

SYNTHESIS AND PROPERTIES OF HEXACYANOFERRATE INTERLAYERED IN HYDROTALCITE. I. HEXACYANOFERRATE(II)

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Abstract—Hydrotalcite (HT) interlayered with hexacyanoferrate(II) ions ($[\text{Mg}_{4.62}\text{Al}_{1.52}(\text{OH})_{12}][(\text{Fe}(\text{CN})_6)_{0.30}(\text{CO}_3)_{0.29}]$) has been synthesized from the carbonate-HT ($[\text{Mg}_{4.52}\text{Al}_{1.50}(\text{OH})_{12}][(\text{CO}_3)_{0.77}]$) through double ion exchange reactions, and the products have been studied by chemical and physical methods. Mössbauer spectroscopy shows that hexacyanoferrate(II) is held rigidly in the interlayer by electrostatic forces and is characterized by a singlet at 0.01 mm s^{-1} at 80 K. X-ray diffraction shows an increase of the basal spacing (d_{003}) from 0.78 to 1.1 nm following exchange. Hexacyanoferrate(II) in the interlayer was oxidized to hexacyanoferrate(III) (up to 20%) by dioxygen on dehydrating the interlayer either by drying at 70°C or by washing with nonaqueous solvents like acetone or ethanol. The CN (ν_6) band of hexacyanoferrate(II) and (III) is found at 2036 cm^{-1} and 2112 cm^{-1} , respectively. The presence of an absorption band at 2080 cm^{-1} , assigned to free cyanide anions in the interlayer, suggests that the hexacyanoferrate(II,III) complexes are not inert in the interlayer, cyanide ligands being substituted with either water or hydroxyls. Oxidation and ligand exchange of the hexacyanoferrate(II) are also indicated by Mössbauer spectroscopy.

Key Words—Anion exchange, FTIR spectroscopy, Hexacyanoferrate(II), Hydrotalcite, Interlayer chemistry, Layered double hydroxides, Mössbauer spectroscopy.

INTRODUCTION

Layered double hydroxides (LDH) belonging to the pyroaurite-sjögrenite group are compounds of great potential mineralogical and technical importance. In nature they may be important as unstable intermediates during mineral alterations (Crovisier *et al.*, 1983), precipitation or corrosion (Castle *et al.*, 1976; Stampfl, 1969) due to their anion exchange capacity and extensive areas of reactive hydroxylated surfaces. LDH compounds and their pillared forms find extensive use in applications, e.g., as molecular sieves (Miyata and Hirose, 1978; Miyata and Kumura, 1973), electrode modifiers (Shaw *et al.*, 1990; Itaya *et al.*, 1987), anion exchangers and adsorbents (Meyn *et al.*, 1990; O'Neill *et al.*, 1989; Miyata, 1983), hosts for photocatalytic processes (Giannelis *et al.*, 1987), and as precursors for basic catalysts (Reichle, 1985).

The structure is derived from brucite, with trivalent cations substituting for divalent in the trioctahedral hydroxide layer. The interlayers contain the charge compensating anions and water (Taylor, 1973; Allmann, 1970). Hence, the distance between consecutive layers mainly depends on the size of the interlayer anion. The general formula may be presented by $[\text{M}_a^{II}{}_{(1-x)}\text{M}_b^{III}{}_x(\text{OH})_2]^{x+}[(\text{A}^{n-})_{x/n}y \text{H}_2\text{O}]^{x-}$, where $0.15 < x < 0.70$, $\text{M}_a = (\text{Mg}, \text{Zn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Cd}, \text{Mn})$, $\text{M}_b = (\text{Al}, \text{Fe}, \text{Cr}, \text{Mn}, \text{Co}, \text{Ni}, \text{Sc}, \text{Ga})$, and A^{n-} is an anion not forming strong complexes with either M_a - or M_b -cations, e.g., CO_3^{2-} , SO_4^{2-} , NO_3^- , Cl^- , $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Fe}(\text{CN})_6^{4-}$. For hydrotalcite (HT) $\text{M}_a = \text{Mg}$ and $\text{M}_b = \text{Al}$. An increasing charge of the interlayer

anion increases its affinity for the interlayer (Mendiboure and Schöllhorn, 1986; Miyata, 1983). However, the affinity for the carbonate anion apparently exceeds all other anions. Hence, carbonate tends to replace any other interlayer ion and halts any further anion exchange. In this study, the different interlayer-anion forms of LDHs will be denoted by preceding the LDH name or its abbreviation with the name of the formal intercalating anion, e.g., hexacyanoferrate(II)-hydrotalcite or hexacyanoferrate(II)-HT.

Complex ions of transition metals are widely used both as probes or pillaring agents for layered structures such as phyllosilicates and LDHs (Newsham *et al.*, 1988; Schoonheydt, 1982). Hexacyanoferrate(II) and hexacyanoferrate(III) have become popular interlayer complex anions and pillaring agents in LDH research because of easy incorporation in the interlayer due to high anion charge, their rapid charge transfer kinetics, and their easy detection and characterization by spectroscopic or voltammetric methods (Dutta and Puri, 1989; Idemura *et al.*, 1989; Carrado and Kostapapas, 1988; Cavalcanti *et al.*, 1987; Itaya *et al.*, 1987; Kikkawa and Koizumi, 1982; Miyata and Hirose, 1978; Miyata and Kumura, 1973). Also, as pointed out in Hipps *et al.* (1988), the study of cyanide complexes adsorbed onto oxides (and hydroxides) is attractive because the CN-stretching frequency falls within the transmission window of these compounds. However, vibrations due to water may interfere inside this spectral window.

Hexacyanoferrate-intercalated LDH compounds

have been synthesized either by direct precipitation from solution (Carrado and Kostapapas, 1988; Kikkawa and Koizumi, 1982; Miyata and Hirose, 1978) or by anion exchange of the chloride, nitrate, or calcined form of LDH (Idemura *et al.*, 1989; Cavalcanti *et al.*, 1987; Itaya *et al.*, 1987). Despite the work done on hexacyanoferrate-LDHs, there is controversy regarding the influence of interlayering on oxidation state and stability of the complexes. Qualitative studies have indicated that hexacyanoferrates may be subject to changes in iron oxidation state as a result of the intercalation (Idemura *et al.*, 1989; Carrado and Kostapapas, 1988; Cavalcanti *et al.*, 1987). No evidence for ligand exchange of hexacyanoferrate(II) in HT has been presented. However, cyclic voltammetry of hexacyanoferrate(III) adsorbed at an electrode modified by a coating of an HT analogue ($M_a = \text{Zn}$, $M_b = \text{Al}$, $A^- = \text{Cl}^-$) has indicated exchange of CN^- ligands to occur (Shaw *et al.*, 1990). Also ligand exchange of hexacyanoferrate(III) has been proposed to explain its reduction upon intercalation in HT (Idemura *et al.*, 1989).

Here we report a study of the synthesis and properties of hexacyanoferrate interlayered HTs formed by ion exchange from the carbonate-HT through an intermediary nitrate form. The properties of the interlayer-hexacyanoferrate complex have been investigated by FTIR and Mössbauer spectroscopy, allowing us to characterize the carbon-nitrogen bonding, the physical state of the complex in the interlayer, and the coordination and oxidation state of the iron.

EXPERIMENTAL METHODS

Synthesis

Carbonate-HT (C1) was precipitated from aqueous solutions of the magnesium and aluminium nitrate salts at room temperature. From a reservoir 100 cm³ 0.80 M solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was slowly (500 min) pumped into 700 cm³ of a vigorously stirred 0.36 M solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ held at pH 9.0 through the automatic addition of 2.0 M NaOH/0.15 M Na_2CO_3 . After separation and washing of the raw product, it was dispersed in 500 cm³ 0.02 M solution of Na_2CO_3 and refluxed for 20 hr to exchange any interlayer nitrate with carbonate and to increase crystallinity. This product was separated, washed with water, and finally dried at 40°C.

Hexacyanoferrate(II)-HT was obtained by anion exchange. Firstly, interlayer carbonate was replaced with nitrate (N1) using hot glycerol as solvent for the exchange reaction (Hansen and Taylor, 1991). Subsequently, nitrate was exchanged with hexacyanoferrate(II) ions by refluxing suspensions of 300 mg nitrate-hydrotalcite in 100 cm³ 0.1 M carbon dioxide-free aqueous solutions of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ for 1 hr. The final hexacyanoferrate(II)-HT (F1-A) was separated by filtration and washed with carbon dioxide-free water. At this

stage, part of the hexacyanoferrate(II)-hydrotalcite was washed with "out of the bottle" acetone (F1-B) or ethanol (F1-C). Samples F1-E (acetone) and F1-F (ethanol) were also washed with these solvents after deoxygenation by bubbling the solvents for 2 hr with oxygen-free argon (30 cm³ min⁻¹). Finally these products were washed with deoxygenated water.

Cyanide-HTs and cyanate-HTs were prepared by ion-exchange of a nitrate-HT in 0.1 M KCN or 0.1 M KCNO solutions at room temperature for 12 hr. Turnbull's blue, approximately $\text{KFeFe}(\text{CN})_6 \cdot \text{H}_2\text{O}$, was synthesized by mixing equivalent amounts of FeCl_3 and $\text{K}_4\text{Fe}(\text{CN})_6$ solutions followed by evaporation of the solvent at reduced pressure.

Except for hexacyanoferrate(II)-HTs dried at 70°C (F1-D) and at 100°C (F1-G) for 16 hr in an open oven, all samples were dried at room temperature over silica gel and soda lime in a dessicator. All samples were kept at 5°C or below in the dark until examination. Throughout the study double-deionized, silica-free water was used. All chemicals used were *pro analysi* quality and were used as received.

Chemical analysis

The content of carbonate in these compounds was determined by digesting the material with perchloric acid and precipitating the liberated CO_2 as BaCO_3 from solutions of $\text{Ba}(\text{OH})_2/\text{BaCl}_2$ in a circulating gas system (Larsen, 1949). The content of metals (magnesium, aluminium, and iron) in the acid digest were determined by atomic absorption spectroscopy (AAS). During acid dissolution of the hexacyanoferrate-hydrotalcites, variable amounts of a blue compound precipitated indicating similarities to Prussian blue. The solutions were made alkaline to dissolve this precipitate, and the newly formed precipitate of iron(III) hydroxide was subsequently redissolved with acid before determination of iron by AAS. The content of hydroxide in the hydrotalcites was calculated by difference.

X-ray diffraction, infrared and Mössbauer spectroscopy

Hexacyanoferrate(II)-HTs were examined by powder X-ray diffraction (XRD) with $\text{CoK}\alpha$ radiation using a computer-controlled Philips PW 1050 diffractometer. Samples as unoriented powders were scanned from 6 to 80° 2θ at 1° 2θ /min. Diffraction data were processed using a PC (Raven and Self, 1988).

FTIR spectra were recorded on a Perkin Elmer FTIR 2000 spectrometer either as transmittance spectra [Nujol mulls between KBr windows, pressed KBr pellets, or aqueous solutions between polyethylene (PE) sheets] or as diffuse reflectance spectra (DRIFT) using a Harrick "praying mantis" diffuse reflectance attachment. Spectra were recorded at a resolution of 2 cm⁻¹ and averaged over 25–50 scans. KBr pellets were pressed under 8 tons for 30 s. For reflectance spectra, 1 mg of

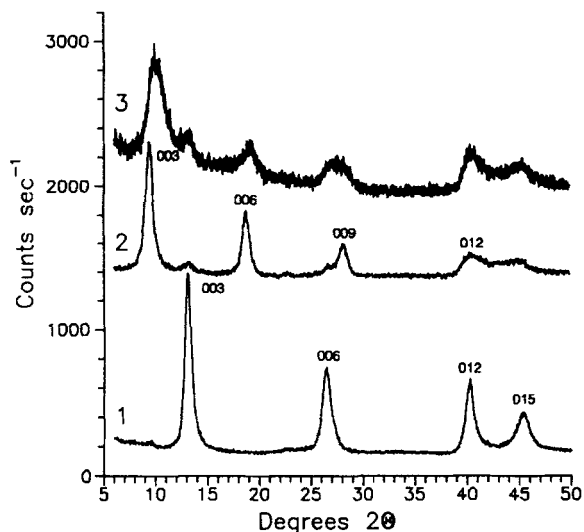


Figure 1. X-ray diffractograms of 1) carbonate-hydroxalcite; 2) nitrate-hydroxalcite exchanged with hexacyanoferrate(II) at 100°C and dried at room temperature (F1-A); and 3) same as (2) but dried at 70°C for 16 hr (ordinate scale expanded 4×).

analytes were mixed and lightly ground with 50 mg KBr in a mortar for 30 s. Pure KBr was run as reference. Reflectance spectra were converted to the Kubelka-Munk function, $f(R_\infty)$ (Kubelka, 1948; Kubelka and Munk, 1931). For dilute samples in low-absorbing matrices, a linear relationship between $f(R_\infty)$ and concentration of the analyte holds provided the scattering coefficient is constant (Kortüm *et al.*, 1963).

^{57}Fe Mössbauer spectra of samples F1-A to F1-F were obtained at 298 K and 80 K using a constant acceleration spectrometer and a Co in Rh source. The spectrometer was calibrated using a thin foil of $\alpha\text{-Fe}$ at room temperature and isomer shifts are given relative to the centroid of the spectrum of this absorber. A detailed study was undertaken of sample F1-A by acquiring several spectra at different temperatures between 80 and 298 K. The HT-hexacyanoferrates were studied as powders held fixed by a lid in a Plexiglas container. For comparison, the spectra of salts and frozen solutions of hexacyanoferrate(II) and hexacyanoferrate(III) were obtained. Frozen solutions in the glassy state were prepared by dissolving the salt in a water/glycerol mixture (60/40% vol) and quenching the solution by freezing a small container ($\sim 0.75\text{ cm}^3$) directly in liquid nitrogen. The frozen solutions were studied at 80 K only.

RESULTS

XRD and chemical analysis

When nitrate-HT is contacted with solutions of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, hexacyanoferrate(II) becomes intercalated in HT. This is demonstrated by the increase in the basal spacing, d_{003} , from 0.78 nm in the carbonate

Table 1. Composition of carbonate and hexacyanoferrate(II) forms of hydroxalcite.

Sample	Weight (mg)	Mg	Al	CO_3^{2-}	Fe
		(μmole)			
C1	21.55	202.8	67.38	33.83	—
C1	21.71	198.68	66.53	33.63	—
C1	25.58	233.24	77.21	40.64	—
N1	28.28	240.64	77.21	9.55	—
N1	29.49	255.86	87.06	8.97	—
N1	25.65	227.48	75.57	8.01	—
F1-A	26.87	214.32	70.24	13.60	14.33
F1-A	21.85	176.47	57.60	10.62	11.34

form to 1.1 nm in the hexacyanoferrate(II) forms (Figure 1). On heating, the hexacyanoferrate(II)-HT at 70°C (F1-D) d_{003} decreases to app. 1.08 nm, and all reflections are broadened (Figure 1). During the exchange reactions, carbonate has not been completely expelled from the interlayer of all HT crystals as seen from a weak diffraction peak at 0.78 nm characteristic of the carbonate form (Figure 1), the chemical analyses (Table 1), and the discovery in the IR spectra of a CO_3^{2-} ν_3 vibration at 1380 cm^{-1} (not shown).

Calculating the content of hydroxide in the hydroxalcites by difference and attributing all iron in the hexacyanoferrate(II)-HT samples to $\text{Fe}(\text{CN})_6^{4-}$, the average compositions of the original carbonate-HT and the hexacyanoferrate(II)-HT (F1-A) are $[\text{Mg}_{4.55}\text{Al}_{1.50}(\text{OH})_{12}][(\text{CO}_3)_{0.77}]$ and $[\text{Mg}_{4.62}\text{Al}_{1.52}(\text{OH})_{12}][(\text{CO}_3)_{0.29}(\text{Fe}(\text{CN})_6)_{0.30}]$, respectively. The intermediary nitrate-HT (N1) has the average composition $[\text{Mg}_{4.49}\text{Al}_{1.51}(\text{OH})_{12}][(\text{CO}_3)_{0.16}(\text{NO}_3)_{1.19}]$. The OH:(Mg + Al) molar ratios are 1.99, 1.95, and 2.00 for the three compounds in good agreement with a theoretical ratio of 2.00 for octahedral metal hydroxide layers. For the three forms, the Mg:Al ratios are 3.01, 2.97, and 3.06, respectively. For the hexacyanoferrate(II)-HT, 30% of the layer charge is compensated by carbonate and not hexacyanoferrate(II), probably due to lack of rigorous exclusion of carbon dioxide during exchange reactions.

FTIR-spectroscopy

The FTIR spectra of the different hexacyanoferrate-HTs differ with respect to number, positions, and intensity of absorptions in the CN-stretching region. A DRIFT spectrum of the untreated hexacyanoferrate(II)-HT (F1-A) is shown in Figure 2, and spectral data are listed in Table 2. The main absorption is seen at 2036 cm^{-1} , followed by weak absorptions at 2080 and 2111 cm^{-1} . This is similar to the spectra of aqueous solutions of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, which show a broad absorption band centered at 2038 cm^{-1} , but different from DRIFT or KBr pellet transmission spectra of the pure $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ salt, which show the major (CN) ν_6 at 2044 cm^{-1} and no absorption at 2111 cm^{-1} (Figure 3A). The 2111 cm^{-1} absorption in DRIFT spectra of

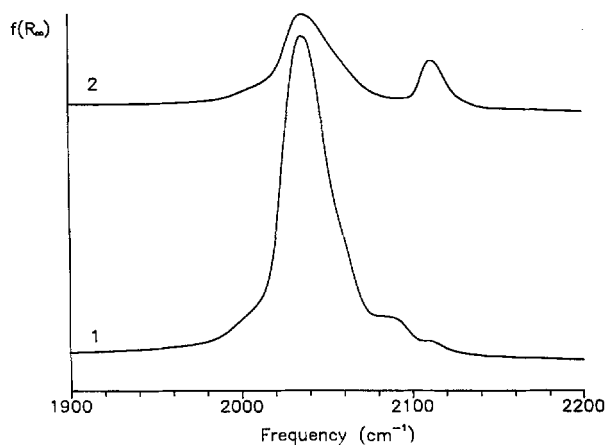


Figure 2. DRIFT spectra of nitrate-HT exchanged with hexacyanoferrate(II) at 100°C: 1) sample was dried at room temperature (F1-A), and 2) sample was dried at 100°C for 16 hr (F1-G).

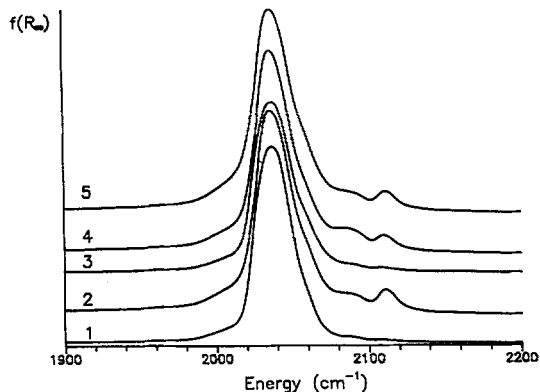


Figure 4. DRIFT spectra of hexacyanoferrate-HTs treated in different ways. Hexacyanoferrate(II)-HT washed with 1) deoxygenated acetone (sample F1-E), 2) nondeoxygenated acetone (F1-B), 3) deoxygenated ethanol (F1-F), 4) nondeoxygenated ethanol (F1-C), and 5) hexacyanoferrate(II)-HT washed with water and dried at 70°C for 16 hr (F1-D).

hexacyanoferrate(II)-HTs washed with oxygen-containing acetone (F1-B) or ethanol (F1-C) is seen to be much more intense compared with the hexacyanoferrate(II)-HT washed with these solvents after deoxygenation (F1-E, F1-F) (Figure 4). Also heating the hexacyanoferrate(II)-HT at 70° or 100°C for 16 hr (F1-D and F1-G) increases the intensity of the 2111 cm^{-1} absorption (Figures 2 and 4, Table 2). Except for the hexacyanoferrate(II)-HT dried at 100°C, all other samples show a broad, weak absorption around 2080 cm^{-1} . The intensity of this absorption was found to depend neither on the time of grinding the sample with KBr during sample preparation nor on how long the sample had been stored before examination. Also, the intensity of the 2080 cm^{-1} absorption did not show any rela-

tionship to the intensity of the 2111 cm^{-1} absorption. Water was found to produce a very broad absorption band centered at 2080 cm^{-1} (Figure 3B).

Cyanate in the interlayer of HT exhibits an intense absorption maximum of CN (ν_3) at 2170 cm^{-1} , i.e., at the same peak position as observed in the spectrum of an aqueous solution of KCNO (Figure 5). In contrast, the intensity from the cyanide ion in HT is very weak, showing a broad absorption at 2039 cm^{-1} and a sharp absorption at 2027 cm^{-1} , which is very different from the intense CN (ν_6) absorption at 2080 cm^{-1} in the spectrum of aqueous solutions of KCN (Figure 5). An absorption at 2170 cm^{-1} for the KCN treated HT is ascribed to an impurity of cyanate found in the KCN salt used for the ion exchange reaction.

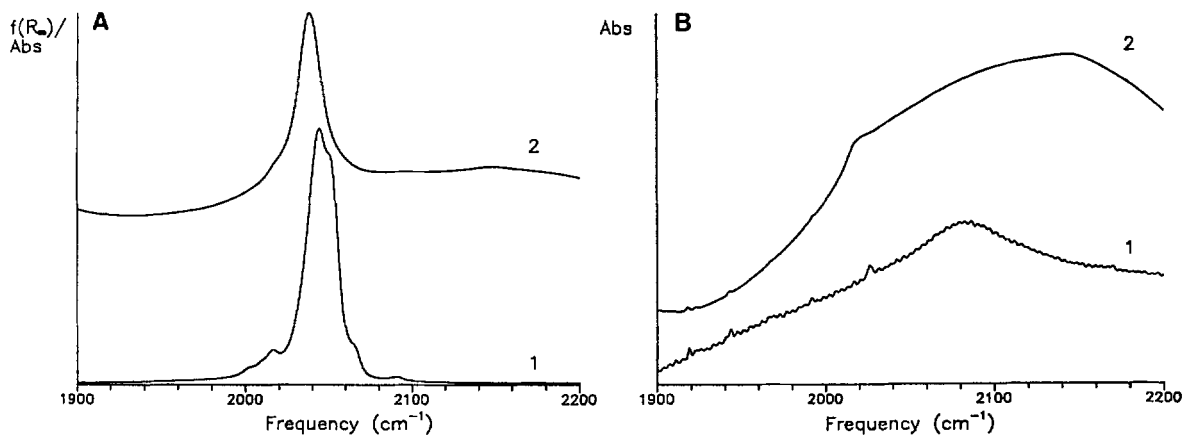


Figure 3. A) represents transmission FTIR spectra of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ in 1) KBr pellet and 2) as aqueous solution between PE sheets (ordinate scale expanded 10 \times); B) shows transmission FTIR spectra of water 1) in KBr pellet (ordinate scale expanded 20 \times) and 2) between PE sheets. (Hump at 2021 cm^{-1} in A(2) and B(2) is due to PE).

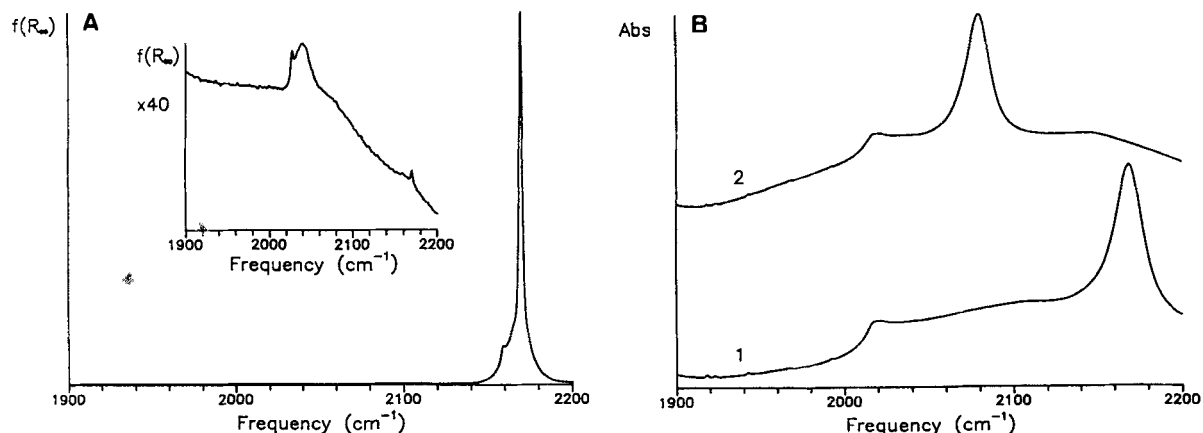


Figure 5. A) shows DRIFT spectra of washed and dried products from shaking nitrate-HT with 0.1 M solutions of KCNO and KCN (insert). (Ordinate scale of insert expanded 40 \times). B) shows transmission FTIR spectra of aqueous solutions of 1) KCNO and 2) KCN between PE sheets (hump at 2021 cm^{-1} is due to PE).

A precipitate of Prussian blue gave one broad absorption band located at 2082 cm^{-1} (not shown) in agreement with results of Wilde *et al.* (1970).

Mössbauer spectroscopy

Mössbauer spectra of the hexacyanoferrate(II)-HTs obtained at 80 K are shown in Figure 6. The spectra of samples F1-A, F1-E, and F1-F all exhibit a single lorentzian-shaped absorption line only. Spectra of samples F1-B, F1-C, and F1-D are also dominated by a single absorption line, but they do deviate significantly from lorentzian shape, demonstrating the presence of more than one component in these spectra. The spectra were fitted using lorentzian-shaped lines, which is an excellent approximation for the singlet. In the case of samples F1-B, F1-C, and F1-D, the extra component(s) was fitted by introducing one doublet to account for the low-intensity broad absorption between approximately $\pm 1 \text{ mm s}^{-1}$. The poor resolution and the low intensity of this doublet cause that no definite line positions may be preferred in the fit. In Table 3 are given the Mössbauer parameters derived from a two-component fit using one singlet and one doublet with a relatively large quadrupole splitting. The parameters of the spectra obtained at 80 K of solid $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, $\text{K}_3\text{Fe}(\text{CN})_6$ salts and $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ ions in frozen solutions are also given in Table 3. The detailed temperature study of sample F1-A revealed only insignificant change of the line width with temperature, and the isomer shift changed monotonously by a magnitude as expected from the second-order Doppler shift. The logarithm of the absorption area for sample F1-A (obtained from the fits) is shown as a function of temperature in Figure 7 and exhibits a non-linear dependence in this temperature range.

DISCUSSION

The 1.1 nm d_{003} basal spacing of the air-dried hexacyanoferrate(II)-HT is within the range reported for hexacyanoferrate-HTs (1.07–1.12 nm); however, all were dried at temperatures above room temperature (60°–110°C). In our experiments, heating at 70°C resulted in a decrease of d_{003} to approx. 1.08 nm. Miyata and Hirose (1978) observed a decrease of basal spacing from 1.12 nm to 1.08 nm on drying at 200°C. Basal spacings of LDHs are known to vary with hydration status of the interlayer, which partly may explain the differences observed, i.e., samples dried at elevated temperatures may have equilibrated with the humidity at room temperature before being examined by XRD. The distribution of residual interlayer-carbonate may also be thought to have a considerable influence on the temperature dependence of the d_{003} decrease. The relative intensity of the 003 spacing (0.76 nm) attributed to crystallites having only carbonate in the interlayer (Figure 1) is much too low to account for the 30% of the layer charge compensated by carbonate as determined from chemical analysis. Furthermore, no indication of random or regular mixing of interlayers can be detected. Hence, carbonate and hexacyanoferrate(II) ions have to occur together in some of the interlayers. Locally, the smaller carbonate ion may contract the interlayer and, thus, favor dehydration. HTs containing less carbonate are then expected to dehydrate at higher temperatures in accordance with what has been observed (Miyata and Hirose, 1978).

For the potassium salt of $\text{Fe}(\text{CN})_6^{4-}$, the CN (ν_6) absorption is located at 2044 cm^{-1} (DRIFT spectra). Substituting other metal cations for potassium in the hexacyanoferrate(II) salt changes the frequency of the main CN peak with up to 50 cm^{-1} (Emschwiller, 1954). The resolution and intensities of the other absorptions

Table 2. FTIR frequency and intensity data for the CN-stretching region of hexacyanoferrate as salt, aqueous solution and interlayered in hydrotalcite.

Sample	Frequency (cm ⁻¹)				Ratio ^c
	Transm-Nujol ^a		Reflect. ^b		
	Fe ^{III}	Fe ^{II}	Fe ^{III}	Fe ^{II}	
F1-A	—	2036	2112	2036	0.002
F1-B	2113	2036	2111	2036	0.024
F1-C	2113	2037	2110	2036	0.012
F1-D	2114	2036	2111	2037	0.012
F1-E	—	—	2109	2037	0.002
F1-F	—	—	2109	2036	0.001
F1-G	—	—	2113	2037	0.207
K ₄ Fe(CN) ₆ ·3H ₂ O ^d	—	2044	—	2044	—
Fe(CN) ₆ ⁴⁻ (aq) ^e	—	2038	—	—	—

^a Transmittance, Nujol mulls.

^b Diffuse reflectance, KBr matrix.

^c Ratio of integrated intensity of ν_6 (CN) of cyanoferrate(III) to the integrated intensity of ν_6 (CN) of cyanoferrate(II) determined from DRIFT spectra.

^d Transmittance, KBr pellets.

^e Transmittance, aqueous solution between polyethylene (PE) sheets.

in the range 2000–2100 cm⁻¹ was found to be highly dependent on the hydration state of the salt. For the Fe(CN)₆⁴⁻ ion in aqueous solution, CN (ν_6) moves to 2038 cm⁻¹ (Table 2). For the K₃Fe(CN)₆ salt, DRIFT spectra showed the main CN absorption at 2117 cm⁻¹, with almost the same peak position found for aqueous solutions of this salt (Koch and Hansen, personal communication). Similar differences in position of the main CN absorption between the iron(II) and iron(III) complexes have also been reported (Emschwiller, 1954). These differences are explained by the decreasing π -bonding between the metal atom and the CN groups for the hexacyanoferrate(III) compared with the hexacyanoferrate(II) (Caglioti *et al.*, 1957).

On intercalation in HT, the hexacyanoferrate(II) CN (ν_6) absorption band loses its fine structure and the band width almost doubles, indicating the near environment of the complex ion to be less homogeneous in the HT-interlayer than in the potassium salt (Figures 2A and 3A-1). For the DRIFT and nujol mull spectra, the frequency for the CN (ν_6) absorption of the air-dried hexacyanoferrate(II) in the HTs is almost identical to the frequency observed for aqueous solutions of hexacyanoferrate(II) (Table 2). However, compared with the potassium salt, the peak has shifted about 8 cm⁻¹ toward lower wave numbers (Table 2). This indicates that the aqueous phase is a good approximation for the environment of the hexacyanoferrate(II) ion within the HT-interlayer. The difference in frequency of the CN (ν_6) absorption band for hexacyanoferrate(III) between HT-intercalates, the potassium salt and aqueous solutions thereof, are small, which indicates that the CN stretch of the hexacyanoferrate(III)

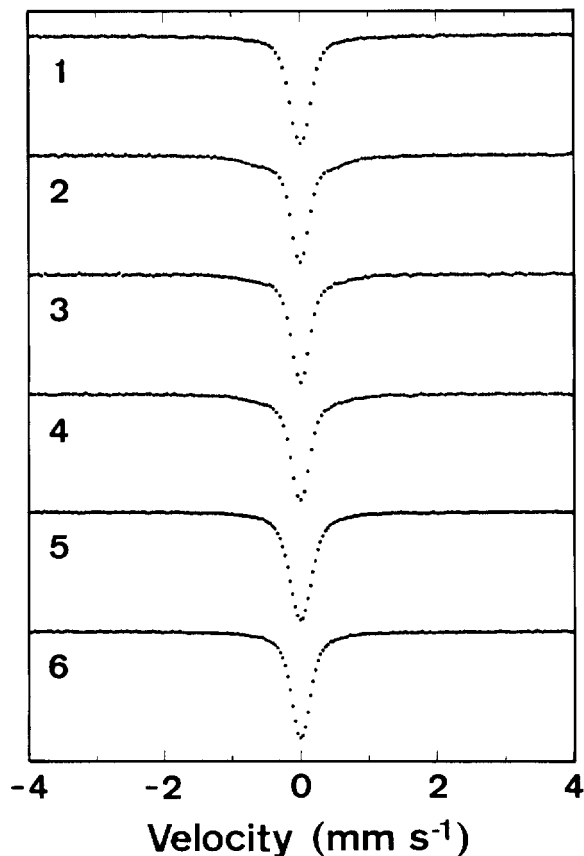


Figure 6. Mössbauer spectra of 1) hexacyanoferrate(II)-HT (F1-A), 2) hexacyanoferrate(II)-HT treated with nondeoxygenated acetone (F1-B), 3) hexacyanoferrate(II)-HT treated with nondeoxygenated ethanol (F1-C), 4) hexacyanoferrate(II)-HT heated at 70°C for 16 hr (F1-D), 5) hexacyanoferrate(II)-HT treated with deoxygenated acetone (F1-E), and 6) hexacyanoferrate(II)-HT treated with deoxygenated ethanol (F1-F). All spectra were obtained at 80 K.

is less sensitive to changes in the environment than the CN stretch of the hexacyanoferrate(II) ion. For the hexacyanoferrate-HT samples, the relative amounts of cyanide in iron(II) and iron(III) complexes may be deduced from the intensities of the 2036 cm⁻¹ and 2111 cm⁻¹ absorptions, respectively (see ratio in Table 2). For air-dried samples, where the extent of ligand exchange is small, this ratio may be taken as an estimate of the relative amount of iron(II) and iron(III) cyanide complexes in the interlayer.

The absorption around 2080 cm⁻¹ observed in all DRIFT and transmission spectra of hexacyanoferrate(II)-HTs in the present study has not been reported in earlier investigations of hexacyanoferrate-HTs. It is located in a frequency range (2080–2090 cm⁻¹) where numerous heavy metal hexacyanoferrate(II)s show CN stretching (Ayers and Waggoner, 1971). For these Prus-

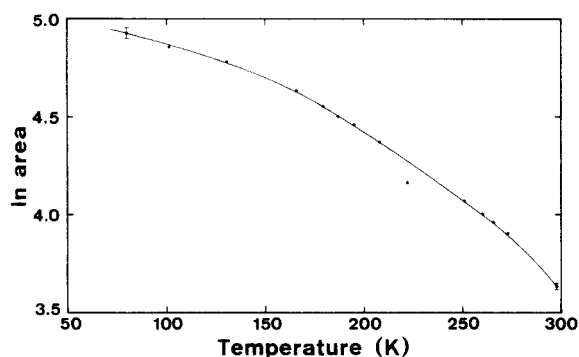


Figure 7. Temperature dependence of absorption area in the Mössbauer spectrum for sample F1-A between 80 and 298 K. Line is only a guide to the eye.

sian blue-like compounds ($M_k^A[M^B(CN)_6]_l \cdot xH_2O$; (k,l) = (1,1), (4,3), (3,2), (2,1)), cyanide forms bridges between M^A and M^B cations (Ludi and Güdel, 1973). Some single bridged binuclear cyanides also absorb around 2080 cm^{-1} , e.g., $Ba_3FeCo(CN)_{11} \cdot 16H_2O$ has a stretching frequency at 2090 cm^{-1} (Dows *et al.*, 1961). Although these observations could indicate the presence of bi- or polynuclear CN-bridged interlayer complexes, attempts to intercalate cyanide-bridged binuclear iron-cyanide complexes in HT were not successful—apparently due to preferential uptake of mononuclear cyano complexes or monomerization of dimers already adsorbed (Hansen and Koch, personal communication). The presence of residual glycerol in the hexacyanoferrate-HT as the cause of the 2080 cm^{-1} absorption is precluded as the nitrate-HT used for anion exchange with hexacyanoferrate(II) did not show any absorption peak around 2080 cm^{-1} and transmission spectra of liquid glycerol or a glycerol-intercalated

HT only showed absorptions of very weak intensity in the $2000\text{--}2100\text{ cm}^{-1}$ region.

Blue precipitates were observed on dissolving all hexacyanoferrate-HTs with dilute mineral acids. Together with the presence of the 2080 cm^{-1} absorption, this could indicate the formation of initial or proto-Prussian blue-like compounds (PPB) in the interlayer. However none of the synthesized hexacyanoferrate-HTs was blue-colored and the interlayer spacing is much too small to accommodate even a monolayer of Prussian blue. Using cyclic voltammetry, Shaw *et al.* (1990) claimed that a Prussian blue-like compound had formed in an HT analogue of Zn and Al contacted with aqueous solutions of $Fe(CN)_6^{3-}$. However, they did not observe the formation of such compounds with HT in agreement with Itaya *et al.* (1987) and Hansen (1990). Furthermore, if the interlayer itself stimulated the formation of cyanide bridged binuclear species the difficulties of placing these in the interlayer would be surprising (Hansen & Koch, personal communication).

From Figure 3B, it appears that water gives rise to a broad absorption band around 2080 cm^{-1} , the absorption being most pronounced in spectra of water in wetted KBr pellets. The fact that no 2080 cm^{-1} absorption is observed for hexacyanoferrate-HT samples dried at 100°C could indicate the 2080 cm^{-1} absorption observed for the air-dried samples was caused by water. The width of the 2080 cm^{-1} band is much smaller in the hexacyanoferrate-HT samples as compared with water in either KBr pellets or in the liquid state (Figure 3B). Therefore, the presence of water in the hexacyanoferrate(II)-HT samples cannot be the only explanation for the 2080 cm^{-1} absorption. Furthermore, the 2080 cm^{-1} band could not be detected for air-dried carbonate- or nitrate-HTs which, as indicated from the presence of a band at 1635 cm^{-1} , do contain water.

Table 3. Mössbauer parameters of hexacyanoferrate in hydrotalcites, potassium salts, and frozen solutions at 80 K.

Sample	Singlet			Doublet			
	δ^1 (mm s^{-1})	Γ^2 (mm s^{-1})	A^3 (%)	δ^1 (mm s^{-1})	ΔE_Q^4 (mm s^{-1})	Γ^4 (mm s^{-1})	A^3 (%)
F1-A	0.012	0.33	100				
F1-B	0.006	0.31	90	-0.045	1.26	0.38*	10
F1-C	0.007	0.30	90	-0.086	1.17	0.80*	10
F1-D	0.002	0.32	93	-0.046	1.31	0.54*	7
F1-E	0.007	0.36	100				
F1-F	0.007	0.31	100				
$K_4Fe(CN)_5 \cdot 3H_2O$	0.038	0.24	100				
$K_3Fe(CN)_6$				-0.044	0.47	0.33	100
$Fe(CN)_6^{4-}$ (glass)	-0.006	0.26	100				
$Fe(CN)_6^{3-}$ (glass)				-0.058	0.93	0.50	100

¹ ± 0.005 .

² ± 0.02 .

³ ± 3 .

⁴ ± 0.05 .

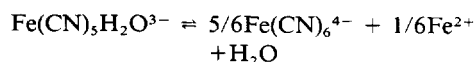
δ = isomer shift; ΔE_Q = quadrupole splitting; Γ = width at half height; A = relative area; * = constrained to be equal.

While neither cyano-bridged iron complexes nor water explain the presence of the 2080 cm^{-1} band, it seems likely that it may be due to the presence of electrostatically bound cyanide ions in the interlayer. As shown earlier, the solvation behavior of water approximates the solvation behavior of the interlayer environment. The stretching frequency of CN^- in aqueous solution is located at 2080 cm^{-1} (Figure 5B). Some cyanide ligands must be lost from the interlayer-hexacyanoferrate in order for Prussian blue precipitates to develop on acid dissolution of the HT. In the interlayer, cyanide ligands of hexacyanoferrate(II) may be partly exchanged by water or hydroxyls:



To maintain charge balance, cyanide ions are not expelled from the interlayer when water is the substituting ligand. This does not contradict the results from exchange of interlayer nitrate with cyanide or cyanate ions. Where cyanate is easily exchanged with nitrate in HT, as seen from the very intense $\text{CN}(\nu_6)$ absorption, cyanide is not (Figure 5A). Free cyanide ions have probably not been incorporated into the interlayer by simple ion exchange, as a frequency shift from 2080 cm^{-1} in aqueous KCN to 2030–2040 cm^{-1} in the interlayer would not be expected if only electrostatic forces were involved. The very weak absorptions at 2027 and 2039 cm^{-1} could be due to cyanide bound to aluminium or magnesium of the hydroxide layers. However Mazur and Hipps (1979) were not able to detect any cyanide absorbed onto alumina using inelastic electron tunneling spectroscopy. Although cyanide ions may show very low affinity for the interlayer during ion exchange, cyanide may be placed in the interlayer when generated *in situ* and, subsequently, caught by electrostatic forces. The lack of the 2080 cm^{-1} band for samples dried at 100°C demonstrates that, when no water or hydroxyls are available in the interlayer, the ligand exchange does not take place following this treatment.

The aquo-substituted complex is more prone to oxidation by dioxygen than the hexacyanoferrate(II) ion (Olabe and Zerga, 1983). Also the $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ ion may decompose in the interlayer (Olabe and Zerga, 1983):



The Fe^{2+} formed in the basic interlayer environment must be expected to be quickly oxidized by dioxygen if present. This sequence of reactions may explain PPB formation during acid dissolution of the HT.

In addition to ligand exchange, interlayer-hexacyanoferrate(II) may itself be directly oxidized. Oxidation of hexacyanoferrate(II) to hexacyanoferrate(III) is seen from IR spectra by increase of the absorption at

2111 cm^{-1} and decrease of the 2036 cm^{-1} absorption (Table 2). Hexacyanoferrate(II) becomes oxidized on washing with nondeoxygenated nonaqueous solvents such as acetone and ethanol, but not when these are deoxygenated (Tables 2 and 3, Figure 4). Heating also induces oxidation, the degree of oxidation increasing with temperature (Table 2). This has also been observed by Idemura *et al.* (1989), Carrado and Kostapapas (1988), and Cavalcanti *et al.* (1987), who ascribed the phenomenon to oxidation by dioxygen. Oxidation of interlayer hexacyanoferrate(II) is easily observed visually by a color change from very faint yellow to intense yellow or green.

The oxidation of hexacyanoferrate(II) on washing with oxygen containing solvents like acetone, ethanol, but not pure water and, on drying, seems to be due to oxidation by dioxygen because oxidation is very limited when deoxygenated nonaqueous solvents are used. This indicates that water hinders the migration of oxygen into the interlayer, or that oxidation by dioxygen cannot take place in the presence of water. The very low activity of water in the nonaqueous solvents, which however are miscible with water, may be expected to dehydrate the interlayer or at least to dehydrate interlayer volumes close to the particle edges and so make the interlayer accessible to gases like dinitrogen and dioxygen as has been observed when hexacyanoferrate(II)-HTs are dried at 100°C (Miyata and Hirose, 1978). This explanation is further supported by the fact that hexacyanoferrate(II)-HT did not become oxidized by heating in an aqueous suspension at 100°C during the intercalation reaction (sample F1-A).

Information on the physical state of the hexacyanoferrate(II) complex in the interlayer may be inferred from the Mössbauer study. In aqueous solution, the small ion-like hexacyanoferrate(II) does not absorb γ -rays without recoil, and it is, thus, not possible to obtain a Mössbauer spectrum in this condition. The fact that a Mössbauer spectrum is observed demonstrates that the complex is held rather rigidly in the interlayer (on the time scale of the excited state) mainly by electrostatic forces. If a Debye crystal model is assumed as an approximation for the hexacyanoferrate(II)-HT system, a non-linear dependence between the logarithm of the spectral area and the temperature is expected from the analytical expression for the f -factor in the Debye model (Wertheim, 1971). This expression may, for temperatures larger than $1/2\theta_D$ (θ_D is the Debye temperature), be simplified to a linear relation between the logarithm of the spectral area and the temperature from which θ_D may be determined. From the data presented in Figure 7, it can be concluded that a linear relation between $\ln A$ and temperature does not hold over the entire temperature range probed in this experiment. However, it appears that, for temperatures above 150 K, a linear relation

is a fair representation of the data (in particular if the observations at 222.0 and 298.0 K are excluded) and from the slope in this range a Debye temperature of approximately 140 K is estimated. The hexacyanoferrate(II) complex is expected to be partly hydrated in the interlayer, and this water is expected to freeze at around 220 K. The absence of a significant change in the area-temperature relation around this temperature indirectly supports the dominance of electrostatic forces in determining the behavior of the hexacyanoferrate(II) complex. The absence of significant changes in the Mössbauer parameters around the expected freezing temperature of the interlayer water also indicates that the interaction of the complex and the interlayer water is secondary compared with the electrostatic forces. It is most likely that the complexes adsorbed to the external surfaces would be less strongly held as compared with complexes in the interlayer and, thus, more susceptible to any effects induced by the freezing of water, but we cannot resolve such a contribution from the present results.

From Table 3, it is noted that the Mössbauer parameters of the dominating singlet in the spectra of the hexacyanoferrate(II)-HT samples are very similar and exhibit a significant change in comparison to the solid potassium salt and the frozen solution both with respect to isomer shift and line width. The different isomer shifts demonstrate that the near environments of the hexacyanoferrate(II) complex are different in the salt, the frozen solution, and the interlayer. We suggest that the difference is similar to the cation effect known from crystalline hexacyanoferrate(II)-salts and explained by the effect of differences in polarizing power of the cations on the π back donation in the hexacyanoferrate(II) complex (Greenwood and Gibb, 1971). From the parameters and the relative areas of the singlet in the samples, it appears that the interlayer hexacyanoferrate(II) ion is the dominant species in samples F1-A–F1-F, and, effectively, the only species in samples F1-A, F1-E, and F1-F in agreement with results from FTIR analysis. A rather large increase in the quadrupole splitting of the hexacyanoferrate(III) complex is noted upon solvation (Table 3) as also reported by Papp *et al.* (1975). Local variation of the polarizing power within the HT interlayer may also cause relatively small changes in isomer shifts partly contributing to the observed broadening of the singlet. The parameters and relative areas (assuming equal *f*-factors of all components) of the spectra of samples F1-A, F1-E, and F1-F and of the singlet in the spectra of the other samples demonstrate that the hexacyanoferrate(II) complex remains essentially unchanged upon intercalation and washing. As indicated by the weak doublet component in samples F1-B, F1-C, and F1-D changes in part of the hexacyanoferrate(II) complexes may be induced by relatively mild treatments. Direct oxidation

of hexacyanoferrate(II) to hexacyanoferrate(III) or a ligand exchange of CN in any of these two ferrates would cause the appearance of a doublet component in the Mössbauer spectrum. Because of the poor resolution of the doublet component(s) in the spectra of samples F1-B, F1-C, and F1-D, the derived parameters may not be considered very significant and, accordingly, they cannot be used to distinguish between the different possibilities. A comparison of the doublet parameters for the hexacyanoferrate-HTs and the parameters for the potassium salt of the hexacyanoferrate(III) show that they are very different (Table 3) and, thus, may be taken to indicate that simple oxidation of the iron in the hexacyanoferrate(II) complex is very limited. However, as demonstrated by the large increase in quadrupole splitting of the hexacyanoferrate(III) in glass as compared with the potassium salt, it is likely that a hexacyanoferrate(III) specie contributes to the doublets in the spectra of the hexacyanoferrate-HT samples.

Essentially the same conclusions may be derived from the spectra obtained at 298 K (not shown). However, due to the relative large decrease in absorption area between 80 and 298 K (a factor of approximately 5), the low-intensity components are poorly defined and the relative absorption areas derived from the fits differ slightly.

CONCLUSIONS

Hexacyanoferrate(II)-HTs synthesized from the carbonate-HT by double ion exchange takes advantage of the easy and reproducible synthesis of the carbonate-HT and its superior crystallinity. Non-oxidized hexacyanoferrate(II)-HTs can be synthesized and stored provided they are not washed with oxygen-containing non-aqueous solvents and not dried at temperatures above room temperature.

On oven drying or washing, the hexacyanoferrate(II)-HT with nonaqueous oxygen-containing solvents interlayer-hexacyanoferrate(II) oxidizes and exchanges ligands. The oxidation is due to reaction with dioxygen penetrating the interlayer after partial or complete removal of water. The interlayer-hexacyanoferrate(II) complex is not inert and probably undergoes ligand exchange reactions where cyanide is exchanged by water or hydroxyls producing free cyanide ions in the interlayer. However, when not produced within the interlayer and held by electrostatic forces the cyanide ion shows little affinity for the interlayer. The presence of interlayer-water is the main determinant of both oxidation and ligand exchange of interlayer-hexacyanoferrate(II).

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