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Physical and Chemical Interactions between Mg:Al Layered Double Hydroxide and Hexacyanoferrate

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The physical and chemical interactions of ferrocyanide (potassium and ammonium salts) and ferricyanide (potassium salt) with Mg:Al layered double hydroxides (LDH) (having Mg:Al ratios of 2 and 3) are investigated using powder XRD and FTIR spectroscopy. Physically, the potassium ferricyanide is shown to intercalate with a small local field deformation similar to that seen for hexacyanocobaltate (III) in similar materials. Chemically, the reduction of ferricyanide to ferrocyanide upon intercalation is confirmed. Physical interactions of ferrocyanide with 3:1 LDH are shown spectroscopically to include the possible generation of anions in differing environments. Chemically, ferrocyanide is shown to generate cubic ferrocyanides (of the type M_2MgFe(CN)$_6$, where $M = K^+$ or NH_4^+) under conditions where free Mg^{2+} is likely present in solution, namely, solutions with a pH lower than ~7.5. It is shown that the reported 2112-cm^{-1} band found in some chemically altered LDH ferrocyanide is indeed due to interlayer ferricyanide, but that the 2080 cm^{-1} band is due to the cubic material. © 2001 Academic Press

Key Words: **layered double hydroxide; hydrotalcite; hexacyanoferrate; ferrocyanide; ferricyanide; FTIR.**

INTRODUCTION

Layered double hydroxides (LDH) are a family of widely distributed, anion-exchanging minerals having the general formula $[M(\text{II})_{1-x}M(\text{III})_x(\text{OH})_2][Y]_x \cdot z\text{H}_2\text{O}$ [Y = e.g. Cl, $\frac{1}{2}\text{SO}_4$], sometimes known as anion-exchanging clays (1–5). The applications and importance of LDH have recently been reviewed both in general (4) and with particular application to the incorporation of anionic metal complexes (5).

Cyanide, in various forms, is thought to have played major roles in the origins of life (6). Generally, cyanides seem to provide the only realistic synthetic routes to purines and pyrimidines under early Earth conditions. For instance, Oró and co-workers have demonstrated the formation of adenine from ammonium cyanide solutions (7–9). Layered double hydroxides have also been invoked in studies of the origins of life (10–12). Our interest in this area arises from the possible concentration and/or activation of cyanide from solution by LDH (13). Cyanide has been shown to be easily introduced into LDH systems through intercalation of metallacyano complexes such as ferricyanide (2, 14–17), ferrocyanide (2, 15–22), nitroprusside (2, 23), and cobalticyanide (23, 24). Thus, the behavior of complex cyanides in the presence of LDH is a matter of some importance in a number of areas.

In the cases of ferricyanide and ferrocyanide, intercalation of the anion into the LDH may be accompanied by changes in the oxidation state of the anion and in the structure of the LDH system itself. The situation regarding ferrocyanide intercalation is the more interesting of the two. Rives and co-workers (19) ascribe a band near 2080 cm^{-1}, in both the Mg:Al and Zn:Al systems, to intercalated ferricyanide formed by oxidation of ferrocyanide, for which Hansen and Koch (20) report a frequency of 2112 cm^{-1}. Hansen and Koch (20) also reported, under certain experimental conditions, the presence of a ν(CN) absorption near 2080 cm^{-1} and suggested (correctly as we shall see) that this 2080-cm^{-1} species could be some form of cubic ferrocyanide. The iron cyanide LDHs reported by Carrado *et al.* (2) would appear, from their strong colors and high Fe:Al ratios, to have been contaminated with iron cyanide decomposition products, perhaps as a result of air exposure under strongly basic conditions during mixing.

We show in this work that, upon intercalation into either 2:1 or 3:1 Mg:Al LDH, ferricyanide undergoes a variable amount of reduction to ferrocyanide, with cyanide itself presumably acting as the reducing agent. We extend our previous use of oriented FTIR spectroscopy to 2:1 and 3:1 Mg:Al LDH ferricyanide and 3:1 Mg:Al LDH ferrocyanide. Intercalated ferricyanide is shown to exhibit a small deviation from local O_h symmetry similar to that found (23) in intercalated cobalticyanide. The oriented spectrum of 3:1 Mg:Al LDH ferrocyanide shows a switch in the relative

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frequencies of the *a*, *b*- and *c*-polarized components relative to the 2:1 case.

We find that when LDH is exposed to solutions of potassium ferrocyanide, under conditions where free Mg^{2+} may exist in solution, two types of material may be formed in varying ratios. The initial product contains intercalated ferrocyanide, while in the presence of free Mg^{2+}, cubic material of nominal composition $K_2MgFe(CN)_6$ is also produced as a distinct solid phase. We also find that treatment of Mg:Al LDH with solutions of ammonium ferrocyanide generates intercalated ferrocyanide and ammonium magnesium ferrocyanide $[(NH_4)_2MgFe(CN)_6]$ in all cases. The ability of these LDH systems to spontaneously generate materials containing cyanides in varied environments with, perhaps, different reactivities places them in good stead to promote and/or control certain cyanide reactions of possible prebiotic importance. The material with $[\nu(CN) \approx 2080\ cm^{-1}]$ formed from exposure of LDH to ferrocyanide, under conditions where free Mg^{2+} is expected to be present, while previously assigned (19) as LDH ferricyanide, would appear to be identical to our cubic material while that formed during a vigorous dehydration process $[\nu(CN) \approx 2112\ cm^{-1}]$ (20) is comparable to conventionally prepared LDH ferricyanide.

EXPERIMENTAL

Pure water (18.2 MΩ-cm obtained from a Millipore Milli-Q Plus water purification system), boiled and purged with nitrogen to remove carbon dioxide, was used throughout this work. All salts were ACS reagent grade. Hydrated metal salts $AlCl_3 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, and NaCl were used as supplied by Aldrich and Fisher. Potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$) and ammonium ferrocyanide hydrate ($(NH_4)_4Fe(CN)_6 \cdot xH_2O$) were used as supplied by Aldrich and potassium ferricyanide ($K_3Fe(CN)_6$) was used as supplied by J. T. Baker. Sodium hydroxide was used as a 50% (w/w) solution obtained from Aldrich.

The starting materials, 2:1 and 3:1 Mg:Al LDH chloride, $[Mg_2Al(OH)_6Cl$ and $Mg_3Al(OH)_8Cl]$, were prepared according to our previously described procedure (13, 23). These materials were washed a minimum of three times by centrifugation. Ferrocyanide- and ferricyanide-exchanged materials were generally prepared as pale cream and yellow colored solids, respectively, by exposure of the appropriate LDH chloride to excess 0.1 M solution of the potassium or ammonium salts under a slow stream of nitrogen. In cases where we desired to investigate the formation of cubic materials, the LDH chlorides were exposed to excess 0.2 M ferrocyanide solutions, also under a slow stream of nitrogen. In all cases, exchanges were performed using a starting material which had been kept damp in a sealed centrifuge tube and reaction times varied between 18 and 24 h. During the reaction and drying periods, and subsequent storage, all ferrocyanide- and ferricyanide-containing reaction mixtures and products were protected from light by aluminum foil to prevent unwanted photolytic reactions involving the anions.

Following exchange with the appropriate anion, the products were repeatedly washed and collected via a centrifuge and allowed to dry in an evacuated desiccator over molecular sieves at ambient temperature. Infrared and powder XRD data were collected as described elsewhere (25–27). Following our usual practice, infrared frequencies were determined by cursor placement and/or by direct reporting by the instrumental software.

Potassium magnesium ferrocyanide ($K_2MgFe(CN)_6$) was prepared by slowly adding, via an addition funnel, 100 mL of a 0.1 $MgCl_2$ solution to 100 mL of a 0.1 M $K_4Fe(CN)_6$ solution over a period of approximately 45 min. The reaction mixture was kept under a slow stream of nitrogen and stirred magnetically for the duration of the addition. The reaction vessel was covered in aluminum foil to prevent photolysis of the ferrocyanide solution and/or the product. The resulting white solid was then collected and repeatedly washed via a centrifuge. Ammonium magnesium ferrocyanide ($(NH_4)_2MgFe(CN)_6$) was prepared similarly.

RESULTS AND DISCUSSION

Physical Interaction with Ferricyanide

Figure 1 shows the observed powder XRD patterns for 2:1 and 3:1 Mg:Al LDH ferricyanide. The observed basal spacings are 11.18 Å for the 2:1 and 9.82 Å for the 3:1. These spacings indicate that the ferricyanide anion intercalates with its three-fold axis perpendicular to the hydroxide layers. Kikkawa first proposed this mode of intercalation for ferrocyanide in LDH and it appears from the basal spacings to be the preferred anion orientation in every $M(CN)_6^-$ intercalated LDH reported to date (2, 14–24). The main peaks from each of these diffraction patterns are compiled in Table 1.

Figures 2 and 3 present both the conventional and oriented FTIR spectra of 2:1 and 3:1 Mg:Al LDH ferricyanide. In each case, two $\nu(CN)$ peaks are observed; one near $2117\ cm^{-1}$ and the other near $2035\ cm^{-1}$. Hexacyanoanions, intercalated into LDH, have been shown (20, 24) to exhibit infrared spectra virtually identical in position to the aqueous anion. Our own data and literature reports (28) indicate that aqueous ferricyanide exhibits a single $\nu(CN)$ IR band at or near $2111\ cm^{-1}$. We therefore assign the $2117\text{-}cm^{-1}$ species as intercalated ferricyanide. We attribute the $2035\text{-}cm^{-1}$ peak to ferrocyanide obtained by reduction of the ferricyanide and discuss it further in the following section. The intercalated ferricyanide shows a slight splitting of the $\nu(CN)$, similar in magnitude to that seen (23) for cobalticyanide. Such similarities in the spectroscopic properties of cobalticyanide and ferricyanide are

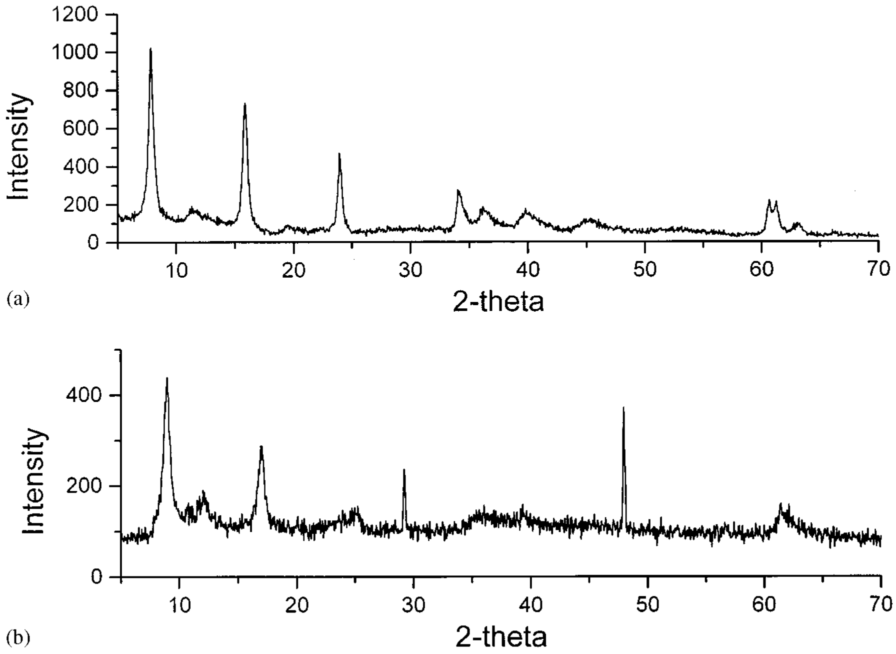

FIG. 1. Powder XRD patterns of (a) 2:1 and (b) 3:1 Mg:Al LDH ferricyanide.

hardly surprising, given the similar sizes and charges of the two anions; one would expect their interaction with the LDH cation layers to be similar. Orientation (22) of 2:1 LDH ferricyanide yields a broad, symmetric peak centered at 2117 cm^{-1}. Similar results are seen for the 3:1 LDH ferricyanide. Significant peaks of the FTIR spectra for 2:1 and 3:1 Mg:Al LDH ferricyanide are summarized in Table 2.

Physical Interaction with Ferrocyanide

The physical interaction of ferrocyanide with 2:1 Mg:Al LDH has been previously discussed in detail (22) and is well understood. In this case, the T_{1u} mode of octahedral ferrocyanide is split into E_u and A_{2u} modes in D_{3h} upon intercalation into LDH. Thus, the FTIR spectrum of the 2:1 Mg:Al LDH ferrocyanide shows two ν(CN) modes; one at 2035 cm^{-1} and the other at 2045 cm^{-1}. The oriented FTIR spectrum shows that the A_{2u} (z-polarized) absorption is that observed at the lower frequency.

TABLE 1
Powder XRD Data (*d* Spacings Given in Å) for 2:1 and 3:1 Mg:Al LDH Ferricyanide

Mg:Al	003	006	009	012
2:1	11.18	5.57	2.63	1.53
3:1	9.82 (7.89)[a]	5.23	2.57	1.51

[a] This value assigned as 003 of either the remaining LDH Cl or contaminant LDH CO_3^{2-} phase.

Figure 4 shows the observed powder XRD patterns for 3:1 Mg:Al LDH chloride and ferrocyanide. The ferrocyanide-exchanged material shows a basal spacing of 10.90 Å, compared with 10.77 Å for the 2:1 LDH ferrocyanide. (The small difference in basal spacings between the 2:1 and 3:1 Mg:Al LDH ferrocyanides is possibly related to variations in hydration state.) Such a spacing is consistent with the intercalated anion being in the expected (21) orientation of having a three-fold axis perpendicular to the hydroxide layers.

Table 3 compiles the significant XRD peaks of the 3:1 Mg:Al LDH chloride and ferrocyanide. The conventional and oriented FTIR spectra of 2:1 Mg:Al LDH ferrocyanide are presented in Figs. 5 and 6 for the sake of comparison together with those of the corresponding 3:1 system, reported here for the first time. Dramatic differences are observed. A comparison of the oriented spectra of the 2:1 and 3:1 LDH ferrocyanides also shows that the relative polarization of the 2035- and 2045-cm^{-1} species is reversed in the 3:1 case relative to the 2:1, with the 2045-cm^{-1} peak being suppressed on orientation in the 3:1 material. Thus, the lower frequency band in each species correlates with the higher frequency band in the other. The reasons for this effect are not clear. In the conventional FTIR spectrum, the 3:1 Mg:Al LDH ferrocyanide shows a more complex ν(CN) region than the 2:1 LDH. In addition to the peaks at 2035 and 2045 cm^{-1}, there are also a number of less intense and less well-defined peaks throughout this region. Such a com-

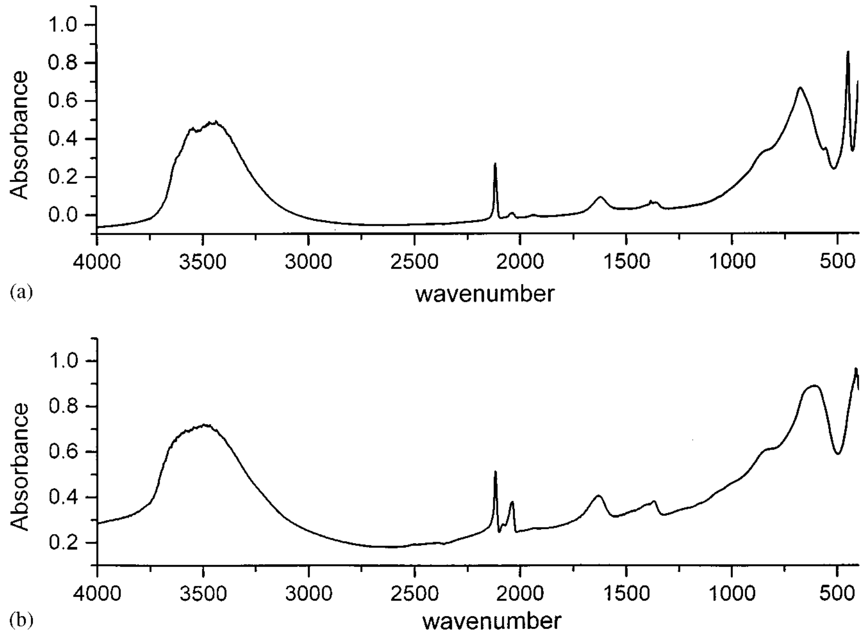

FIG. 2. Full-scale FTIR spectra of (a) 2:1 and (b) 3:1 Mg:Al LDH ferricyanide.

plex ν(CN) spectrum suggests a situation where ferrocyanide is in several distinct interlayer environments. Interlayer ferrocyanide ions in 3:1 LDH are expected to be positioned further away from each other than in the 2:1 case. The extra room in the 3:1 case may well provide a more diverse range of opportunities for the anion to hydrogen bond to nonequivalent lattice OH groups. Significant peaks of the FTIR spectra for 2:1 and 3:1 Mg:Al LDH ferrocyanide are summarized in Table 4.

Presence of High-Frequency OH Bands

The presence of non-hydrogen-bonded OH groups in LDHs intercalated with ML_6-type anions is expected as a geometric consequence of the interaction of such anions with the hydroxide layers. High-frequency hydroxide stretches attributable to such groups are clearly resolved in conventional spectra of 2:1 LDH ferrocyanide and in oriented LDH ferricyanide samples. The high-frequency ν(OH) is clearly seen near 3622 cm^{-1} in Fig. 5a. (One might be tempted to assign this peak to brucite ($Mg(OH)_2$) present in the solid, but our own experiments and published literature (30, 31) indicate that brucite exhibits its sharp peak at ~3700 cm^{-1}.) We have observed (32) similar high-frequency ν(OH) peaks in 2:1 Mg:Al LDH nickelocyanide and oriented samples of 2:1 Mg:Al LDH ferricyanide but not in nonoriented 3:1 Mg:Al LDH ferrocyanide, 2:1 Mg:Al LDH ferricyanide, or 3:1 Mg:Al LDH nickelocyanide. The exact origin of these high-frequency OH bands is, as yet, unknown.

Chemical Interaction with Ferricyanide

Figures 2 and 3 represent the conventional and oriented FTIR spectra of 2:1 and 3:1 Mg:Al LDH chloride treated with aqueous potassium ferricyanide. As previously discussed, we attribute the near-symmetric peaks having a maximum absorbance of ~2117 cm^{-1} to intercalated ferricyanide. We always observe a secondary peak near 2040 cm^{-1} when we make this material. The structure of this peak, and its behavior under orientation, clearly indicate that it is identical to intercalated ferrocyanide. Idemura *et al.* (15) observed similar behavior from LDH–ferricyanide systems. It is likely that cyanide itself acts as the reducing agent in this particular system.

Chemical Interaction with Ferrocyanide

Figures 4–6 depict the FTIR spectra and powder XRD patterns for the product of treatment of Mg:Al LDH chloride with potassium ferrocyanide. Both sets of data are indicative of a well-ordered, single-phase LDH, namely, Mg:Al LDH ferrocyanide (with very minor contamination by carbonate, but with no other iron cyanide containing phase). We will refer to this material (having a basal spacing of ~10.9 Å, a split ν(CN) peak with maximum absorption near 2035 cm^{-}1, a high-frequency ν(OH) (~3622 cm^{-}1, not $Mg(OH)_2$), and a characteristic LDH lattice vibration at ~450 cm^{-}1) as LDH ferrocyanide and its component ferrocyanide as "intercalated" ferrocyanide. In our normal exchange procedures, used to prepare LDH ferrocyanide,

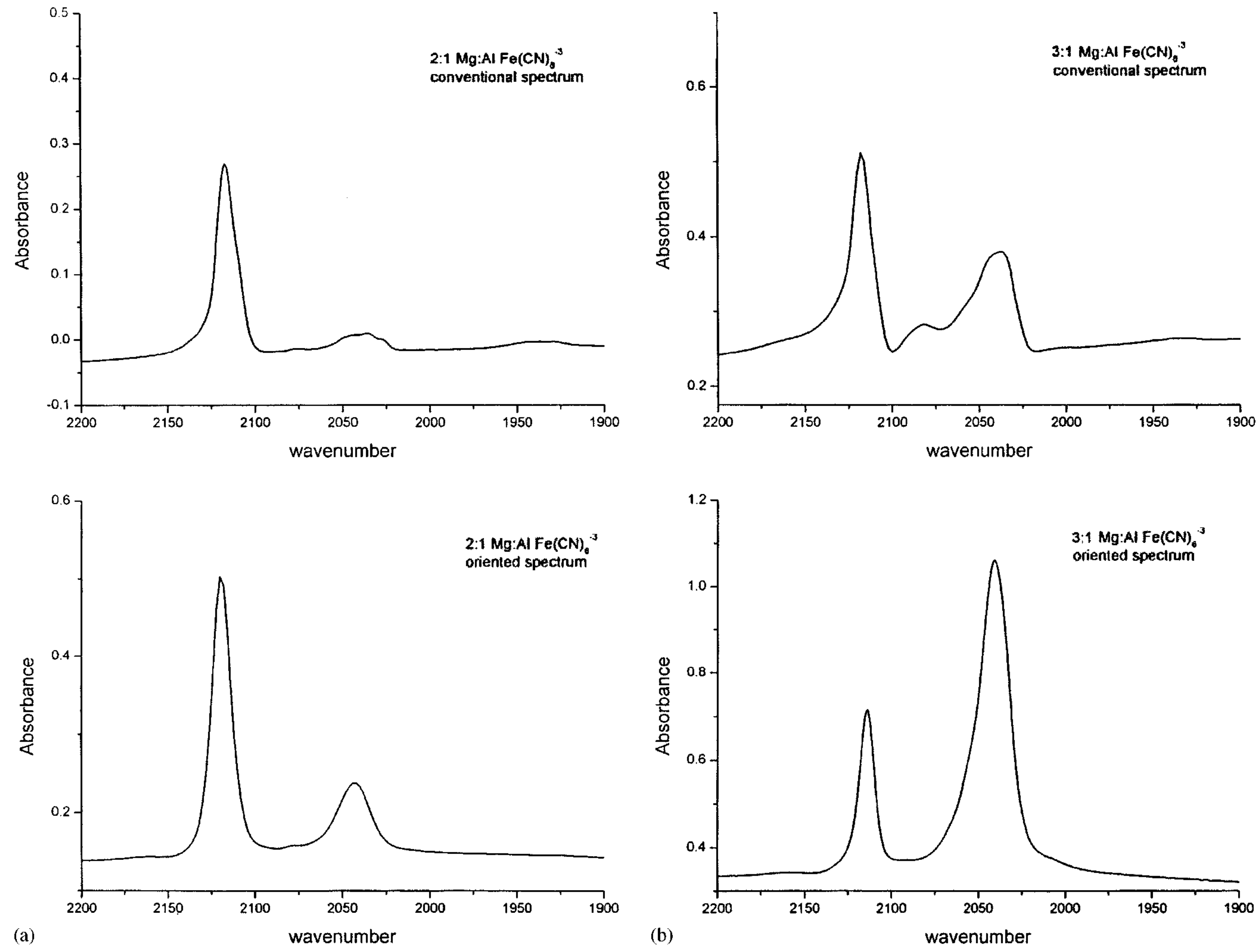

FIG. 3. Expanded-scale FTIR spectra, conventional (upper) and oriented (lower), of (a) 2:1 and (b) 3:1 Mg:Al LDH ferricyanide.

we see only "intercalated" ferrocyanide. There have been several reports (18–20) in the literature of ferrocyanide oxidizing to ferricyanide upon intercalation into LDH, largely based upon the appearance of a second ν(CN) band near 2085 cm^{-1}. Our infrared evidence does not support such a claim. As previously stated, intercalated ferricyanide shows a ν(CN) maximum near 2112 cm^{-1}, very much like the aqueous anion.

Figures 7 and 8 show the FTIR spectra and powder XRD patterns for the cubic ferrocyanide species $K_2MgFe(CN)_6$ and $(NH_4)_2MgFe(CN)_6$. The infrared spectra show ν(CN) absorptions of ~2083 cm^{-1} for the potassium species and ~2082 cm^{-1} for the ammonium species. Other absorptions of interest include the NH stretching and bending vibrations for the ammonium material and *M*–C stretches and *M*–C–N bends for both compounds. Significant infrared

TABLE 2
FTIR Data for 2:1 and 3:1 Mg:Al LDH Ferricyanide

Mg:Al	ν(OH)	δ(OH)	ν(CN)	δ(*M*CN)	ν(C=O)	Lattice peaks
2:1	3544, 3436	1621	2117, 2035	554	1384, 1371	673, 448
3:1	3495	1632	2118, 2037	—	1371	614

Note. All values in cm^{-1}. The presence of ν(C=O) is due to adventitious carbonate.

TABLE 3
Powder XRD Data (*d* Spacings Given in Å) for 3:1 Mg:Al LDH Ferrocyanide and Chloride

Anion	003	006	009	012
Cl –	7.70	3.89	2.56	1.53
$[Fe(CN_6)]^{4-}$	10.90	5.50	2.58	1.53

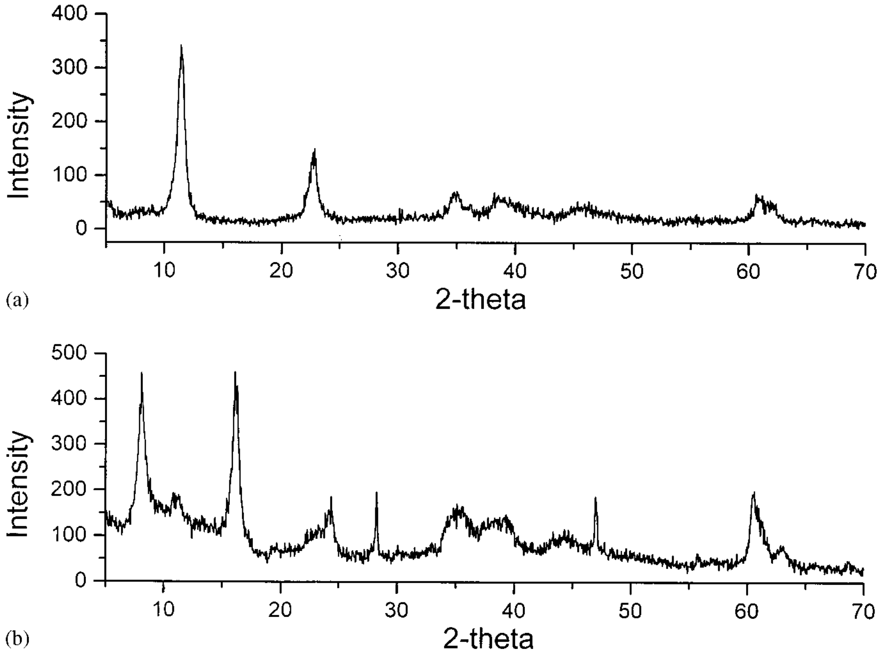

FIG. 4. Powder XRD patterns of 3:1 Mg:Al LDH (a) chloride and (b) ferrocyanide.

absorptions are listed, along with their assignments, in Table 5. Table 6 lists our observed XRD data for these cubic materials along with literature values. Our data are completely consistent with a cubic structure, as commonly found (33) for $M(I)_2M(II)$ ferrocyanides.

We then decided to treat 2:1 Mg:Al LDH chloride with ammonium ferrrocyanide. Figure 9 shows the infrared spectrum and powder XRD pattern for the product of that reaction. The infrared spectrum shows features from both Mg:Al LDH ferrocyanide and ammonium magnesium

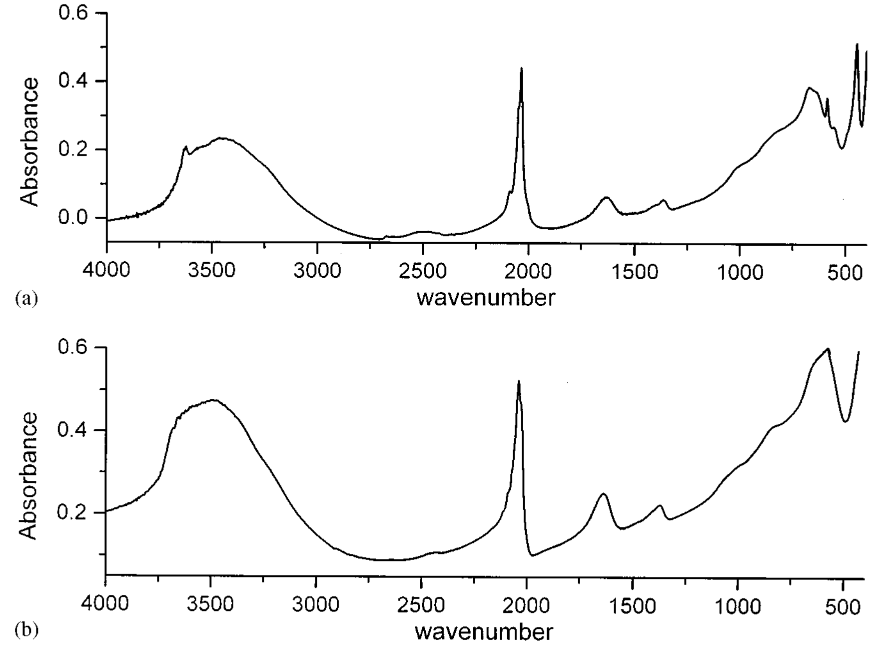

FIG. 5. Full-scale FTIR spectra of (a) 2:1 and (b) 3:1 Mg:Al LDH ferrocyanide.

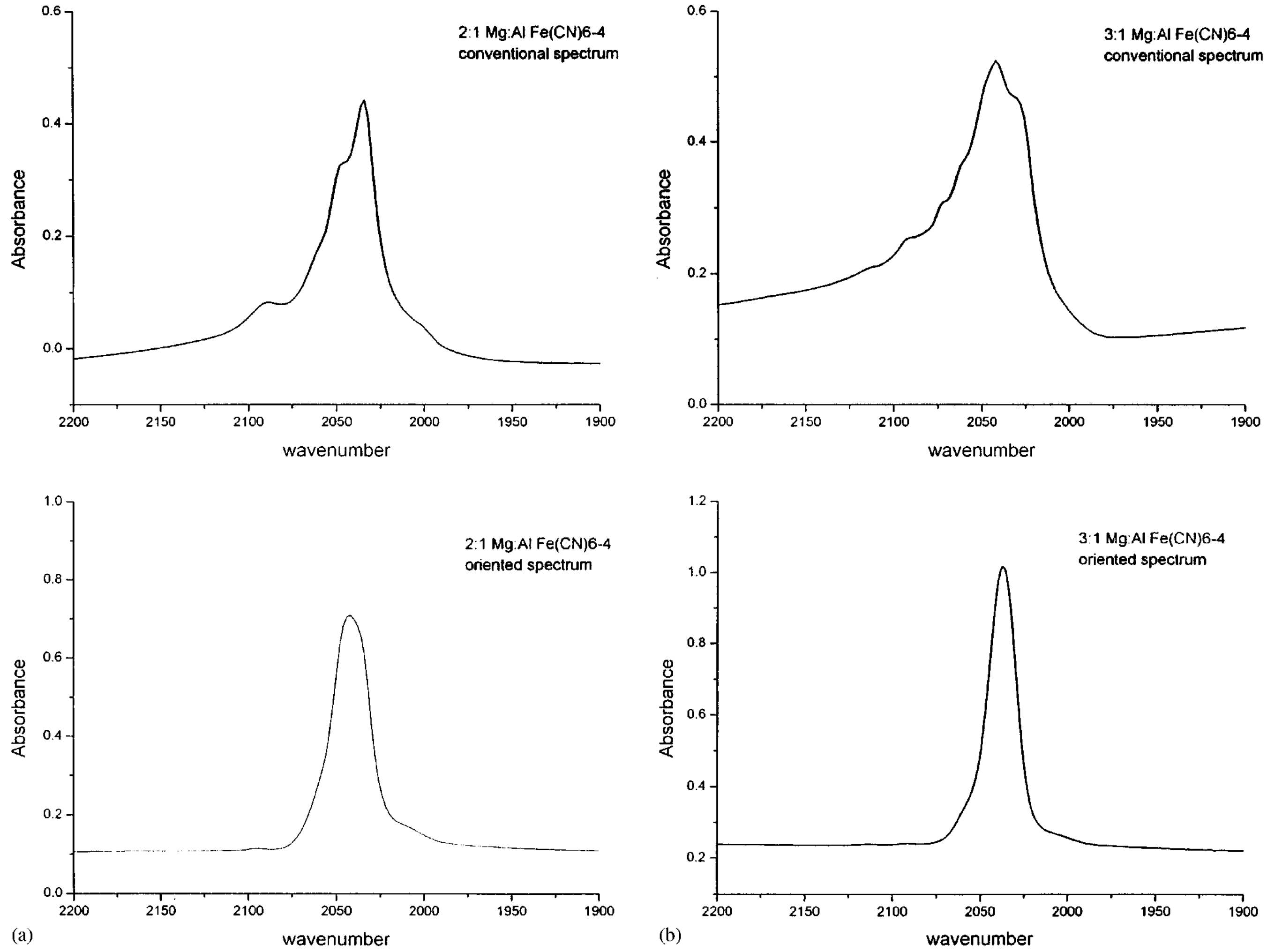

FIG. 6. Expanded-scale FTIR spectra, conventional (upper) and oriented (lower), of (a) 2:1 and (b) 3:1 Mg:Al LDH ferrocyanide.

ferrocyanide. The ν(CN) region shows two well-defined peaks: one having a maximum absorbance of ~2034 cm^{-1} and the characteristic shape of intercalated ferrocyanide within 2:1 Mg:Al LDH and the other a symmetric peak with a maximum near 2086 cm^{-1}, very similar to the ammonium magnesium ferrocyanide. The region between 3600 and 2500 cm^{-1} shows ν(OH) stretches of ~3500 and 3623 cm^{-1} corresponding to the usual LDH OH stretch and the previously discussed high-frequency peak found in LDH metallocyanides as well as peaks near 3400 cm^{-1} (ν(NH), overlapping ν(OH)) and 1400 cm^{-1} (δ(NH)), corresponding to those found in ammonium magnesium ferrocyanide. The XRD pattern (Fig. 9b) also supports our claim of a two-phase system. The diffraction pattern is dominated by peaks from the highly symmetric cubic species, but peaks are also seen that exactly match the d_{003} and d_{006} reflections

TABLE 4
FTIR Data for 2:1 and 3:1 Mg:Al LDH Ferrocyanide

Mg:Al	ν(OH)	δ(OH)	ν(CN)	δ(MCN)	ν(C=O)	Lattice peaks
2:1	3622, 3467	1630	2034, 2045(sh)	586	1364	670, 446
3:1	3646(sh), 3468	1642	2087, 2032(sh), 2045(sh)	—	1372	586

Note. All values in cm^{-1}. The presence of ν(C=O) is due to adventitious carbonate.

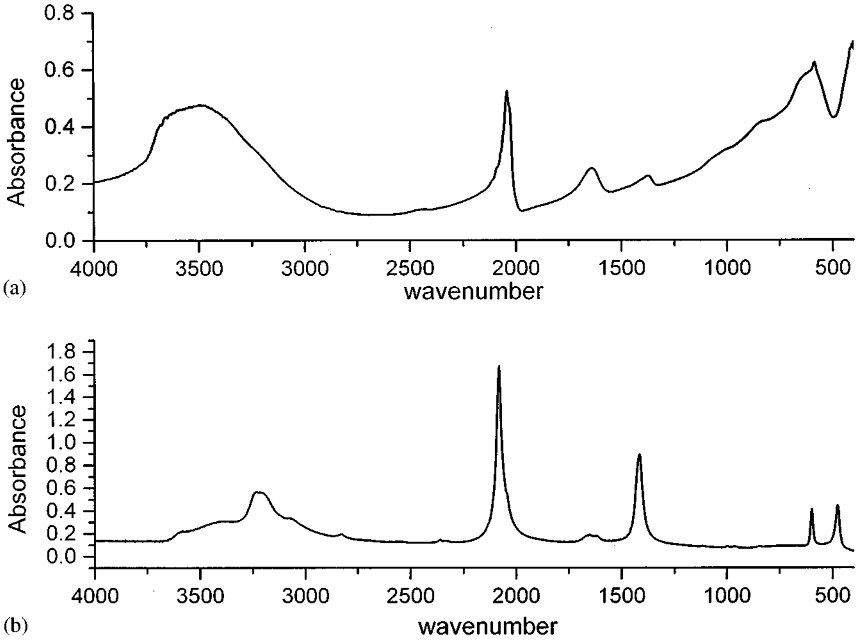

FIG. 7. FTIR spectra of (a) $K_2MgFe(CN)_6$ and (b) $(NH_4)_2MgFe(CN)_6$.

for LDH ferrocyanide. The features associated with the 2080-cm^{-1} material develop over time and are thus not due to entrained soluble magnesium salts.

As previously stated, in our hands, treatment of LDH with potassium ferrocyanide usually yields only intercalated ferrocyanide. We have, however, shown that more of the "reacted" ferrocyanide species is formed if the exchange reaction is carried out at lower pH (29). Additionally, those literature preparations described as leading to the 2085-cm^{-1} species involved either low stated pH (19) or

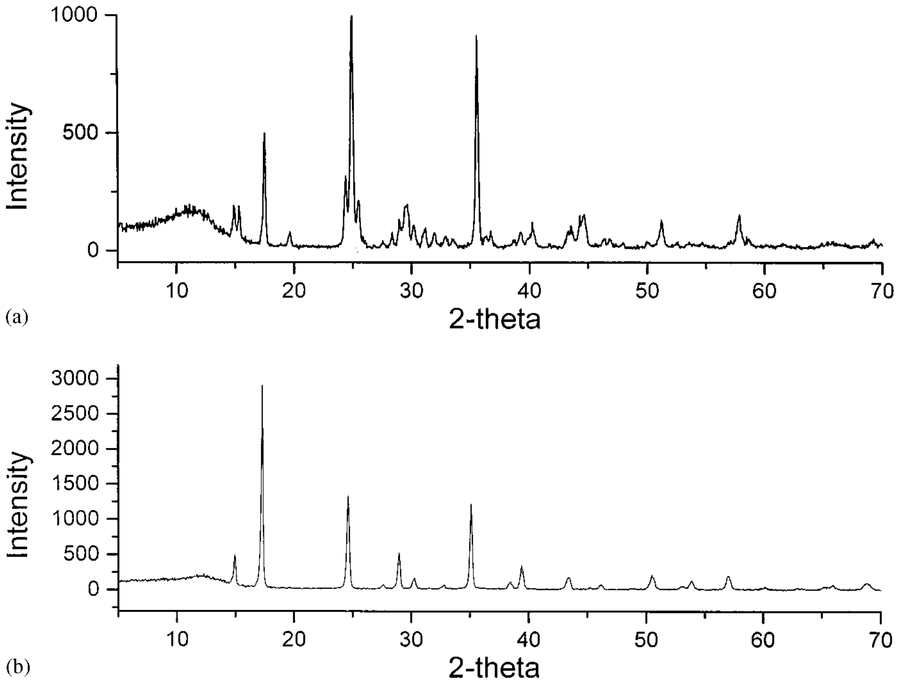

FIG. 8. Powder XRD pattern of (a) $K_2MgFe(CN)_6$ and (b) $(NH_4)_2MgFe(CN)_6$.

TABLE 5
FTIR Data (All Values in cm^{-1}) for $M_2MgFe(CN)_6$, Where $M = K^+$ or NH_4^+

M	ν(NH)	ν(CN)	δ(OH)	δ(NH)	δ(*M*CN)	ν(*M*C)
K^+		2083	1620	—	597	470
NH_4^+	3234	2082	1652	1417	600	477

TABLE 6
Powder XRD Data (*d* Spacings Given in Å) for $M_2MgFe(CN)_6$

h	*k*	*l*	$K_2MgFe(CN)_6$	$(NH_4)_2MgFe(CN)_6$
1	1	1	5.936 (6.071)	5.920 (5.930)
2	0	0	5.053 (5.149)	5.122 (5.146)
2	1	0	4.515 (4.606)	—
2	2	0	3.646 (3.645)	3.617 (3.627)
2	1	2	3.572 (3.534)	—
3	1	1	—	3.082 (3.087)
2	2	2	3.011 (3.053)	2.949 (2.951)
3	2	0	2.866 (2.858)	—
3	2	1	2.799 (2.789)	—
3	2	1	—	2.725 (2.734)
4	0	0	—	2.555 (2.557)
3	2	2	2.523 (2.534)	—
4	1	0	2.470 (2.499)	—
3	3	1	—	2.342 (2.345)
4	2	0	—	2.287 (2.287)

Note. Literature values, given in parentheses, are from Ref. 33.

direct contact of a soluble magnesium (or zinc) salt and potassium ferrocyanide solutions (18). In the former case, our own pH studies (26) indicate that at pH values below ~7.5, the Mg:Al LDH would be expected to partially dissolve, yielding free magnesium ions (which could then form potassium magnesium ferrocyanide) and either $Al(OH)_3$ or an aluminum-rich LDH phase. Cubic material would be expected to form in these cases in the same manner as in our direct reaction of magnesium ions with ferrocyanides.

We conclude that the two different ν(CN) peaks sometimes observed in LDH ferrocyanide are caused by ferrocyanide existing in two different environments: as the intercalated anion in an LDH phase and as a component of a distinct cubic (potassium or ammonium) magnesium ferrocyanide phase, for the following reasons:

(1) Potassium magnesium ferrocyanide and ammonium magnesium ferrocyanide are cubic (or near cubic) materials. Cubic ferrocyanides of this type generally show ν(CN) absorptions near 2085 cm^{-1} (28). Specifically for potassium magnesium ferrocyanide and ammonium magnesium ferrocyanide, our infrared investigations show ν(CN) stretches at 2083 cm^{-1}.

(2) Mg:Al LDH chloride, upon exposure to excess ammonium ferrocyanide solution, develops two ν(CN) peaks: one at 2035 cm^{-1}, expected for hydrogen-bonded, intercalated ferrocyanide, and the other near 2085-cm^{-1}. The 2085-cm^{-1} peak shows no effect from sample orientation, consistent with its cubic nature. Intercalated ferricyanide, by

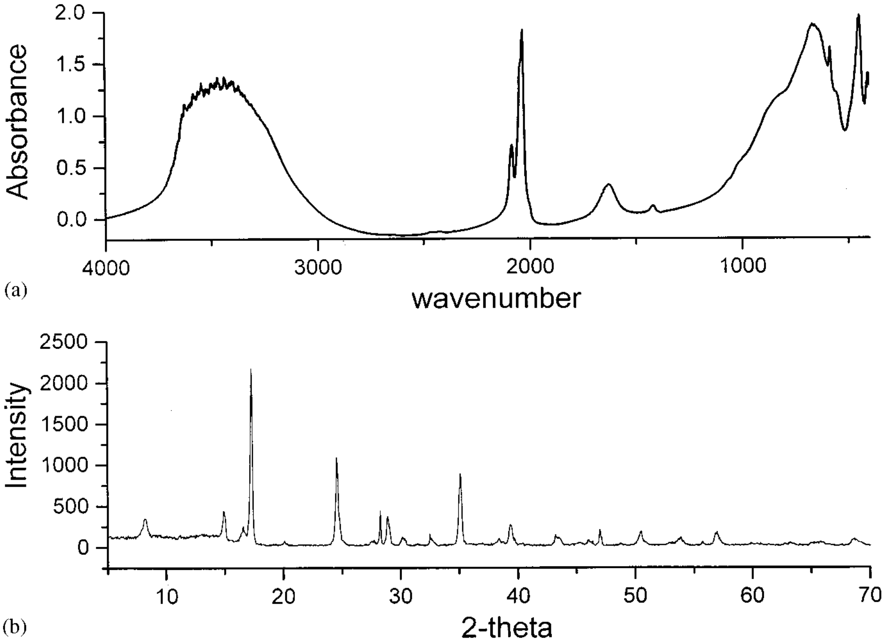

FIG. 9. FTIR spectrum (a) and powder XRD pattern (b) of product obtained by treating 2:1 Mg:Al LDH chloride with ammonium ferrocyanide.

contrast, exhibits its ν(CN) stretch near 2112 cm^{-1} and shows a detectable, if small, orientation effect.

(3) Mg:Al LDH chloride, upon exposure to excess ammonium ferrocyanide solution, develops two sets of X-ray diffractions: one corresponding to LDH ferrocyanide and the other to ammonium magnesium ferrocyanide.

(4) The published work (19) leading to the formation of the 2085-cm^{-1} species involved reaction conditions expected to provide free magnesium ions in contact with dissolved potassium ferrocyanide.

We have also treated zinc-containing LDH chloride (both Zn:Al and Zn:Cr) with ferrocyanide solution and found that these materials form cubic zinc ferrocyanide much more readily than their Mg-containing counterparts. In LDH-containing zinc, appreciable amounts of cubic ferrocyanide are seen in the infrared spectra of materials obtained by treatment of the LDH with potassium ferrocyanide at room temperature. Our infrared spectra for such zinc-containing materials are consistent with those reported in the literature for similar Zn:Al materials (18).

The reactions between Mg:Al LDH and either ferrocyanide or ferricyanide provide some interesting, and hopefully exploitable, chemistry. In both cases, most of the anion ends up as intercalated species within the layered system. During ferricyanide intercalation, some of the ferricyanide is reduced to ferrocyanide, which also intercalates into the LDH. Treatment of LDH with ferrocyanide provides perhaps the most exciting chemical possibilities. When Mg:Al LDH is exposed to a solution of ferrocyanide at a reduced pH (either by addition of acid or use of ammonium ferrocyanide), varying amounts of cubic ferrocyanides are formed. Such a situation presents the possibility of having ferrocyanide in any of three distinct environments: intercalated into the LDH interlayer, adsorbed (34) onto the outer surface (35) of the LDH, or in a cubic material. Such varied environments suggest the possibility of varied chemistry as well. The formation of ammonium magnesium ferrocyanide from the treatment of Mg:Al LDH with ammonium ferrocyanide is particularly exciting in connection to the origins of life because it presents a method for concentrating cyanide and ammonia in the same, easily formed, insoluble substance. However, our general method of preparing ferrocyanide–intercalated LDH, which we present here, provides a method which limits this conversion to cubic ferrocyanide in those cases where a pure LDH ferrocyanide is required.

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