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Preparation, Characterization, and Mössbauer Spectroscopy of Organic Anion Intercalated Pyroaurite-like Layered Double Hydroxides

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Pyroaurite is a layered double hydroxide, a hydrotalcite-like lamellar mineral of formula $Mg_6Fe_2(OH)_{16}CO_3{\cdot}4H_2O$. Organopyroaurite derivatives, of general formula $[Mg_6Fe_2(OH)_{16}]$-$[O_2C-(CH_2)_p-CO_2H]_2{\cdot}xH_2O$ with $1 \le p \le 14$, were prepared by coprecipitation of the corresponding nitrates in basic medium. The interlamellar distance of these organominerals depends on the size of the intercalated anion. In the case of the dicarboxylate anions, it is directly related to the number of C atoms in the aliphatic chain, which, plausibly, adopts an all-trans conformation, almost perpendicular to the mineral layers. ^{13}C CP/ and DD/MAS NMR show the high rigidity of the aliphatic chain. Mössbauer spectroscopy measures the average degree of distortion of the Fe(III) local environment (via the average quadrupole splitting, $\langle QS \rangle$) and the intrasample Fe(III) local environment variability (via the width, σ_{QS}, of the QS distribution). Both $\langle QS \rangle$ and σ_{QS} are found to change discontinuously on going from CO_3^{2-} to dicarboxylate intercalates, to be continuous functions of p for $1 \le p \le 12$, and to change discontinuously again on going from $p = 12-14$. These behaviors have simple structural interpretations.

Introduction

Layered double hydroxides (LDH) are a family of lamellar solids, of general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$-$[A^{n-}_{x/n}{\cdot}mH_2O]^{x-}$, with positively charged layers between which anions (A^{n-}) are intercalated. The positive charges in the hydroxide layers result from the isomorphous replacement of a fraction of divalent cations (Mg(II), Zn(II), ...) from the brucite–type parent structure ($Mg(OH)_2$) by trivalent cations (Al(III), Fe(III), Cr(III), ...).[1]

Hydrotalcite[2] ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$) and pyroaurite[3] ($Mg_6Fe_2(OH)_{16}CO_3{\cdot}4H_2O$) are naturally occurring anionic clay minerals belonging to the LDH family.[4] A large variety of hydrotalcite-like materials can be synthesized, varying the nature of the divalent and trivalent cations and of the accompanying anion.[5] Thus far, pyroaurite has been much less studied than hydrotalcite.

Allmann[3] published the crystal structure of pyroaurite in 1968, showing a rhombohedral structure consisting of positively charged brucite-like layers $(Mg_6Fe_2(OH)_{16})^{2+}$ alternating with disordered negatively charged interlayer hydrated carbonate anions $(CO_3{\cdot}4H_2O)^{2-}$. To the best of our knowledge, there is no report in the literature of the intercalation of organic anions into pyroaurite in replacement of carbonate, in a way similar to what has been reported for other members of the LDH family.[1,6]

In this paper, we report the synthesis and the characterization of a series of such organopyroaurites, resulting from the incorporation of dicarboxylate anions in the interlamellar spaces of synthetic pyroaurite and of some analogs with various Mg/Fe ratios.

Experimental Methods

Synthesis. The synthetic procedures, adapted from refs 5b,c and 6c, were as follows:

(*a*) *Synthesis of Pyroaurite* ($Mg_6Fe_2(OH)_{16}CO_3{\cdot}4H_2O$). A solution of $Mg(NO_3)_2{\cdot}6H_2O$ (Aldrich, ACS Reagent, 99%; 2.4 mol) and of $Fe(NO_3)_3{\cdot}9H_2O$ (Aldrich, ACS Reagent, 98+%; 0.8 mol) in 1.28 L of distilled water was slowly added during 90 min at room temperature, under a vigorous agitation, to a solution containing sodium carbonate (Na_2CO_3; 0.8 mol) and NaOH 50% (8.19 mol) in 1.6 L of distilled water. At the end of the addition, the reaction mixture was in a gel form. It was then heated to 65–70 °C during 18 h, washed, and vacuum-dried at 125 °C.

(*b*) *Synthesis of Organic Intercalates of Pyroaurite and Analogs.* The same procedure as in (a) above was followed. The appropriate amounts (0.8 mol) of dicarboxylic acids (p = 0 (oxalic), 6 (suberic), 8 (sebacic), 10 (decanedicarboxylic), 12 (dodecanedicarboxylic), 14 (tetradecanedicarboxylic)) were used instead of sodium carbonate. All dicarboxylic acids were

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purchased from Aldrich, with the highest purity available, and used without further purification. The reaction was done under a nitrogen atmosphere, using decarbonated water after double distillation under nitrogen.

Characterization. The ratio Mg/Fe was measured by X-ray fluorescence on all the samples and found to be 3.1 ± 0.2.

Thermal gravimetric analysis (TGA) shows weight losses from 7 to 10% for the various samples between 100 and 200 °C, corresponding to the loss of physisorbed water. A second loss occurs between 300 and 550 °C, the position of the transition depending upon the length of the methylene chain. This second loss was attributed to the organic component. The amount of organic material could be calculated on the basis of this second weight loss, and the following approximate general formula could be derived:

$$Mg_6Fe_2(OH)_{16}(O_2C{-}(CH_2)_p{-}CO_2H)_2xH_2O$$

In all cases the stoichiometry of the organic component was calculated to be close to 2, indicating a large amount of packing of the organic chains. One can speculate that the organic intercalate is a statistical mixture of dianion, monoanion, and neutral diacid.

The powder X-ray patterns were obtained on a Phillips PW1050/81 diffractometer, with Cu Kα radiation. Samples were prepared for XRD measurements by dispersing about 15 mg of sample in water and then applying the dispersion on a glass slide and allowing to air dry.

The FTIR spectra were performed on a Bomem Michelson MB 100 spectrometer using the KBr pellet technique. Typically, 16 scans were acquired with a resolution of 4 cm^{-1}.

TGA measurements were taken with a Polymer Labs STA 1500H using alumina reference and sample pans under flowing nitrogen (40 cm^3/min). The heating rate ranged from 15 to 20 °C/min.

The ^{13}C CPMAS and DDMAS (dephasing period of 40 μs) NMR spectra were recorded at 45.22 MHz on a Bruker CXP 180 with a spinning rate of 4000 Hz.

Room temperature (RT, 22 °C) ^{57}Fe absorption Mössbauer spectra were collected in the usual transmission geometry using a ^{57}Co/Rh source, constant acceleration drive, and calibration with respect to α−Fe at RT. The spectra were folded to ensure a flat background.

The Mössbauer spectral analysis was performed using the quadrupole splitting distribution (QSD) method of Rancourt and Ping[9] with a single Gaussian component ($N = 1$). This amounts to assuming that the QSD is Gaussian in shape, centered on the average quadrupole splitting ⟨QS⟩, and has a Gaussian width of σ_{QS}. No coupling was allowed ($\delta_1 \equiv 0.0$) between the distributed QS and the center shift (CS). The Lorentzian full width was frozen at $\Gamma \equiv 0.4$ mm/s for all spectra because this value gave good fits with $N = 1$. Area asymmetry was allowed via the parameter h_-/h_+, which is defined as the ratio of low-to-high velocity Lorentzian line heights in the elemental doublet.

More reasonable values of Γ ($\Gamma \simeq 0.2$ mm/s) are obtained with $N > 1$; however, the purpose here was to use the simplest possible spectral analysis in order to identify unambiguous trends. Also, it was shown that the Mössbauer absorbers are ideal random-orientation powder absorbers and that the true area asymmetry is probably due to the Goldanskii−Kariagan effect. The details of this study will be published in a forthcoming paper.

Results and Discussion

The basal spacings were obtained from the 001 reflections of the X-ray diffraction patterns. The X-ray spectrum of pyroaurite was characterized by a basal spacing of 7.8 Å, in good agreement with previously reported values for similar LDHs[1a]. Upon intercalation of the sebacate dianion, a shift of the 001 reflection toward larger values was observed (from 7.8 to 18.7 Å).

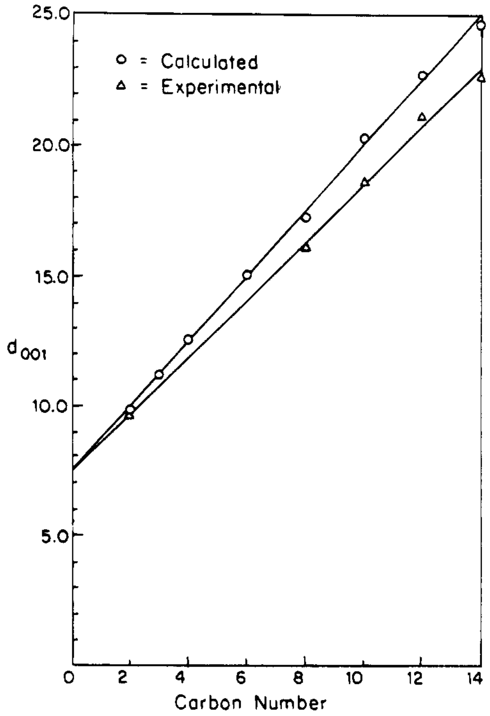

Figure 1. Plots of the interlayer spacing d_{001} versus the carbon number p + 2 for $[HO_2C{-}(CH_2)_p{-}CO_2H]$.

Table 1. Comparison between the Experimentally Determined Basal Spacings Values and the Value Estimated from CPK Models for a Series of Dicarboxylates in an All-Trans Conformation

anion	length (Å)	d_{001} (Å) exp[a]	d_{001} (Å) calc[b]
$(O_2C{-}CO_2)^{2-}$	5.0	9.7	9.8
$(O_2C{-}(CH_2)_6{-}CO_2)^{2-}$	12.5	16.2	17.3
$(O_2C{-}(CH_2)_8{-}CO_2)^{2-}$	15.5	18.7	20.3
$(O_2C{-}(CH_2)_{10}{-}CO_2)^{2-}$	18.0	21.2	22.8
$(O_2C{-}(CH_2)_{12}{-}CO_2)^{2-}$	19.9	22.8	24.7
$(O_2C{-}(CH_2)_{14}{-}CO_2)^{2-}$	23.0	21.7	27.8

[a] Obtained from XRD patterns. [b] Anion size + brucite layer thickness (4.8 Å).

An increase of the basal spacing was observed in all the cases when the carbonate anion was replaced by an organic anion (Figure 1). The basal spacing was linearly related to the carbon number (p) of the intercalated dicarboxylate anions (Figure 1). Table 1 gives the comparison between the experimentally determined basal spacings values for a series of dicarboxylates and the calculated value from a molecular model of the dicarboxylate in an all-trans conformation to which 4.8 Å was added to take the thickness of the brucite-like layer into account.

The infrared spectra of pyroaurite and of the sebacate intercalate are shown in Figure 2a,b, respectively. In the case of pyroaurite, the OH stretching and H_2O bending bands are observed respectively at 3464 cm^{-1} and at 1637 cm^{-1}, and the characteristic carbonate absorptions are observed at 1376 cm^{-1} and 695 cm^{-1}.[7] For the sebacate intercalate, the OH stretching band is moved to 3439 cm^{-1}, the carbonate band at 1376 cm^{-1} is replaced by the two bands characteristic of the carboxylate group at 1563 cm^{-1} and 1383 cm^{-1} and the

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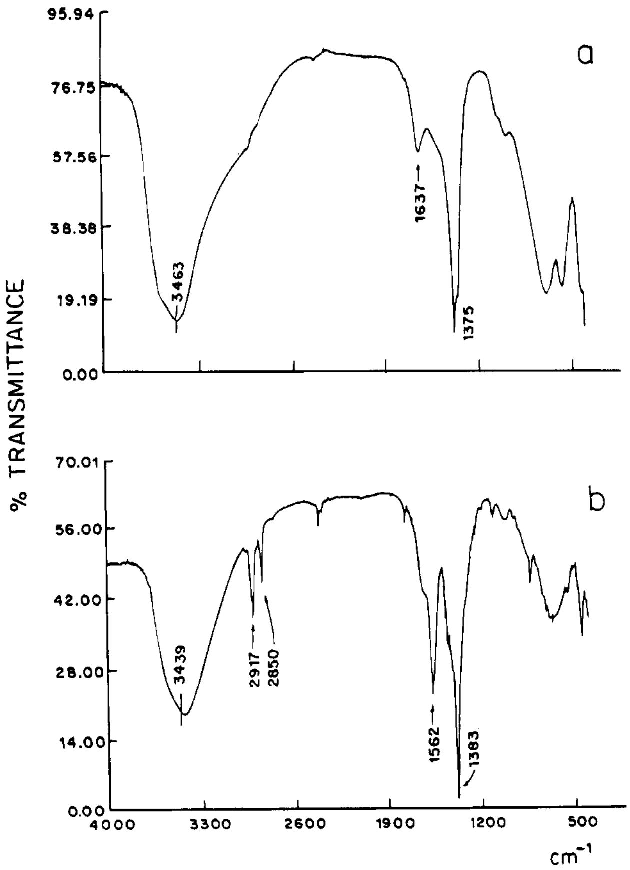

Figure 2. Infrared spectra for (a) pyroaurite and (b) the sebacate–pyroaurite intercalated compound.

H_2O bending band appears as a shoulder of the 1563 cm^{-1} band. Similar IR spectra were obtained for all the dicarboxylate intercalates of this study.

The ^{13}C CP/MAS NMR spectrum of the sebacate intercalate is shown on Figure 3a. A spectrum could be recorded despite the presence of large amounts of paramagnetic Fe(III). The ^{13}C NMR chemical shifts of the carbonyl and of the methylenic carbons are respectively 182 ppm and approximately 30 ppm. Upon dipolar dephasing (DD) conditions[8,9] the broad absorption at 30 ppm disappeared almost completely. For comparison, the similar ^{13}C CP/MAS and DD/MAS NMR spectra are shown on Figure 3b for the corresponding Zn/Al LDH ($Zn_6Al_2(OH)_{16}OOC{-}(CH_2)_8{-}COO$), characterized by a basal spacing of 18.5 Å. The ^{13}C carbonyl chemical shift is 185.3 ppm, and three different resonances can be distinguished at 28.6, 34.2, and 35 ppm for the methylenic carbons. Upon dipolar dephasing conditions, the methylenic ^{13}C signals completely disappear. In both cases, the almost complete disappearance of the $-^{13}CH_2-$ signal upon dipolar dephasing conditions is indicative of the rigidity of the methylenic chain, in good agreement with its all-trans conformation, almost perpendicular to the pyroaurite layers. On the basis of the charge density on the layers, and of the degree of packing, as obtained from the chemical analysis, one can calculate an estimate of the distance between the methylenic chains. On average, it comes to a value of 2.5 Å. This is in agreement with the lack of microporosity as shown, on these materials, and on similar Al,Zn double hydroxides,[10] by nitrogen adsorption isotherms.

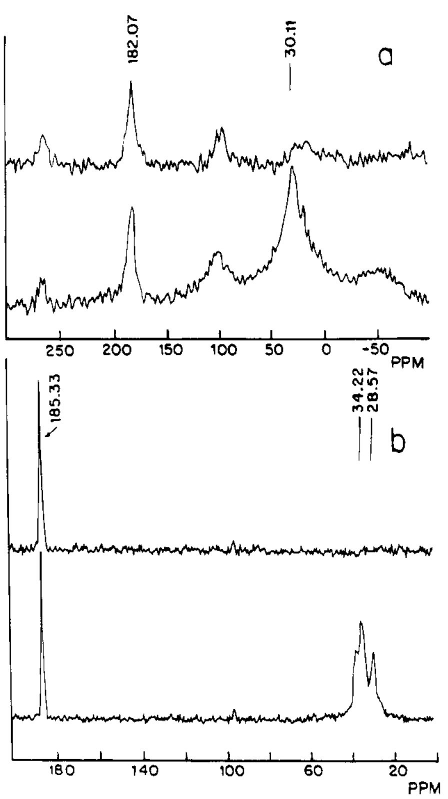

Figure 3. (a) ^{13}C CP/MAS and DD/MAS NMR spectra of the sebacate–pyroaurite intercalated compound. (b) ^{13}C CP/MAS and DD/MAS NMR spectra of the sebacate intercalate in the Zn–Al LDH.

Figure 4a shows the Mössbauer spectrum of the synthetic pyroaurite ($Mg_6Fe_2(OH)_{16}CO_3{\cdot}4H_2O$) with fit and difference spectrum, whereas Figure 4b shows the spectrum of one of the dicarboxylate ($p = 14$) intercalated layered double hydroxide with fit and difference spectrum. All spectra have CS = 0.33 ± 0.01 mm/s (with respect to α-Fe at RT) which, along with ⟨QS⟩ in the range 0.5–0.7 mm/s, is characteristic of ferric iron. No ferrous ion is detected, nor are any iron-containing impurities.

⟨QS⟩ is an accurate measure of the average degree of distortion of the local environment of the Fe(III) cation, but also of the precise unit cell dimensions and composition because of the lattice sum contribution to the hyperfine electric field gradient at the probe. It is found to change discontinuously on going from CO_3^{2-} to dicarboxylate anion intercalates and to increase monotonically as p is increased. These features are shown in Figure 5 where ⟨QS⟩ is plotted as a function of the number of carbon atoms per interlayer molecule. Figure 5 suggests that, just as the interlayer spacing (d_{001}) is anomalously small for the $p = 14$ material (Table 1), the ⟨QS⟩ for this compound is smaller than what might be expected from the trend observed for the $p \leq 12$ compounds.

If ⟨QS⟩ is mostly a measure of the average degree of local distortions for the particular material, then σ_{QS} (the width of the QSD) is a measure of the Fe(III) local environment variability for the given compound. That

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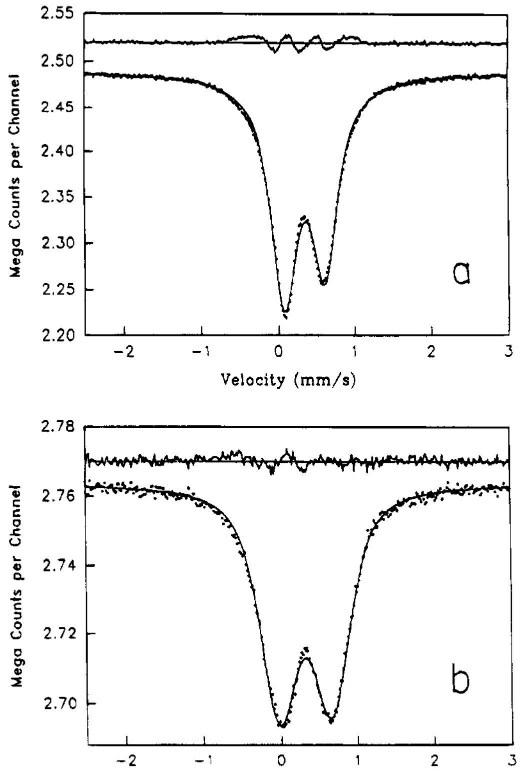

Figure 4. RT Mössbauer spectra of (a) pyroaurite and (b) the hexadecanedioic acid ($p = 14$) intercalated compound.

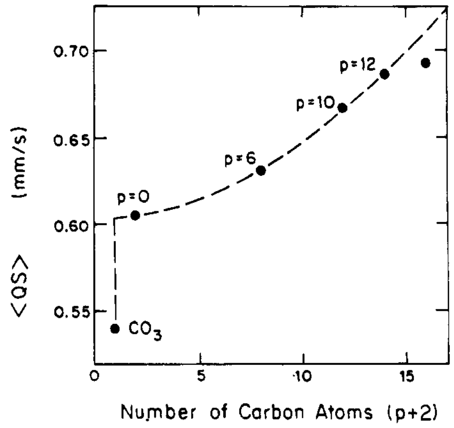

Figure 5. Variation of ⟨QS⟩ as a function of $p + 2$ (the number of carbon atoms in $[HO_2C-(CH_2)_p-CO_2H]$).

is, σ_{QS} measures how different the Fe(III) local environment can be from point to point in the structure. Figure 6 shows that σ_{QS} again changes discontinuously on going from CO_3^{2-} to dicarboxylates intercalates. It then has a constant value of $\sigma_{QS} \simeq 0.20$ mm/s in the range $p = 0-12$ followed by an abrupt and significant increase on going to $p = 14$.

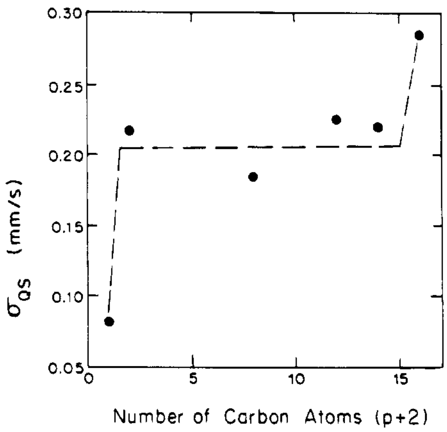

Figure 6. Plots of σ_{QS} versus $p + 2$.

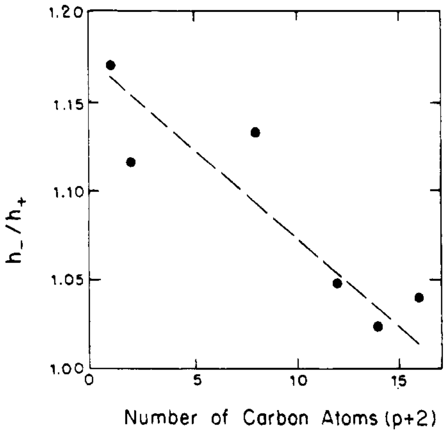

Figure 7. Variation of h_-/h_+ as a function of $p + 2$.

The first abrupt change in σ_{QS} on going from synthetic pyroaurite to dicarboxylate intercalates is evidence for an increased disorder due to the presence of two types of intercalation sites, protonated or deprotonated carboxylate group. The second abrupt increase in σ_{QS}, on going from $p = 12$ to 14, again shows an increased disorder and may be due to decreased alignment with the *c* axis or buckling of the organic molecules. The latter suggestions are consistent with the observed behavior of d_{001} (Table 1).

Finally, given the presence of the Goldanskii–Kariagan effect, h_-/h_+ is a measure of the anisotropy of Fe(III) vibrations and, consequently, of its bonding to the lattice. The greater the difference from 1 of the ratio h_-/h_+, the greater the anisotropy. Isotropic bonding gives $h_-/h_+ = 1$. Figure 7 shows h_-/h_+ as a function of the number of carbon atoms per interlayer molecule. The vibrational (and bonding) anisotropy decreases with increasing interlayer distance. This is probably more a consequence of the long-range ionic binding forces than of compression of the octahedral (double hydroxide) layer.

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