

THE CO-ORDINATION OF HYDRATED Cu(II)- AND Ni(II)-IONS ON MONTMORILLONITE SURFACE

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Abstract—The optical spectra of Cu^{2+} and Ni^{2+} on Camp Berteau montmorillonite after lyophilization and evacuation at room temperature are characteristic for the presence of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ and $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ in the interlamellar space. The most probable ligand field parameters for $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ are $D_{q_{xy}} = 1310 \text{ cm}^{-1}$, $D_s = 1807 \text{ cm}^{-1}$ and $D_t = 664 \text{ cm}^{-1}$. The covalent character of the Cu^{2+} -OH₂ bond is not negligible as indicated by the orbital reduction factors $k_{\parallel}^2 = 0.66$ and $k_{\perp}^2 = 0.76$. This is also the case for $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ which is characterized by a ligand field strength, $D_q = 850 \text{ cm}^{-1}$ and an electronic repulsion parameter $B = 920 \text{ cm}^{-1}$. After desorption in vacuum the optical spectra of Cu^{2+} were poorly resolved, while Ni^{2+} was present partially as $(\text{O}_1)_3\text{Ni}^{2+}$, partially as $(\text{O}_1)_3\text{Ni-OH}_2$ where O_1 means an oxygen of the hexagonal rings in the tetrahedral layers.

INTRODUCTION

Much effort was devoted to the study of the co-ordination of Cu^{2+} with water on smectite surfaces with EPR. The work was recently reviewed and need not be repeated here (Pinnavaia, 1976). Typical EPR parameters for $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ were $g_{\parallel} = 2.33$ – 2.34 ; $A_{\parallel} = -0.0175 \text{ cm}^{-1}$ and $g_{\perp} = 2.08$ – 2.09 (Clementz *et al.*, 1973; Pinnavaia, 1976). They differ from the parameters of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ on reduced charge montmorillonites, $g_{\parallel} = 2.30 \pm 0.01$, $A_{\parallel} = -0.0154 \text{ cm}^{-1}$ and $g_{\perp} = 2.085 \pm 0.005$ (Clementz *et al.*, 1974). On a completely hydrated Cu^{2+} -hectorite ($d_{001} = 16$ – 19.5 \AA) most of the Cu^{2+} was present as $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, but a small amount of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ was also reported with $g_{\parallel} = 2.31$, $A_{\parallel} = -0.0151 \text{ cm}^{-1}$ and $g_{\perp} = 2.04$ (McBride, 1976). It seems then that the EPR parameters of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ significantly depend on the environment. Moreover, on the basis of his parameters McBride predicted the d - d transitions of Cu^{2+} in the range 20000 – 30000 cm^{-1} , far above the 12500 cm^{-1} found in solution and in hydrated synthetic faujasites (McBride, 1976; Holmes and McClure, 1957; De Wilde *et al.*, 1977). We measured the electronic spectra of hydrated Cu^{2+} on a montmorillonite surface to verify McBride's predictions and to account for eventual differences with the solution spectra. An hydrated Ni^{2+} montmorillonite was added to establish differences in behavior between these two transition metal ions and to supplement the work of Tarasevich and Sivolov (1975a,b).

EXPERIMENTAL

Samples

The Camp Berteau (CB) montmorillonite was prepared by the method of Cremers and Thomas (1966)

with slight modifications. The crude clay was immersed in a 1 M NaCl solution, which was renewed several times to obtain a monoionic Na^+ -clay. During subsequent washings with distilled water and centrifuging at $1800 \text{ rounds min}^{-1}$ for 15 min the fraction $< 0.5 \mu\text{m}$ remained in suspension and was collected. It was flocculated again in 1 N NaCl, washed with an acidified (pH = 3.5–4) and a neutral 1 N NaCl solution to remove hydroxy-aluminium compounds, possibly generated during the repeated washings. The clay was dried in an oven at 70°C and stored as such.

For each sample, 2 g of this clay stock were immersed in $\sim 150 \text{ ml}$ distilled water, brought into dialysis tubings and washed salt-free. The dry weight was determined by drying 10 ml of the suspension at 110°C until constant weight. The salt-free suspensions were equilibrated with solutions of $\text{Ni}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$ for 24 hr. The total Cu^{2+} - or Ni^{2+} -contents were three times the cation exchange capacity (CEC) of the clay. The samples were washed three times with distilled water, freeze-dried and stored as such. The exchangeable cation and water contents are given in Table 1.

Procedures and techniques

Diffuse reflectance spectra in the region 5000 – 30000 cm^{-1} were taken with a Cary 17 instrument with a type I reflectance unit. The reflectance cell is shown in Figure 1. The reference was MgO fitted in a matching reflectance cell. In the case of NiCB the reference was NaCB. Spectra were taken of the samples as such and after evacuation between room temperature and 150°C . At each temperature, the equilibration time was at least 48 hr. The spectra were digitalized with a Hewlett-Packard 3480C digital voltmeter and punched on paperband with a Hewlett-Packard 3489A data punch. These spectra were computerized and plotted with an off-line Calcomp

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Table 1. Exchangeable cation and water contents

Samples	Na ⁺ (mequiv. g ⁻¹)	M ²⁺ (mequiv. g ⁻¹)	H ₂ O/M ²⁺ + Na ⁺
CuCB	0.05	1.27	5.29
NiCB	0.06	1.27	7.17

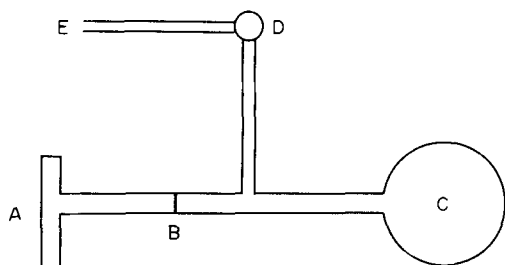


Figure 1. Reflectance cell: A, Suprasil quartz optical window; B, quartz-pyrex transition; C, reservoir for treatment of the samples; D, greaseless valve; E, exit to vacuum line.

plotter as $F(R_{\infty})$ against wavenumber. $F(R_{\infty})$ is the Kubelka-Munck function:

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{K}{S}$$

R_{∞} is the experimental reflectance. K and S are respectively the absorption and scattering coefficients (Kortüm, 1969).

RESULTS

CuCB

The diffuse reflectance spectra of CuCB as such and after evacuation at room temperature were presented in Figure 2. In the hydrated state the spectrum showed a maximum near 13100 cm⁻¹, asymmetric both at the low and high frequency sides of the band maximum. This spectrum was decomposed in three

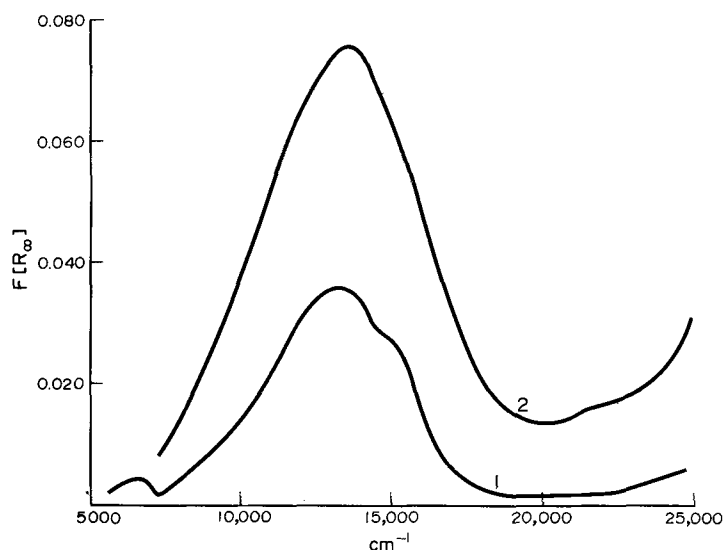


Figure 2. Reflectance spectrum of CuCB: 1, hydrated; 2, after evacuation at room temperature.

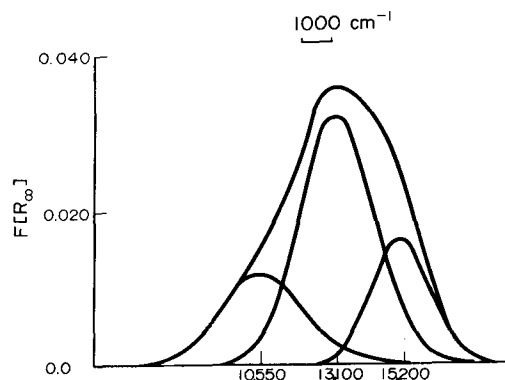


Figure 3. Decomposition in three Gaussian bands of the spectrum of Cu²⁺ in hydrated CuCB.

Gaussian-shaped bands with a Dupont type 310 curve resolver as shown in Figure 3. The band maxima were at 10550, 13100 and 15200 cm⁻¹. The overall band intensity increased significantly after evacuation at room temperature (Figure 2). Dehydration *in vacuo* at 131°C increased the background and the Cu²⁺-band could not be unambiguously resolved, although a shift to higher frequencies was visible. Prolonged equilibration with water vapor at room temperature generated a new band around 11200 cm⁻¹ at the expense of the 13100 cm⁻¹ band (Figure 4). The process was very slow and even after 5 days the 13100 cm⁻¹ band remained the most intense. The spectrum in Figure 4 also shows the overtones and

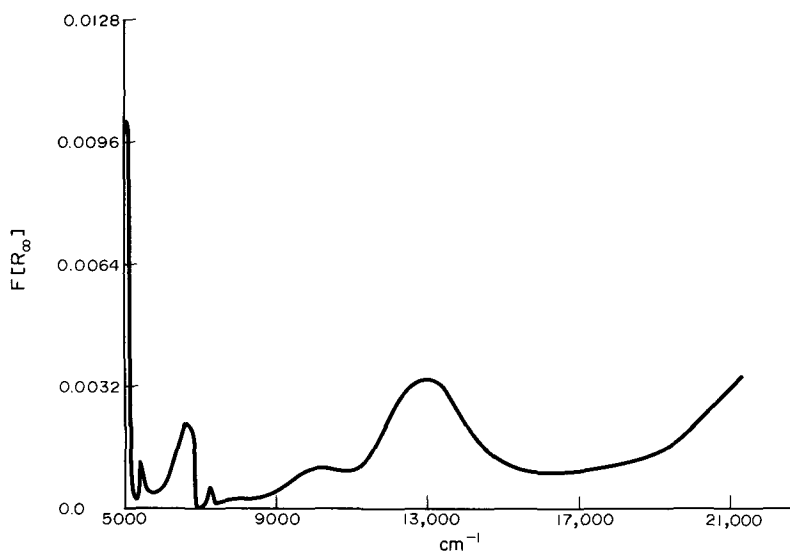


Figure 4. Reflectance spectrum of CuCB after exposure to water vapour at room temperature for 72 hr.

combination bands due to the vibrations of the H_2O molecule and/or lattice hydroxyl groups in the region $5000\text{--}7500\text{ cm}^{-1}$. Because of the large background, the Cu^{2+} spectra on reduced charge montmorillonites were not well resolved.

NiCB

The spectra of NiCB were recorded against NaCB. They were shown in Figure 5. The spectrum of NiCB as such contained—besides the overtones of water and hydroxyls at 7000 cm^{-1} —a band at 8400 cm^{-1} , a double band at 13800 and 15450 cm^{-1} and a strong background starting at 23000 cm^{-1} . Upon degassing at room temperature, the same spectrum was observed together with a band at 25300 cm^{-1} . As for

CuCB, the pretreatment at 140°C *in vacuo* increased considerably the overall background. The 7100 cm^{-1} band was nearly eliminated. The 8400 cm^{-1} was only visible as a broad shoulder on a 14400 cm^{-1} band. A band at 24800 cm^{-1} emerged clearly. The negative dip at 7000 cm^{-1} was due to the instrument.

DISCUSSION

CuCB

On air-dried Cu^{2+} -montmorillonite a monolayer of water was adsorbed between the clay sheets (Clementz *et al.*, 1973), giving rise to the formation of a square planar complex, $\text{Cu}(\text{H}_2\text{O})_4^{2+}$, in the *ab* plane of the mineral. We ascribe the composite band at

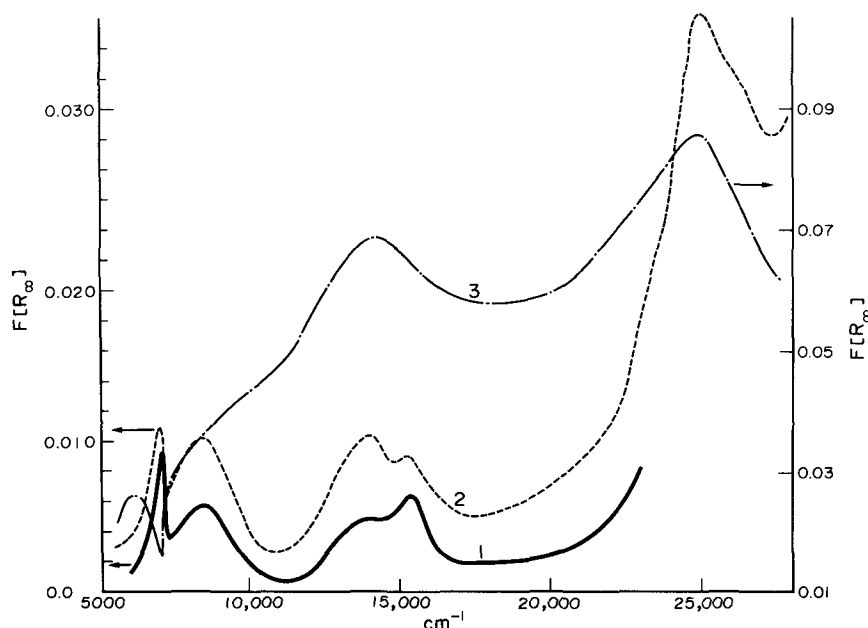


Figure 5. Reflectance spectra of NiCB: 1, hydrated; 2, after evacuation at room temperature; 3, after dehydration *in vacuo* at 140°C .

Table 2. Band assignments and ligand field parameters for $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ on montmorillonite as compared to single crystal values

Species	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	$D_{d_{xy}}$ (cm^{-1})	D_s (cm^{-1})	D_t (cm^{-1})	D_t/D_q	D_q/D_s
CuCB (1)	10,550	13,100	15,200	1310	1807	664	0.51	0.72
(2)	13,100	10,550	15,200	1055	2535	591	0.56	0.42
(3)	15,200	10,550	13,100	1055	2535	1011	0.96	0.42
$\text{Cu}(\text{H}_2\text{O})_4(\text{HCO}_2)_2$	9200	11,200	13,200	1120	1600	560	0.50	0.70
$\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$	13,000	12,000	15,000	1200	2286	771	0.64	0.52
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	10,500	13,000	14,500	1300	1714	729	0.56	0.76
$\text{CaCuSi}_4\text{O}_{10}$	18,800	12,900	15,800	1290	3100	1280	0.99	0.42

13100 cm^{-1} to this species. Our experimental water: cation ratio of 5.29 is accounted for by the presence of physically adsorbed water. We rule out the presence of some $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ because our prolonged hydration experiments indicated the development of a band around 11200 cm^{-1} at the expense of the 13100 cm^{-1} band. Such a frequency decrease is indicative for the transformation of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ to $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ (Hathaway and Billing, 1970). The ligand field expressions of the $d-d$ transitions for square planar Cu^{2+} -complexes are (Kobinata, 1974):

$$\nu_1 ({}^2A_{1g} \leftarrow {}^2B_{1g}) = 4D_s + 5D_t \quad (1)$$

$$\nu_2 ({}^2B_{2g} \leftarrow {}^2B_{1g}) = 10D_{q_{xy}} \quad (2)$$

$$\nu_3 ({}^2E_g \leftarrow {}^2B_{1g}) = 10D_{q_{xy}} + 3D_s - 5D_t, \quad (3)$$

from which it follows that

$$4\nu_3 = 2\nu_2 + 3\nu_1 \quad (4)$$

and

$$D_t/D_q = \frac{4}{7}. \quad (5)$$

Here, $D_{q_{xy}}$ and D_t are one electron radial integrals of the fourth order in r , the d -orbital distance from the Cu^{2+} nucleus. D_s is the corresponding second order integral. $D_{q_{xy}}$ is a measure of the strength of the ligand field due to H_2O . D_t and D_s express the tetragonal component of the ligand field. In Table 2 we give three possible band assignments for $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ on the surface of Camp Bertheau montmorillonite together with the values of their corresponding parameters D_q , D_s and D_t . These parameters and frequencies are compared with those derived from polarized single crystal spectra of Cu^{2+} salts with $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ entities and of a Cu^{2+} silicate (Hathaway and Billing, 1970; Holmes and McClure, 1957). In the latter case Cu^{2+} is strictly

co-planar. The first two possibilities ($\nu_1 < \nu_2 < \nu_3$ and $\nu_2 < \nu_1 < \nu_3$) agree very well with the spectra and parameters of the Cu^{2+} salts. This means that $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ between the clay sheets behaves as a tetragonally elongated octahedral complex with the clay surfaces acting as weak axial ligands. The strength of the ligand field due to the clay surfaces, D_{q_z} , is obtained from: $D_t = \frac{4}{7}(D_{q_{xy}} - D_{q_z})$ (Lever, 1968). It follows that D_{q_z} equals 148 and 21 cm^{-1} for (1) and (2) in Table 2, respectively (we neglect covalent bonding). The third hypothesis ($\nu_2 < \nu_3 < \nu_1$) resembles the strictly co-planar case of $\text{CaCuSi}_4\text{O}_{10}$, although the frequency of each individual component of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ on CB is at least 2000 cm^{-1} lower. This assignment seems therefore less likely. We can obtain an idea about the covalent character of the bonding in $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ on montmorillonite from a combination of our band assignments and the EPR parameters (Clementz *et al.*, 1973). To the first order in the spin orbit coupling constant λ we have (Hathaway and Billing, 1970):

$$g_{\parallel} - 2.0023 = \frac{-8\lambda k_{\parallel}^2}{\nu_2} \quad (6)$$

$$g_{\perp} - 2.0023 = \frac{-2\lambda k_{\perp}^2}{\nu_3} \quad (7)$$

K_{\parallel} and k_{\perp} are the so-called orbital reduction factors, which allow for the nephelauxetic effect and the covalent character of the Cu—O bonds. $\lambda = -829 \text{ cm}^{-1}$ for the free Cu^{2+} ion. Table 3 shows the results for $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ on montmorillonite and compares them with those of similar Cu^{2+} salts. It is striking that on the montmorillonite surface $k_{\perp} > k_{\parallel}$, the reverse of what is usually observed for Cu^{2+} complexes. The fact that g_{\perp} for $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ on montmorillonite is larger than g_{\parallel} for the same species in Cu^{2+} salts is

Table 3. g -values, hyperfine splitting constants, orbital reduction factors and M.O. coefficients of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ systems

Species	g_{\parallel}	A_{\parallel} (cm^{-1})	$g_{\perp} \pm 0.005$	k_{\parallel}^2	$k_{\perp}^2 \pm 0.05$	α^2	β^2	β_1^2
CuCB (1)	2.335	0.0175	2.085	0.66	0.76	0.91	0.88	0.75
(2)	2.335	0.0175	2.085	0.53	0.76	0.91	0.88	0.60
(3)	2.335	0.0175	2.085	0.53	0.65	0.91	0.80	0.60
$\text{Cu}(\text{H}_2\text{O})_4(\text{HCO}_2)_2$	2.35	—	2.06	0.59	0.46	—	—	—
$\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$	2.3554	—	2.0676	0.64	0.59	—	—	—
$\text{CaCuSi}_4\text{O}_{10}$	2.326	—	2.054	0.63	0.49	—	—	—

also the reverse of our observations for Cu(en)_2^{2+} (en = ethylenediamine) on the same montmorillonite and on zeolites (Velghe *et al.*, 1977, Peigneur *et al.*, 1977). The reason for this is not clear at this moment. The coefficients of the M.O.s of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$, calculated with the Kivelson and Neiman theory (1961), are also displayed in Table 3. Here, α , β_1 and β are respectively the coefficients of $dx^2 - y^2$, dxy and dxz (or dyz) in the M.O. expressions of the in-plane σ bond, in-plane π -bond and out-of-plane π -bond. If we adhere to the hypothesis that π -bonding is very small ($\beta_1^2 \rightarrow 1$ and $\beta^2 \rightarrow 1$), as is usually the case with simple ligands (Hathway and Billing, 1970), then case 1 is nearest to the real situation. It should be helpful to have available A_{\perp} values to substantiate this idea.

CuCB after evacuation

The intensity increase after room temperature evacuation is best ascribed to a change of the scattering power of the powder as the band maxima positions of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ remain the same, and thus also the structure of the complex. After the 130°C evacuation, the spectrum becomes poorly resolved due to a strong background, although there seems to be a shift to higher frequencies. Tarasevich observed the same shift upon dehydration of a Cu^{2+} montmorillonite at 150°C (Tarasevich, 1975a). He assumed that the Cu^{2+} ions after entering the ditrigonal holes of the mineral, caused this frequency shift. The inability of part of the Cu^{2+} ions to complex with adsorbed ethylenediamine confirms this assignment (Velghe *et al.*, 1977).

NiCB

Although the $\text{H}_2\text{O}:\text{Ni}^{2+}$ ratio is 7.29, the spectrum of NiCB as such agrees perfectly with that of octahedral $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ in solution. The ligand field theory satisfactorily accounts for the spectrum (Liehr and Ballhausen, 1959) with the strength of the ligand field D_q equal to 850 cm^{-1} and with Racah's electronic repulsion parameter B equal to 920 cm^{-1} (König, 1971). The ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transition around 25300 cm^{-1} is not observed in our experimental spectra, as it is masked by the strong background in that region, typical for all clay minerals (Sindberg and Snyder, 1972). After dehydration at room temperature the spectrum shows the same features and the $25,300\text{ cm}^{-1}$ band, indicating a $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ on the surface. After desorption at 140°C the intensity increase of the spectrum is strong evidence for a symmetry lowering, although a change in scattering cannot be excluded. The intense band at 14000 cm^{-1} is considered to be the ${}^3T_1(P) \leftarrow {}^3T_1(F)$ transition of tetrahedral Ni^{2+} (Lever, 1968). The ${}^3A_2(F) \leftarrow {}^3T_1(F)$ transition is expected around 7000 cm^{-1} in tetrahedral fields. Its low-frequency tail can be observed, but the maximum is masked by OH and H_2O overtones and a negative dip due to the instrument. The two other bands, a shoulder near 9000 cm^{-1} and the band at $24,800\text{ cm}^{-1}$ are the same as observed on a dehydrated NiA zeolite (Klier and Ralek, 1968).

Therefore we ascribe them to Ni^{2+} co-ordinated to the oxygens of the hexagonal rings of the tetrahedral layers of the mineral. The corresponding symmetry is D_{3h} , when Ni^{2+} is in the plane of the sixring, but more probably C_{3v} , i.e. Ni^{2+} is somewhat recessed from the center of the hexagonal ring toward the interlamellar space. A third band is expected around 4000 cm^{-1} in this symmetry, but this is outside our experimental frequency range and therefore not observed.

We conclude that after dehydration at 140°C under vacuum part of the Ni^{2+} is present as a tetrahedral complex, formed with three oxygens of the hexagonal rings in the tetrahedral layers and one residual water molecule. The other Ni^{2+} ions are completely dehydrated and co-ordinated only to the three surface oxygens of the hexagonal rings in the tetrahedral layers.

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