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Intercalation of iron hexacyano complexes in Zn,Al hydrotalcite. Part 2. A mid-infrared and Raman spectroscopic study

J. Theo Kloprogge,[a,*] Matt Weier,[a] Inmaculada Crespo,[b] Maria A. Ulibarri,[b]
Cristobalina Barriga,[b] V. Rives,[c] Wayde N. Martens,[a] and Ray L. Frost[a]

[a] *Inorganic Materials Research Group, School of Physical and Chemical Sciences, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane Q 4001, Australia*
[b] *Departemento de Química Inorgánica e Ingeniería Química, Facultad de Ciencias, Universidad de Córdoba, Córdoba 14004, Spain*
[c] *Departamento de Química Inorgánica, Universidad de Salamanca, Salamanca 37008, Spain*

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Abstract

Combined mid-IR and Raman spectroscopies indicate that intercalation of hexacyanoferrate (II) and (III) in the interlayer space of a Zn,Al hydrotalcite dried at 60°C leads to layered solids where the intercalated species correspond to both hexacyanoferrate(II) and (III). This is an indication that depending on the oxidation state of the initial hexacyanoferrate, partial oxidation and reduction takes place upon intercalation. The symmetry of the intercalated hexacyanoferrate decreases from O_h existing in the free anions to D_{3d}. The observation of a broad band around $2080\,\text{cm}^{-1}$ is indicative of the removal of cyanide from the intercalation complex to the outside surface of the crystals. Its position in the intercalation complex is probably filled by a hydroxyl group.

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1. Introduction

Although many inorganic layered compounds with negatively charged layers compensated by intercalated cations are known, only a few families of compounds are known with the opposite charge distribution. One of these families corresponds to layered double hydroxides (LDHs), also known as hydrotalcite-like or hydrotalcite-type compounds, following hydrotalcite, a natural mineral with the composition $[Mg_6Al_2(OH)_{16}]CO_3{\cdot}4H_2O$. Partial isomorphous Mg^{2+}/Al^{3+} substitution gives rise to a net positive charge in the brucite-like layers, balanced by interlayer anions (carbonate in the case of hydrotalcite). The nature of the cations in the hydroxide layers and of the interlayer anions can be varied substantially. The resulting synthetic materials exhibit applications in a broad range of fields, e.g., catalysts and catalyst supports, antacids, anion scavengers (due to the ability of calcined LDHs to recover the layered structure when contacted with anions), etc. The properties and applications of these materials have been recently reviewed [1].

The calcination of hydrotalcites leads to formation of homogeneous mixed oxides. In the particular case of hydrotalcites containing iron, it has been reported [2] that the properties of the final oxides depend on the original location of the iron cations, i.e., in the brucite-like layers, or as part of a complex anion in the interlayer. The iron-containing anions most widely used to intercalate in hydrotalcites are hexacyanoferrates [1–12] and many efforts have been made to explain the precise nature of the interlayer hexacyanoferrate species, as oxidation/reduction processes from Fe(II) to Fe(III) and vice versa have been reported [6,12]. In the present paper, we report a detailed mid-infrared and Raman study of Zn,Al hydrotalcites containing intercalated hexacyanoferrate (II) and (III), in order to gain insight in the processes taking place in the interlayer.

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[*] Corresponding author. Fax: +61-7-3864-1804.
E-mail address: t.kloprogge@qut.edu.au (J.T. Kloprogge).

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2. Experimental

2.1. Synthesis

Synthesis of these samples has been described elsewhere [3]. Sample HTFE2 was prepared by direct synthesis from Zn and Al nitrate solutions (Zn/Al molar ratio = 2.0) in decarbonated water and degassed with nitrogen for 20 min. A solution of $K_4[Fe(CN)_6]$ was added (Al/Fe molar ratio = 2.0) with vigorous stirring at pH = 10.2 and 60°C. This pH produces the co-presence of carbonate in the interlayer but a lower value yields to precipitation of $K_2Zn_3[Fe(CN)_6]_2$. After ageing for 24 h, the solid was filtered and washed, and dried at 60°C for 24 h ($c = 32.561$ Å, $a = 3.066$ Å). The same procedure was used with hexacyanoferrate (III) to obtain sample HTFE3 ($c = 32.561$ Å, $a = 3.066$ Å) but in this case, no precipitation of salts at low pH was found so it was maintained at 9 to avoid carbonate presence. However, in this case, the presence of an impurity corresponding also to a layered material with the hydrotalcite-like structure and intercalated carbonate anions is present, even at this lower pH.

A better method to obtain pure hexacyanoferrate hydrotalcite is anion exchange of a Zn,Al hydrotalcite-like material (ZNALTA) with intercalated terephthalate first prepared by direct synthesis. A portion of 1.5 g of the solid was suspended in 100 mL of decarbonated water and then NaOH was added until a pH of 10.2 was reached. Next, the amount of $K_4[Fe(CN)_6]$ required for a Al/Fe ratio close to 1 was dissolved in 100 mL of decarbonated water and drop-wise added to the ZNALTA slurry with strong stirring and maintaining the pH at 10.2. After ageing for 24 h, the solid was filtered and washed, and dried at 60°C for 24 h, leading to sample TAFE2 ($c = 32.825$ Å, $a = 3.072$ Å). Synthesis of TAFE3 was not possible because no exchange of ZNALTA with $K_3[Fe(CN)_6]$ occurred. The powder XRD patterns for samples HTFE2, HTFE3 and TAFE2 are shown in Fig. 1.

Chemical analysis of Zn, Al and Fe was carried out by atomic absorption for HTFE2 (Zn/Al = 2.02, Al/Fe = 4.26), HTFE3 (Zn/Al = 1.85, Al/Fe = 3.54) and TAFE2 (Zn/Al = 2.10, Al/Fe = 3.24). The atomic Zn/Al ratios are very close to the value existing in the starting solutions (2.0) used to prepare the samples. However, the values for the Al/Fe ratios are somewhat unexpected. As the interlayer anion balances the positive charge in the layers due to incorporation of Al^{3+}, an Al/Fe ratio equal to 3 and 4 would be expected for those samples containing $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, respectively. Values larger than expected in HTFE2 and HTFE3 can be due to the co-presence of carbonate in the interlayer. The Al/Fe lower than 4 in TAFE2, where no evidence of carbonate was found, suggests the simultaneous presence of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ after a redox process occurs in the interlayer space.

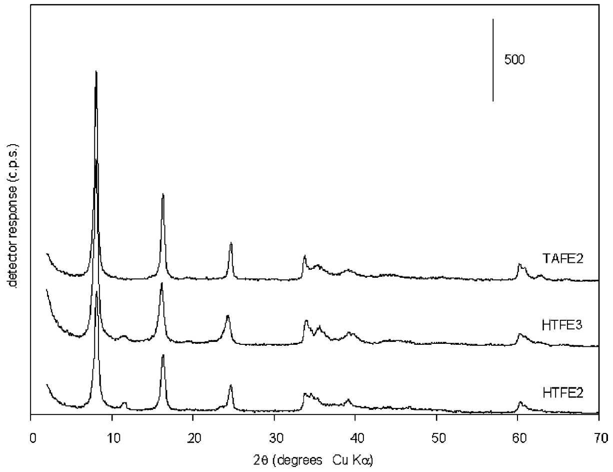

Fig. 1. Powder X-ray diffraction patterns of the samples used in this study.

2.2. Analytical procedures

2.2.1. Mid-infrared spectroscopy

The samples were finely ground for 1 min, combined with oven-dried spectroscopic grade KBr (containing approximately 1 wt% sample) and pressed into a disc under vacuum. The transmittance spectrum of the sample was recorded in triplicate by accumulating 512 scans at $4\,cm^{-1}$ resolution between 400 and $4000\,cm^{-1}$ using the Perkin-Elmer 1600 series Fourier transform mid-infrared spectrometer equipped with an LITA detector.

2.2.2. Raman spectroscopy

The micromount and single crystal samples were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10 ×, 20 ×, and 50 × objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He–Ne laser producing highly polarized light at 633 nm and collected at a resolution of $3.6\,cm^{-1}$ and a precision of $\pm 1\,cm^{-1}$ in the range between 200 and $4000\,cm^{-1}$. Repeated acquisition on the crystals using the highest magnification (50 ×) was accumulated to improve the signal-to-noise ratio in the spectra. Spectra were calibrated using the $520.5\,cm^{-1}$ line of a silicon wafer.

2.2.3. Spectral manipulations

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic

Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

3. Theoretical analysis

The hexacyanoferrate anion forms a regular octahedron with cyanide ligands in the corners leading to site symmetry of O_h. Selection rules imply that A_{1g}, E_g and T_{2g} will be Raman active only, while $2T_{1u}$ is infrared active only and T_{2u} is inactive [13]. Kikkawa and Koizumi [4] and Braterman et al. [5] suggested that the C_3 axis of the octahedron is oriented perpendicular to the hydroxide sheets of the hydrotalcite. Braterman et al. [5] reasoned that theoretically the C–N vibrations would correspond to A_{1g}, E_g and T_{1u} from which the first two are Raman active while the last one is infrared active. However, the first two modes are also observed in the infrared spectrum as very weak bands, while the T_{1u} bands split in two bands assigned to E_u and A_{2u} indicative of a decrease in symmetry from O_h to D_{3d} [5].

4. Results and discussion

Fig. 2a shows the infrared spectra of the three samples. In addition to the vibrations normally observed for hydrotalcites, weak bands are visible around 1363 and 1612 cm^{-1} plus a complex set of bands around 2100 cm^{-1}. Fig. 2b shows the corresponding Raman spectra. The two bands around 1363 and 1612 cm^{-1} are not observed in the Raman spectra but the complex set, best resolved, around 2100 cm^{-1} is. The 1363 cm^{-1} band has been previously ascribed to adsorbed carbonate on the external surface of the hydrotalcite. However, XRD indicated the presence of an impurity, possibly hydrotalcite with carbonate in the interlayer, at least for samples HTFE2 and HTFE3. So, in these cases this band is due to interlayer carbonate instead of adsorbed carbonate. The other band at 1612 cm^{-1} is due to the bending mode of water. In comparison to normal liquid water, the band has shifted towards lower wavenumbers by about 30 cm^{-1}, indicating that this water is present in the hydrotalcite interlayer, where it has some sort of hydrogen bond type interaction with the hexacyanoferrate anions.

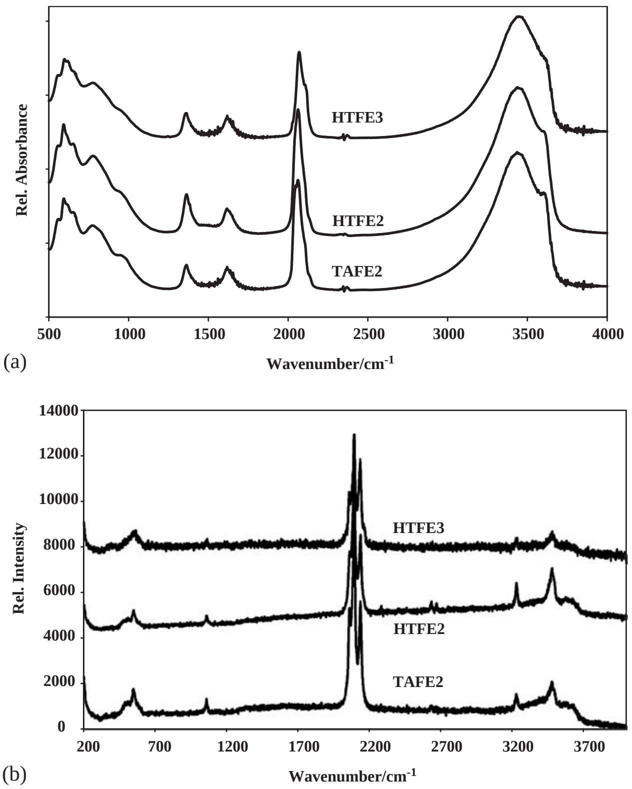

Fig. 2. (a) Infrared spectra in the region between 500 and 4000 cm^{-1}, and (b) the Raman spectra in the region between 200 and 4000 cm^{-1} of the intercalated hydrotalcites TAFE2, HTFE2 and HTFE3.

The potassium salts of hexacyanoferrate(II) and hexacyanoferrate(III) are characterized by a characteristic IR band at 2038 and 2116 cm^{-1}, respectively, ascribed to the C–N stretching mode. In addition, two weak bands are present in the hexacyanoferrate(III) spectrum at 2046 and 2076 cm^{-1}. The corresponding Raman spectra reveal bands at 2064 and 2092 cm^{-1} for the hexacyanoferrate(II) and at 2127 and 2133 cm^{-1} plus a very weak band at 2076 cm^{-1} for the hexacyanoferrate(III) (Fig. 3). A change in the oxidation state of the iron in cyanoferrate complexes is reflected in the C$\equiv$N stretching frequency, which shifts roughly from 2050–2070 cm^{-1} for Fe(II) to 2115–2125 cm^{-1} for Fe(III) [14,15]. This shift can be explained by the decreasing π-bonding between the iron and the CN groups for hexacyanoferrate(III) compared to hexacyanoferrate(II) [16].

In earlier work [3], the intercalated hydrotalcites were described as having two bands in all cases. The detailed band component analysis of the IR and Raman spectra in this study (Fig. 4 and Table 1) reveal that there are actually three bands present in the intercalated samples prepared from the hexacyanoferrate(II) anion and four bands in the sample prepared from the hexacyanoferrate(III) anion. In addition, all bands are observed at slightly higher wavenumbers. The weak band observed at 2039 cm^{-1} and the associated strong band at 2063 cm^{-1} in the IR spectra of TAFE2 and HTFE2 indicate the presence of hexacyanoferrate(II) in the interlayers of these hydrotalcites. The corresponding Raman band is observed at 2065 cm^{-1}. The presence of two additional bands around 2136 and 2103 in the IR spectra and around 2136 and 2094 cm^{-1} in the Raman spectra indicate the presence of hexacyanoferrate(III). These results suggest that the samples undergo redox processes resulting in a mixture of hexacyanoferrate(II) and (III). Holgado et al. [6] provided evidence for the partial reduction–oxidation of the iron in the interlayer hexacyano-complex by Fe–K XANES measurements, while Idemura et al. [7] observed the reduction of Fe(III) to Fe(II) in $Fe(CN)_6^{3-}$ intercalated LDH by Mössbauer spectroscopy. In addition to the shift observed due to oxidation or reduction of the iron, Crespo et al. [3] pointed out that the precise position of the $C\equiv N$ stretching frequency in hexacyanoferrate(II) is probably also influenced by the hydrogen bonding between the interlayer water molecules or the hydroxyl groups of the LDH sheets and the cyano groups. However, this is not reflected in the positions associated with the OH modes in the IR spectra with a single OH-bending mode at 1612 cm^{-1} and in the OH-stretching region in both the IR and Raman spectra between roughly 2500 and 4000 cm^{-1}.

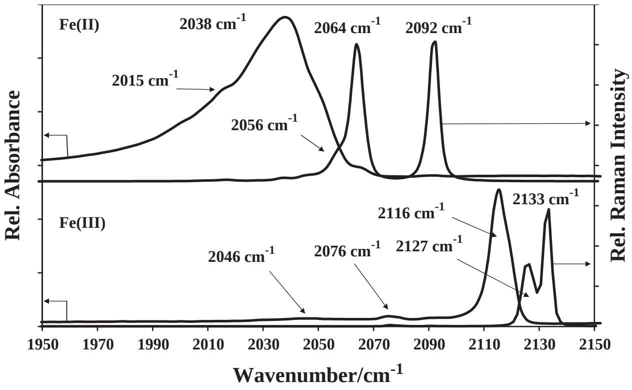

Fig. 3. Infrared and Raman spectra in the region between 1950 and 2200 cm^{-1} of the potassium salts of hexacyanoferrate(II) and hexacyanoferrate(III).

Similar patterns can be observed for HTFE3, although all bands are slightly shifted towards lower wavenumbers for the hexacyanoferrate(II) anion and towards higher wavenumbers for the hexacyanoferrate(III) anion. The relative intensity of the bands indicate, especially in the Raman spectrum, that in this sample more hexaferrate(III) is present than in the other two samples (more intense bands at ca. 2110–2130 cm^{-1}). This may cause changes in the interactions between the hexaferrate(II) and (III) anions resulting in the observed shifts in the IR and Raman spectra. In a comparable study, Idemura et al. [7]

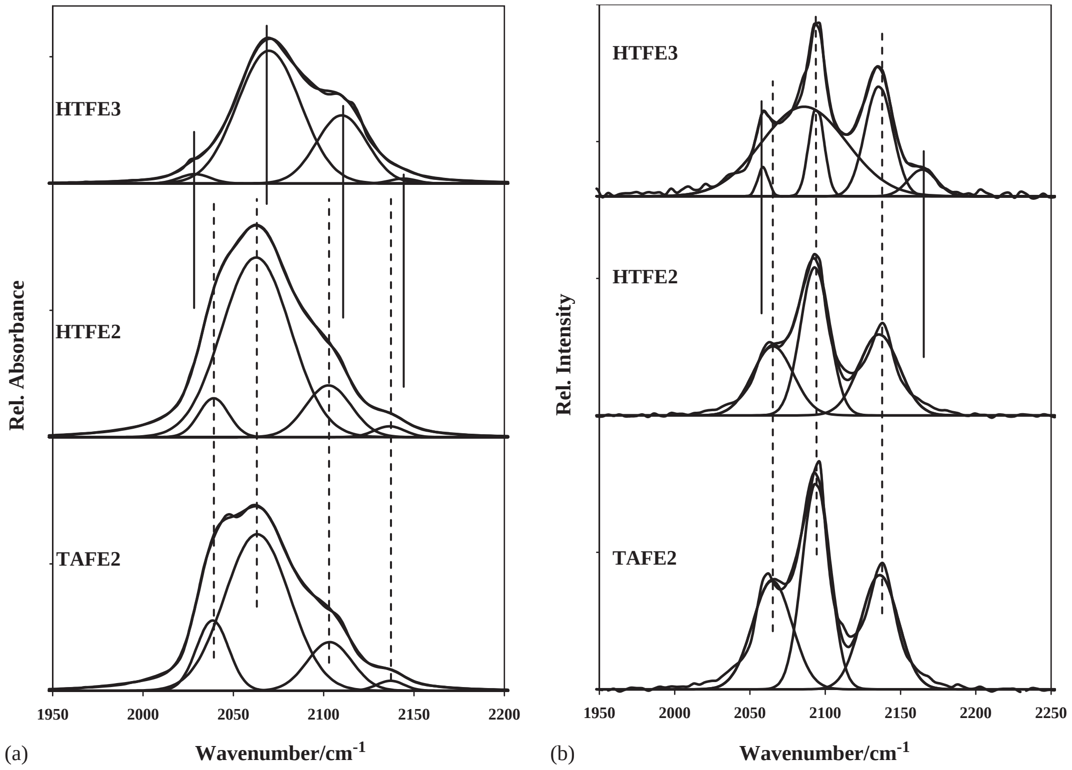

Fig. 4. Band component analysis in the region between 1950 and 2200 cm^{-1} of (a) the IR spectra, and (b) the Raman spectra of TAFE2, HTFE2 and HTFE3.

Table 1
Band component analysis of the C≡N stretching region

	Free ion		TAFE2		HTFE2		HTFE3	
	IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})
T_{1u}		2044	2039		2039		2029	
A_{1g}	2062		2063	2065	2063	2065	2070	2059
E_g	2098		2103	2094	2103	2093	2110	2094
			2137	2136	2136	2136	2144	2136
								2164

prepared for 84% $Fe(CN)_6^{3-}$ intercalated LDHs by anion exchange of a nitrate-LDH with potassium and sodium salt solutions under careful exclusion of carbonate. The IR spectrum showed two bands around 2120 and 2040 cm^{-1} indicating that a part of the Fe(III) was reduced to Fe(II) during intercalation. Intercalation with pure $Fe(CN)_6^{4-}$ resulted in only a single band around 2040 cm^{-1} if the sample was dried in vacuum but the other band appeared when dried in air. Similar observations of partial oxidation and reduction of Fe(II) and Fe(III) in intercalated cyanoferrate complexes have been reported by various groups, although small shifts have been reported depending on the starting source of the cyano-complex [6,8–10,17].

Since the three samples were dried at 60°C in air, it cannot be excluded that the partial oxidation and reduction of the iron in the hexacyanoferrate complex in the hydrotalcite interlayer is caused by the heating in air. Hansen and Koch [10] found that partial oxidation occurred when the cyanoferrate exchanged hydrotalcite was dried in an oven at 70–100°C. However, when the sample was dried at room temperature no oxidation was observed. Based on these observations, they concluded that the oxidation takes place because of the oxygen dissolved in the solvent during the preparation of the hydrotalcites and when the solid is dried above room temperature the fast removal of water from the interlayer favors migration of oxygen into the interlayer causing the oxidation of the Fe(II) to Fe(III). Oxidation of Fe(II) to Fe(III) in the hexacyano-complex requires some adjustments in the interlayer in order to maintain the charge balance with the positively charged hydroxide sheets of the hydrotalcite. One possibility is an exchange of a cyanide ligand by water or hydroxyls according to the reaction:

$$Fe(CN)_6^{4-} + H_2O \rightarrow Fe(CN)_5H_2O^{3-} + CN^-.$$

These cyanide ions are thought not to be expelled from the interlayer when water is the replacing ligand. Hansen and Koch [10] reported a very weak and broad absorption band around 2039 cm^{-1} and a sharp band at 2027 cm^{-1}, which is quite far from the normally observed band for free cyanide around 2080 cm^{-1}. This may indicate that the cyanide is bound to the cations in the LDH hydroxide sheets. The above-mentioned aquo-substituted complex oxidizes easier than the initial hexacyanoferrate(II) [18]. The results of this study, however, do not support the presence of free cyanide in the interlayer, based on the fact that the sharp band at 2027 cm^{-1} is not present, while the 2039 cm^{-1} band has been thought to be due to the hexacyanoferrate(II) complex in the interlayer. However, the observation of a broad band around 2080 cm^{-1} in the Raman spectrum of HTFE3 might indicate that the cyanide has moved out of the interlayer instead. Most probably, it is weakly adsorbed on the external surface of the crystallites.

Information about the symmetry of the hexacyanoferrate anion and its reduction and oxidation behavior when intercalated in LDHs can be gained from comparison of the Raman spectra with the infrared spectra [19]. As already indicated above, free $Fe(CN)_6^{4-}$ will give three vibrational modes with A_{1g} at 2098 cm^{-1} and E_g at 2062 cm^{-1} in the Raman spectrum and T_{1u} at 2044 cm^{-1} in the infrared spectrum. For the intercalated hydrotalcites, bands were observed in the Raman spectrum at 2136, 2094 and 2065 cm^{-1} for TAFE2 and HTFE2, and at 2164, 2136, 2094 and 2059 cm^{-1} for HTFE3, clearly supporting the fact that a change (reduction and oxidation) in the site symmetry has taken place. Lowering of the site symmetry to C_3 would predict four bands in the Raman for both the Fe(II) and Fe(III) hexacyano anions resulting in theoretically eight modes. In practice, one can expect that several of these modes will overlap resulting in the observation of less than eight bands. Braterman et al. [5] argued, in accordance with the findings of this study, that the activation of A_{1g} and E_g in the infrared spectrum while the T_{1u} band splits in two bands assigned to E_u and A_{2u} indicate a decrease in symmetry from O_h to only D_{3d} (from which C_3 forms a subgroup).

5. Conclusions

Combined mid-IR and Raman spectroscopies confirmed that intercalation of hexacyanoferrate(II) or (III) in the interlayer of Zn,Al hydrotalcite leads, in the samples studied here, to partial oxidation/reduction processes. This resulted in a mixed-valence situation in the interlayer, with both Fe(II) and Fe(III) interlayer species present, whichever the starting hexacyanoferrate. Deconvolution analysis of the recorded spectra has proved the presence of bands originated by both hexacyanoferrates, which probably also undergo a lowering in their site symmetry due to the restricted movement within the interlayer and the formation of hydrogen bonds with the hydroxide layers of the hydrotalcite. A small amount of free cyanide is expelled from the interlayer during the reduction of hexacyanoferrate(III).

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