjustment	2.195	0.0169	2.06
Cu(dien)$_2$-solution	pH = 10.30		g_{iso} = < 2.070	
Cu(dien)$_2$H	10% exchange no pH adjustment	2.197	0.0200	2.05
Cu(dien)$_2$H2	freeze-dried	2.182	0.0196	2.06
Cu(dien)$_2$H2	evacuated at 373°K	2.174	0.0203	2.05
Cu(tetren)-solution	no pH adjustment	2.195	0.0164	2.06
Cu(tetren)-solution	pH = 10.30	2.193	0.0164 g_{iso} = < 2.094	2.07
Cu(tetren)H	10% exchange no pH adjustment	2.203	0.0190	2.06
Cu(tetren)H1	freeze-dried	2.197	0.0185	2.06
Cu(tetren)H1	evacuated at 373°K	2.184	0.0194	2.06

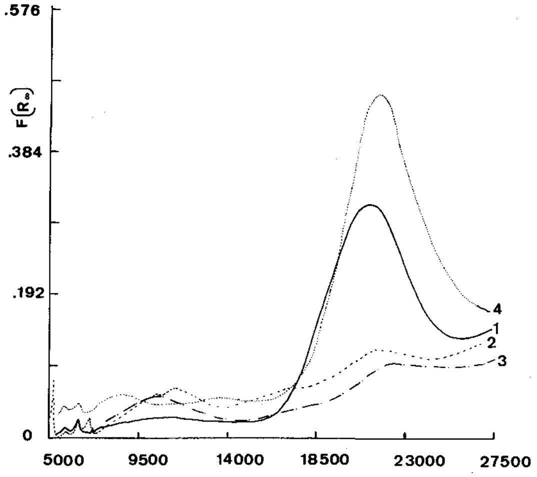

Figure 8. Reflectance spectra of Ni(dien)$_2$H2′ and Ni(tetren)H2′. (1) Ni(dien)$_2$H2′, evacuated at 373°K; (2) Ni(dien)$_2$ H2′, freeze-dried; (3) Ni(tetren)H2′, freeze-dried; (4) Ni(tetren)H2′, evacuated at 373°K.

$A_{\parallel}^{Cu}$ is systematically ~0.0030 cm^{-1} larger for the complexes on the clay than for the same complexes in aqueous solution.

Reflectance spectroscopy of Ni(dien)$_2$- and Ni(tetren)-hectorites

Two groups of d–d transitions are found on the spectra of Figures 6, 7, and 8. After the clays were exchanged at pH = 10.30, the spectra are dominated by three bands at 11,400 cm^{-1}, 18,800 cm^{-1}, and 28,000 cm^{-1} for [Ni(dien)$_2$]$^{2+}$ and at 10,600 cm^{-1}, 18,900 cm^{-1}, and 27,500 cm^{-1} for Ni(tetren)-hectorites. The latter band overlaps with a lattice absorption and is not unambiguously assigned. It must be present on theoretical grounds. Indeed, these three bands are typical for Ni(II) in an octahedral or pseudo-octahedral environment (Lever, 1968a). They are also found after exchange without excess ligand. In that case, they are weak and especially the first band is asymetric, indicating the presence of several components, and at lower frequencies than in the corresponding samples exchanged at pH = 10.30 (11,000 cm^{-1} for Ni(dien)H1′ and 10,300 cm^{-1} for Ni(tetren)H1′).

The second group of d–d transitions is characterized by one band around 22,000 cm^{-1}. It is weakly present on the suspension spectra of all the samples. After freeze-drying it is clearly visible on Ni(dien)$_2$H1′,2′ and Ni(tetren)H1′,2′. It grows in intensity upon evacuation of water at the expense of the octahedral bands. However, very weak octahedral bands remain visible in the range 10,000–11,000 cm^{-1}, but for Ni(tetren)H2′ new bands appear around 8600 cm^{-1} and 13,450 cm^{-1}. For the samples prepared at pH = 10.30, the transformation from octahedral bands into the 22,000 cm^{-1} band is much less pronounced, especially for Ni(dien)$_2$H1,2. The UV bands of Ni(dien)$_2$H1,2 are clay-lattice absorptions. The UV-bands of Ni(tetren)H1,2, when recorded against Na$^+$-hectorite, have maxima at 43,500 cm^{-1} with a shoulder around 40,000 cm^{-1}.

Table 3. d_{001} spacings of the complex-loaded hectorites after freeze-drying.

Sample	d_{001} (Å)	Sample	d_{001} (Å)
Cu(dien)$_2$H1	13.13	Ni(dien)$_2$H1	13.88
Cu(dien)$_2$H1′	12.63	Ni(dien)$_2$H1′	13.31
Cu(dien)$_2$H2	13.29	Ni(dien)$_2$H2	14.21
Cu(dien)$_2$H2′	12.77	Ni(dien)$_2$H2′	13.66
Cu(tetren)H1	13.83	Ni(tetren)H1	14.08
Cu(tetren)H1′	13.11	Ni(tetren)H1′	13.90
Cu(tetren)H2	14.04	Ni(tetren)H2	14.19
Cu(tetren)H2′	13.83	Ni(tetren)H2′	13.75

Thermogravimetry and d_{001} spacings

The weight-loss curves confirm the spectroscopic data in that water is completely removed below 393°K. No clear decomposition temperature of the complexes is revealed, but only a continuous weight loss starting from 400°K. Probably, both protonated amines and complex amines desorb by gradual decomposition. The d_{001} spacings (Table 3) confirm the presence of the complexes in the interlamellar space of the clays. The spacings are not rational, indicating the presence of several types of molecules in the interlamellar space.

The following qualitative observations can be made from Table 3:

(1) Exchange at pH = 10.30 gives the largest spacings.
(2) For the same exchange conditions, the spacing increases with increasing complex loading.
(3) The spacings of the Ni^{2+}-clays exceed those of the corresponding Cu^{2+}-clays.
(4) For Cu^{2+}, the tetren-complexes give larger spacings than the dien-complexes. This is also true for Ni^{2+}, but only at small loadings.

Infrared spectroscopy

The tetren-systems and the dien-systems at low transition-metal ion loading gave poorly resolved spectra. We therefore report in Figure 9 only the IR spectra of Ni(dien)$_2$H2 and Cu(dien)$_2$H2 in comparison with that of an hectorite sample, fully exchanged with dien at pH = 10.30.

Common features of the spectra are the low resolution below 1400 cm^{-1} due to lattice vibrations, and the water and lattice hydroxyl bands at 3690 cm^{-1}, 3650 cm^{-1}, 3450 cm^{-1}, and 1650 cm^{-1}. The other bands are due to complexes and protonated dien molecules. A complete assignment was not attempted, but protonated and complexed dien molecules were distinguished. For the protonated forms the symmetric NH$_3^+$ defor-

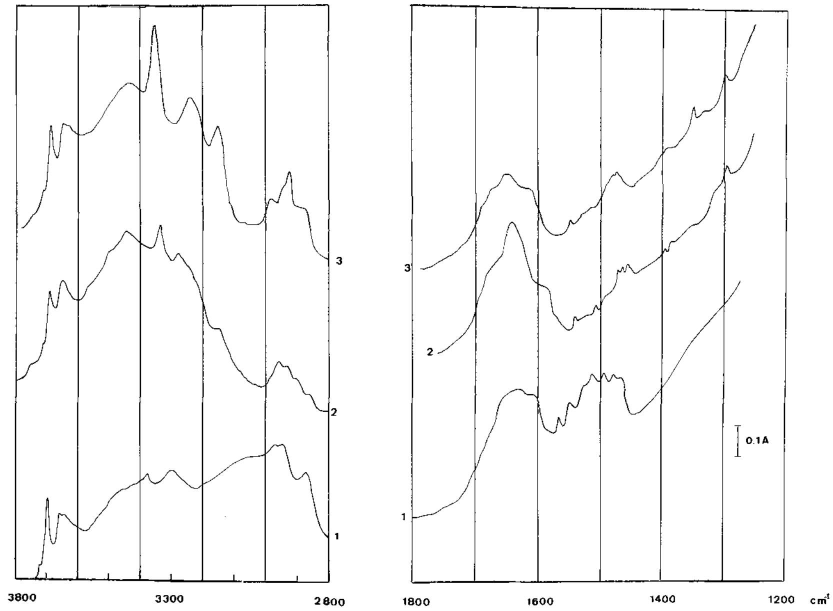

Figure 9. (1) IR spectra of dien-hectorite; (2) Cu(dien)$_2$H2; (3) Ni(dien)$_2$H2.

mation is diagnostic and occurs at 1510 cm^{-1} for ethylenediammonium on montmorillonite (Cloos and Laura, 1972). Four bands were noted between 1500 and 1570 cm^{-1} for dienH-loaded hectorite, probably indicating different environments for dienH molecules and interaction with H_2O or other dien molecules. These bands are barely visible on the complex-loaded clays, indicating that they contain much fewer protonated species. This is confirmed by the presence of the broad NH stretching band in the region 3000–3100 cm^{-1} on dienH-hectorite and its absence on the complex-loaded clays. It is, however, impossible to quantify these bands. Other bands in the deformation region are NH-bands at 1610 cm^{-1} for Ni(dien)$_2$H2 and dienH-hectorite but extending down to 1585 cm^{-1} for Cu(dien)$_2$H2. This 1585 cm^{-1} component is typical for planar complexes (Schoonheydt *et al.*, 1979). CH_2 deformations occur between 1500 and 1450 cm^{-1}. The weak bands at 1350 cm^{-1} and 1300–1295 cm^{-1} for the complex-loaded hectorites are due to coordinated NH and CH_2 groups respectively (Schoonheydt *et al.*, 1979). The NH stretching bands of the complexes are at slightly different frequencies; for Ni(dien)$_2$H2: 3355 cm^{-1}, 3240 ± 20 cm^{-1}, and 3150 cm^{-1} and for Cu(dien)$_2$H2: 3355 cm^{-1}, 3260 ± 20 cm^{-1}, and 3150 cm^{-1}. These bands are typical for the octahedral complexes. The CH_2-stretchings of the protonated molecules overlap strongly with those of the complexes, especially in the region 2900–3000 cm^{-1}. Only the 2860 cm^{-1} band seems to be typical for the protonated dien. It is present as a shoulder in Cu(dien)$_2$H2, but again quantitative estimates are difficult to make.

DISCUSSION

The suspensions of transition metal ions, aliphatic polyamines, and hectorite clay have a complex composition which follows directly from the protonation and complexation constants (Sillén and Martell, 1964), summarized in Table 4. At pH = 10.30, the initial solution (Table 5) contains uncharged ligand complexes and monoprotonated ligands as the major cationic species. The actual surface composition however depends on the selectivity of the clay for each of the cations in solution and their equilibrium concentration.

Indirect evidence for the presence of protonated dien and tetren molecules on the surface is offered by the cation deficiency of the hectorites in Table 1. Thus, the larger the excess dien or tetren with respect to the concentration of complexes, the more protonated molecules are exchanged. The direct spectroscopic obser-

Table 4. Complexation and protonation constants of dien and tetren in decimal logarithmic form (Sillén and Martell, 1964).

	H^+	Cu^{2+}	Ni^{2+}
dien	$K_1 = 9.92$ $K_2 = 9.11$ $K_3 = 4.38$	$K_1K_2 = 21.3$	
tetren	$K_1 = 9.68$ $K_2 = 9.10$ $K_3 = 8.08$ $K_4 = 4.72$ $K_5 = 2.98$	$K_1 = 21.80$	$K_1 = 17.43$

Table 5. Initial compositions of the exchange solutions at pH = 10.30 in mmol/cm^3.

	Cu(tetren)H1	Cu(tetren)H2	Ni(tetren)H1	Ni(tetren)H2
tetren	3.98×10^{-4}	3.98×10^{-4}	3.98×10^{-4}	3.98×10^{-4}
tetren H$^+$	9.56×10^{-5}	9.56×10^{-5}	9.56×10^{-5}	9.56×10^{-5}
[tetren H$_2$]$^{2+}$	6.03×10^{-6}	6.03×10^{-6}	6.03×10^{-6}	6.03×10^{-6}
Cu^{2+}/Ni^{2+}	1.49×10^{-23}	4.97×10^{-23}	3.50×10^{-18}	1.17×10^{-17}
[Cu,Ni(tetren)]$^{2+}$	3.75×10^{-4}	1.25×10^{-3}	3.75×10^{-4}	1.25×10^{-3}
[Cu,Ni(tetren H)]$^{3+}$	2.84×10^{-9}	9.48×10^{-9}	1.53×10^{-9}	5.09×10^{-9}
[Cu,Ni(tetren H$_2$)]$^{4+}$	9.00×10^{-16}	3.00×10^{-15}	1.06×10^{-16}	3.52×10^{-16}

vation of protonated amines is qualitative. Only minor NH_3^+ bands and a weak 2860 cm^{-1} C–H vibration were observed in the IR spectra of protonated dien in the presence of the complexes. Moreover, it was impossible to distinguish between protonated dien molecules and dien molecules simultaneously complexed and protonated.

Nature of the Ni^{2+}-complexes on the surface

As for [Ni(en)$_3$]$^{2+}$-loaded clays (Schoonheydt *et al.*, 1979) there are two types of Ni^{2+} complexes on the surface: octahedral and planar, diamagnetic. The latter is characterized by a d–d band around 22,000 cm^{-1} (Lever, 1968b; Donini *et al.*, 1968; Donini *et al.*, 1975). Its concentration on the surface depends on the ion-exchange conditions and the water content. Thus, partial exchange, removal of water and exchange without excess ligand (=low pH) favor the diamagnetic planar form at the expense of the octahedral Ni^{2+} complexes. The spectra of Figures 6, 7, and 8 allow an understanding of these transformations. After exchange at pH = 10.30, the majority species on the surface are distorted octahedral complexes [Ni(dien)$_2$]$^{2+}$ and [Ni·(tetren)(H$_2$O)]$^{2+}$. The presence of one water molecule in the sixth coordination position of [Ni(tetren)·(H$_2$O)]$^{2+}$ is evidenced by ν_1 = 10,600 cm^{-1}, 800 cm^{-1} below the ν_1 of [Ni(dien)$_2$]$^{2+}$. In the latter case, ν_1 = 11,400 cm^{-1} as for [Ni(en)$_3$]$^{2+}$, indicating that Ni^{2+} is surrounded by six nitrogen atoms. The lower ν_1 band frequencies and the band asymmetries observed after exchange without excess ligand indicate increasing contribution of complexes of the type [Ni(dien H)$_2$(H$_2$O)$_2$]$^{4+}$ and [Ni(tetren H)(H$_2$O)$_2$]$^{3+}$, where the two water molecules are axially coordinated. The removal of these water molecules gives the diamagnetic planar complexes [Ni(dien H)$_2$]$^{4+}$ and [Ni(tetren H)]$^{3+}$. This is also the case after exchange at pH = 10.30, indicating that a small amount of these complexes have been exchanged. In view of their extremely small initial concentration in the exchange solution (Table 5), this observation points to the high selectivity of the surface for these planar complexes. The fact that they are already observed in the suspensions indicates their preference for the interlamellar space, probably between the clay platelets with the highest charge density.

Two other mechanisms of formation of these protonated planar complexes can be envisaged. The first one is based on the high dissociation constant of clay-adsorbed water with respect to bulk water (Touillaux *et al.*, 1968; Fripiat, 1971; Poinsignon, 1978). Two weak bands at 8600 cm^{-1} and 13,460 cm^{-1} are formed after dehydration of Ni(tetren)H2′. It may be argued that they are due to a hydroxylated complex $Ni(H_2O)_{6-x}(OH)_x^{+2-x}$ where the OH groups come from the reaction between water and coordinated tetren. The second mechanism is a surface equilibrium

$$\text{tetren H}^+ + [\text{Ni(tetren)(H}_2\text{O)}]^{2+} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} \text{tetren} + [\text{Ni(tetren H)}]^{3+} + H_2O$$

or

$$2\ \text{dien H}^+ + [\text{Ni(dien)}_2]^{2+} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} 2\ \text{dien} + [\text{Ni(dien H)}_2]^{4+}$$

These equilibria are pushed to the right by the removal of water and by the much larger ligand field strength of the amines in planar, diamagnetic Ni-complexes than in octahedral complexes. Indeed, typical Ni–N distances in the latter case are 2.1 Å and 1.8–1.9 Å for the former case (Martin *et al.*, 1977). If and how these 2 mechanisms are operating cannot be decided from the present experimental results. The data indicate, however, that the exchange of protonated ligand complexes and the removal of axially coordinated water molecules constitute the major process for formation of the diamagnetic species.

The nature of the Cu^{2+} complexes on the surface

At Cu:dien and Cu:tetren ratios of 2 and 1, respectively, the main species in solutions are tetragonally distorted complexes [Cu(dien H)$_2$(H$_2$O)$_2$]$^{4+}$ and [Cu(tetren H)(H$_2$O)$_2$]$^{3+}$. This is derived from the similarity between the g-values of these complexes and those of [Cu(en)$_2$(H$_2$O)$_2$]$^{2+}$ (Velghe *et al.*, 1977b; Hathaway and Billing, 1970; Procter *et al.*, 1968; Hathaway *et al.*, 1969a, 1969b). At pH = 10.30, the main species is the pseudo-octahedral [Cu(dien)$_2$]$^{2+}$ (g_{iso} = 2.070), but with tetren both [Cu(tetren H)(H$_2$O)$_2$]$^{3+}$ and

$Cu(tetren)H_2O^{2+}$ are the dominant species. The latter is characterized by $g_{iso} = 2.094$, somewhat smaller than $g_{iso} = 2.126$ for $Cu(NH_3)_5(BF_4)^{2+}$ (Hathaway and Tomlinson, 1970). For the interpretation of the reflectance spectra it must be kept in mind that replacement of H_2O by N-containing ligands in axial positions of the coordination sphere of Cu^{2+} shifts the d–d absorption band maximum to higher wavenumber up to four coordinated N ligands. The band frequencies decrease again for five or six coordinated N-containing ligands.

Thus, the suspension spectrum of $Cu(dien)_2H$ at pH = 10.30 with maximum around 15,800 cm^{-1} is that of the pseudo-octahedral $[Cu(dien)_2]^{2+}$ (Hathaway and Billing, 1970; Stephens, 1969; Kennedy and Lever, 1973) and the shoulder around 19,000 cm^{-1} is to be ascribed to $[Cu(dien\ H)_2]^{4+}$. This is derived from the similarity of the frequency with that of $[Cu(en)_2]^{2+}$ on Camp Berteau montmorillonite (Velghe *et al.*, 1977b). The ratio of the band intensities 15,800:19,000 is in good agreement with the ratio of the isotropic and axially symmetric EPR signals in solution. Upon removal of water the hypsochromic shift of the band maximum indicates the transformation of pseudo-octahedral to planar geometry around the Cu(II) ion. The extent to which this transformation occurs depends on the ion-exchange level and the ion-exchange conditions in a similar way as for $Ni(dien)_2$-hectorites. Thus, exchange at low pH and partial exchange are in favour of the formation of planar complexes. The position of the band maxima for $Cu(dien)_2H1$ and $Cu(dien)_2H2$ after removal of water is 18,600 cm^{-1} and 17,500 cm^{-1}, respectively. This means that the ratio of planar to octahedral is larger for $Cu(dien)_2H1$ than for $Cu(dien)_2H2$. Thus, the clay prefers the planar complexes more than the octahedral. The difference between the spectra of the suspensions of $Cu(dien)_2$-hectorites and the dried samples cannot solely be explained by removal of axially coordinated water molecules. In that case one should observe a shift from ~18,000 cm^{-1} for $[Cu(dien\ H)_2(H_2O)_2]^{4+}$ to the region 19,000–20,000 cm^{-1} for $[Cu(dien\ H)_2]^{4+}$ (Velghe *et al.*, 1977a). The band shift is from 15,800 cm^{-1} to the region 18,000–19,000 cm^{-1}. This implies the transformation $[Cu(dien)_2]^{2+} \rightarrow [Cu(dien\ H)_2]^{4+}$, upon removal of water. Thus, the two other mechanisms must be operative: protonation of coordinated dien by clay-adsorbed water and proton exchange between dien H^+ and coordinated dien driven by removal of H_2O and the ligand field stabilization energy of Cu^{2+} in planar geometry. The transformation octahedral → planar is more pronounced for Cu^{2+} than for Ni^{2+}, suggesting that the second mechanism is predominant. Indeed, Cu^{2+} prefers the planar geometry much more than Ni^{2+} because of the Jahn-Teller effect (Lever, 1968a).

The behavior of the Cu(tetren) complexes on the surface with respect to $[Cu(dien)_2]^{2+}$ is governed by the availability of only five coordinating N atoms. This gives a C_{4v} environment for Cu^{2+}. The band maximum at 15,800 cm^{-1} with low frequency shoulder obtained on Cu(tetren)H1, Cu(tetren)H2, and Cu(tetren)H2′ can then be ascribed to $[Cu(tetren)]^{2+}$ together with the EPR spectrum with $g_{\parallel} = 2.195$. The band systems are broad and may encompass a high frequency component due to $[Cu(tetren\ H)]^{3+}$. This is especially so for Cu(tetren)H2′. The hypsochromic shift observed for this sample after evacuation of water supports this idea. Moreover, for Cu(tetren)H1′ this high frequency band system is already present after freeze-drying indicating again that the surface preferentially picks up the planar complexes. After exchange at pH = 10.30, Cu^{2+} is in a C_{4v} environment with an orbitally nondegenerate groundstate, $d_{x^2-y^2}$, and there is no driving force for it to go to the planar form. Thus, there is no major hypsochromic band shift. Within this explanation, the EPR spectra of $[Cu(tetren\ H)(H_2O)_2]^{3+}$ and $[Cu(tetren)(H_2O)]^{2+}$ are not significantly different. The removal of the axial water molecules however is seen in the increase of $A_{\parallel}$ on the surface with respect to aqueous solutions. This is also evident from the d_{001} distances of Table 3. In no case is a value typical for octahedral complexes found. The trends in the d_{001} distances confirm the spectroscopic variations. Thus, the larger d_{001} distances of $Cu(dien)_2$- and $Ni(dien)_2$-hectorites after exchange at pH = 10.30 translate the increasing amounts of octahedral-like complexes on the surface. Ni^{2+} has greater preference for these octahedral complexes than Cu^{2+} as evidenced by its larger spacings. The larger spacings of Cu(tetren)-hectorites with respect to $Cu(dien)_2$-hectorites indicates the predominance of the pentacoordinated species $[Cu(tetren)]^{2+}$, especially after exchange at pH = 10.30. The d_{001} distances of Ni(tetren)-hectorites are similar to those of $Ni(dien)_2$-hectorites, especially at high exchange levels. At small exchange levels, larger values are found in the former cases probably due to the predominance of the octahedral $[Ni(tetren)(H_2O)]^{2+}$. Finally, the appearance of charge transfer (CT) bands with at least two components after freeze-drying can be traced back also to the change from octahedral complexes (suspension) to complexes with D_{4h} symmetry on the surface (Kennedy and Lever, 1973). The overall shift to lower wavenumbers translates the solvent dependence of the CT bands, the solvent H_2O being partially replaced by the solvent "clay" (Endicott *et al.*, 1975).

CONCLUSIONS

Our study clearly indicates that the solutions of aliphatic polyamines and transition metal ions contain several cationic species depending on the pH. At pH = 10.30, octahedral-like complexes are dominant. At M(II):dien and M(II):tetren ratios of 2 and 1, respectively, the tetragonally distorted complexes $[M(II)(dienH)_2(H_2O)_2]^{4+}$ and $[M(II)(tetren H)(H_2O)_2]^{3+}$ predominate. The composition of the surface after exchange follows this trend, but preferences for the tetragonally distorted complexes have been observed. Some of these complexes have already lost their axial water molecules during the exchange reaction, with the remaining water molecules being removed by freeze-drying and evacuation. The Ni-complexes become diamagnetic, indicating that the surface is an extremely weak ligand. Mechanisms for the transformation of octahedral to planar on the surface of hectorite are protonation by "acid" clay-adsorbed water and proton exchange between protonated amines and complexed amines. Protonated, noncomplexed amines are also exchanged but their direct spectroscopic identification was weak.

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Резюме—Природа соединений в водных растворах Cu(II) и Ni(II) с диэтилентриамином (диен) и тетраэтиленпентамином (тетрен) зависит от pH. При M(II):диен = 2 и M(II):тетрен = 1, главными соединениями являются $[M(\text{диен}\ H)_2(H_2O)_2]^{4+}$ и $M(\text{тетрен}\ H)(H_2O)_2]^{3+}$. При избытке лиганда (pH = 10,30) большинство соединений представляют собой $[M(\text{диен})_2]^{2+}$ и $[M(\text{тетрен})\ (H_2O)]^{2+}$, при этом адсорбируются значительные количества монопротоновых аминов. Во всех исследованных случаях поверхность гекторита предпочитает тетрагонально искаженные соединения. Эти комплексы легко теряют свои координированные по оси водные молекулы, образуя плоские соединения на межслойной поверхности. Плоские Ni(II)-соединения являются диамагнитными, указывая, что поверхность образована очень слабым осевым лигандом. Двухвалентные соединения $[M(\text{диен})_2]^{2+}$ и $[M(\text{тетрен})\ (H_2O)]^{2+}$ также могут быть частично преобразованы на поверхности в соответствующие плоские формы, особенно в случае $[Cu(\text{диен})_2]^{2+}$. Предполагается, что движущими силами являются кислотная природа адсорбированной глиной воды и увеличение в поле кристалла стабилизационной энергии ионов переходных металлов.

Resümee—Die Natur der Cu(II) und Ni(II) Komplexe mit diäthylentriamin (dien) und tetraäthylenpentamin (tetren) in wäßrigen Lösungen ist pH abhängig. Bei M(II):dien = 2 und M(II):tetren = 1 sind die hauptsächlichen Komplexe $[M(\text{dien H})_2(H_2O)_2]^{4+}$ und $[M(\text{tetren H})(H_2O)_2]^{3+}$. Bei Überschuß an Ligand (pH = 10,3) sind die Hauptsorten $[M(\text{dien})_2]^{2+}$ und $[M(\text{tetren})(H_2O)]^{2+}$ und beträchtliche Mengen monoprotonierter Amine werden adsorbiert. Die Oberfläche des Hektorit bevorzugt in allen untersuchten Fällen die tetraädrisch verformten Komplexe. Die Komplexe verlieren ihre axial koordinierten Wasser Moleküle, um planare Komplexe auf der interlamellaren Oberfläche zu formen. Die planaren Ni(II)-Komplexe sind diamagnetisch und zeigen, daß die Oberfläche ein sehr schwacher axialer Ligand ist. Die divalenten Komplexe $[M(\text{dien})_2]^{2+}$ und $[M(\text{tetren})(H_2O)]^{2+}$ können auch teilweise auf der Oberfläche in die entsprechenden planaren Formen übergehen, besonders im Falle von $[Cu(\text{dien})_2]^{2+}$. Die saure Natur des auf Ton adsorbierten Wassers und die Zunahme in Kristallfeldstabilisierungsenergie der Übergangsmetallionen werden als treibende Kräfte angenommen.

Résumé—La nature des complexes en solutions aqueuses de Cu(II) et de Ni(II) avec la diethylenetriamine (dien) et la tétraethylenepentamine (tetren) est dépendante du pH. Pour M(II):dien = 2 et M(II):tetren = 1, les complexes principaux sont $[M(\text{dien H})_2(H_2O)_2]^{4+}$ et $[M(\text{tetren H})(H_2O)_2]^{3+}$. En excès de ligand (pH = 10.30), les espèces majoritaires sont $[M(\text{dien})_2]^{2+}$ et $[M(\text{tetren})(H_2O)]^{2+}$, et des quantités considérables d'amines monoprotonées sont adsorbées. La surface d'hectorite préfère les complexes déformés tétragonalement dans tous les cas étudiés. Les complexes perdent aisément leurs molécules d'eau coordonnées axialement pour former des complexes planes sur la surface interfeuillet. Les complexes planes Ni(II) sont diamagnétiques, montrant que la surface est un ligand axial très faible. Les complexes divalents $[M(\text{dien})_2]^{2+}$ et $[M(\text{tetren})(H_2O)]^{2+}$ peuvent aussi être partiellement transformés en les formes planes correspondantes sur la surface, surtout dans le cas de $[Cu(\text{dien})_2]^{2+}$. On pense que les forces motrices sont la nature acide de l'eau adsorbée par l'argile et le gain d'énergie de stabilisation du champ cristallin par les ions du métal de transition.