

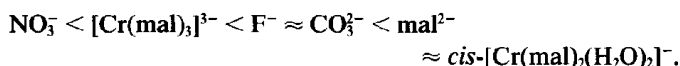
Malonate Intercalation into Layered Chromium–Zinc Double Hydroxides

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Received September 30, 1994; in revised form May 1, 1995; accepted June 8, 1995

Layered double hydroxides of type $[\text{Zn}_2\text{Cr}(\text{OH})_6]X \cdot n\text{H}_2\text{O}$ where $X^- = 1/2 \text{ mal}^{2-}$, $\text{cis-}[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$, and $1/3 [\text{Cr}(\text{mal})_3]^{3-}$ (mal = malonate) were synthesized by anion exchange reactions. These compounds were characterized by X-ray powder diffractometry and IR spectroscopy and the results were compared with those of the compounds where $X^- = \text{F}^-$, $1/2 \text{ CO}_3^{2-}$, and NO_3^- . The IR data allow the significant distinction between hydroxide layer OH-groups forming H-bonds with (i) crystal water and (ii) intercalated anions. With reference to the forces regarding the second H-bonding interaction the following order became obvious:



Propositions of the malonate arrangements in the interlayer were discussed. The malonate ligands of both anionic complexes are situated with an angle of 54.75° to the plane of OH close packing. The found differences between both are assumed to be caused by spatial reasons. © 1995 Academic Press, Inc.

INTRODUCTION

Layered double hydroxides (LDHs) consist of positive charged brucite-like metal hydroxide layers which are separated by negative charged interlayers in which anions and water molecules are intercalated. They can be considered as antitype of the clay minerals montmorillonite, smectite, and others with mean layers and counterions containing interlayers of opposite charge. The general composition can be described as $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}X_{x/2}^{z-} \cdot n\text{H}_2\text{O}$ where M^{2+} is a bivalent metal ion, M^{3+} is a trivalent metal ion, and X^{z-} is an interlayer anion.

In general, LDHs are nonstoichiometrical and the M^{2+}/M^{3+} ratio can vary between $4/1$ ($x = 0.2$) and $3/2$ ($x = 0.4$) since, due to approximately equal ionic radii, the geo-

metrically equivalent octahedral spaces can be occupied statistically (1, 2). Ordered cationic hydroxide layers are known for Ca–Al (3, 4) as well as for Zn–Cr compounds (5). The mineral types occurring in nature are for instance the pyroaurite–sjögrenite group $[\text{Mg}_6\text{Fe}_2(\text{OH})_{16}]\text{CO}_3 \cdot 4\text{H}_2\text{O}$ and the hydrotalcite–manasseite group $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]\text{CO}_3 \cdot 4\text{H}_2\text{O}$, having the in minerals widespread M^{2+}/M^{3+} ratio of about $3/1$. They appear in a hexagonal as well as in a rhombohedral structure variation (sjögrenite/manasseite and pyroaurite/hydrotalcite, respectively). The stacking of the hydroxide layers can also be realized in lower symmetry (polytypes) (1).

A considerably large number of synthetical LDHs exists created by varying the combination of M^{2+} , M^{3+} , and X^{z-} (6, 7). In general, the anions X^{z-} are exchangeable so that just this fact gives the possibility of a very high variety breadth of compounds. At present, exchange reactions of a number of anions have been investigated. Miyata (8) and Mendiboure and Schöllhorn (9) have pointed out selectivity sequences for the interlayer intercalation of many inorganic anions. Additionally, the introduction of carboxylates, organic sulfates, and sulfonates into the interlayers has been carried out (11–14). El Malki *et al.* (10) have discussed the influence of the nature of the incorporated anion (geometrie, size, charge, hydration state) especially on the stacking sequence of the hydroxide layers. Recently, the intercalation of isopoly- and heteropolyoxometalate anions has gained high interest (15–18). The aim of preparing such pillared LDHs is the production of porous molecular-sieve-like materials and/or oxidation catalysts (19).

This work concerns the intercalation of the malonate ion and the malonate containing complex anions $\text{cis-}[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$ and $[\text{Cr}(\text{mal})_3]^{3-}$ and draws a comparison with the “customarily” intercalated anions NO_3^- , CO_3^{2-} , and F^- .

EXPERIMENTAL

Materials Synthesis

The chromium salts $\text{K cis-}[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ and $\text{K}_3[\text{Cr}(\text{mal})_3] \cdot 3\text{H}_2\text{O}$ were prepared by following the meth-

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ods described by Chang (20). For preparing the compound $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ the method of Boehm *et al.* (12, 21) was used. This method implies the reaction of a slurry of ZnO with a concentrated aqueous Cr^{3+} solution ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in this case). The other applied LDHs were obtained by ion exchange. In detail, for preparation of the fluoride and the carbonate, respectively, 500 mg of $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ were suspended in 20 ml of corresponding 1 M sodium salt solution and allowed to stand for 2 hr with occasional shaking. Afterwards, the solution was removed and replaced by a fresh one. After another 2 hr the solid was filtered off, washed with water until being electrolyte-free, and dried at 65°C. For preparing the malonate, *cis*-diaquo-bismalonatochromate(III), and trimalonatochromate(III) compounds, respectively, 0.1 M potassium salt solutions were used. Quantities of 500 mg of $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ were suspended in 20 ml of these solutions and were held with occasional shaking for 24 hr at room temperature. Then it was decanted, replaced by fresh solution, and again allowed to stand for an additional 24 hr. This was repeated twice after the solid was filtered off, washed, and dried at 65°C.

In addition to the *cis*- $[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$ ion an attempt was made to intercalate the *trans*-isomere but this failed, however, since it converted in the *cis*-complex more rapidly than expected. The Vis spectroscopical investigation of the *trans*- $[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$ solution, being the first one which was brought in contact with the hydroxy nitrate, indicated a nearly complete *trans-cis* isomerization already for 5 hr. According to the data given by Casula *et al.* (22) a half-life period of 107 hr under such conditions was expected. In the following studies of ion exchange solutions the second proved to be a mixture of the isomers whereas the third remained nearly unchanged after 24 hr contact with the solid phase. Consequently, the initial LDH composed seems to accelerate the *trans-cis* isomerization catalytically.

In order to control the completeness of yield of both the initial hydroxy nitrate and the ion exchange reactions the compounds were characterized by chemical analysis and X-ray powder diffractometry. After previous separation with the strong basic anion exchanger Dowex-1, the metal contents were determined complexometrically for Zn^{2+} and according to Stünzi and Marty (23) photometrically as CrO_4^{2-} for Cr^{3+} . The separation is based on the better adsorbability of Zn^{2+} ions from hydrochloric acid solution (24), whereas Cr^{3+} ions do not interact with the exchanger resin. The adsorbance of the Zn^{2+} ions on the resin was carried out by a 2 M HCl solution. For their desorbance a solution containing 0.2 M HNO_3 and 0.2 M HCl was used. The anionic complexes of the corresponding LDHs have to be aquated before separation by boiling of the hydrochloric acid solution for 1 hr. The contents of fluoride and nitrate were determined potentiometrically by

use of the sensitrodes F 500 and NO 500 (WTW Weilheim), respectively, the contents of carbonate and malonate by C-H-N analysis. The results of chemical analyses in detail are: $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$ Zn^{2+} 34.16% (calc.), 34.65% (det.); Cr^{3+} 13.58%, 13.74%; NO_3^- (16.20%, 16.50%; $n_{\text{calc}} = 2.0$, $n_{\text{det}} = 1.7$); $[\text{Zn}_2\text{Cr}(\text{OH})_6](\text{CO}_3)_{0.5} \cdot n\text{H}_2\text{O}$ Zn^{2+} 38.25%, 37.64%; Cr^{3+} 15.21%, 14.99%; CO_3^{2-} 8.78%, 8.65%; $n_{\text{calc}} = 1.5$, $n_{\text{det}} = 1.8$); $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{F} \cdot n\text{H}_2\text{O}$ Zn^{2+} 38.48%, 38.10%; Cr^{3+} 15.30%, 15.12%; F^- 5.59%, 5.40%; $n_{\text{calc}} = 2.0$, $n_{\text{det}} = 2.2$); $[\text{Zn}_2\text{Cr}(\text{OH})_6](\text{mal})_{0.5} \cdot n\text{H}_2\text{O}$ Zn^{2+} 35.16%, 35.05%; Cr^{3+} 13.98%, 14.00%; mal^{2-} 13.72%, 13.80%; $n_{\text{calc}} = 2.0$, $n_{\text{det}} = 2.0$); $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{cis}-[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$ Zn^{2+} 21.98%, 22.05%; Cr^{3+} 17.48%, 17.54%; mal^{2-} 34.31%, 35.50%; $n_{\text{calc}} = 1.0$, $n_{\text{det}} = 0.9$); $[\text{Zn}_2\text{Cr}(\text{OH})_6][\text{Cr}(\text{mal})_3]_{0.33} \cdot n\text{H}_2\text{O}$ Zn^{2+} 30.97%, 30.80%; Cr^{3+} 16.46%, 16.36%; mal^{2-} 24.17%, 24.20%; $n_{\text{calc}} = 1.0$, $n_{\text{det}} = 1.1$.

Instrumentation

The X-ray powder diffraction measures were carried out by a diffractometer URD 6 (Freiberger Präzisionsmechanik) with a LiF monochromator using MoK_α radiation. For FTIR absorption spectroscopy a spectrometer IRF 180 (ZWG Berlin) was used by application of samples prepared as KBr pellets.

RESULTS AND DISCUSSION

X-Ray Powder Diffraction Patterns

The intercalation of different anions into the Cr-Zn hydroxide framework achieved not only varying basal spacings c' at nearly unchanged lattice parameter a (Table 1), but also the arrangement of the brucite-like hydroxide layers to each other was influenced. Especially the voluminous anion complexes *cis*- $[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$ and $[\text{Cr}(\text{mal})_3]^{3-}$, but also the malonate ion noncoordinated to a central ion, produce strong turbostratic disorder. Typical for all the diffractograms (Fig. 1) are the nearly undisturbed basic reflections giving evidence of higher order in the c -direction. The turbostratic disorder represents itself in the range of small d -values (large angles, respectively).

TABLE 1
Basal Spacings c' and Lattice Parameters a of
Applied $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{X} \cdot n\text{H}_2\text{O}$

X^-	c' (nm)	a (nm)
NO_3^-	0.881	0.309
$\frac{1}{2} \text{CO}_3^{2-}$	0.755	0.311
F^-	0.747	0.311
$\frac{1}{2} \text{mal}^{2-}$	1.074	0.310
<i>cis</i> - $[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$	1.026	0.309
$\frac{1}{3} [\text{Cr}(\text{mal})_3]^{3-}$	1.042	0.310

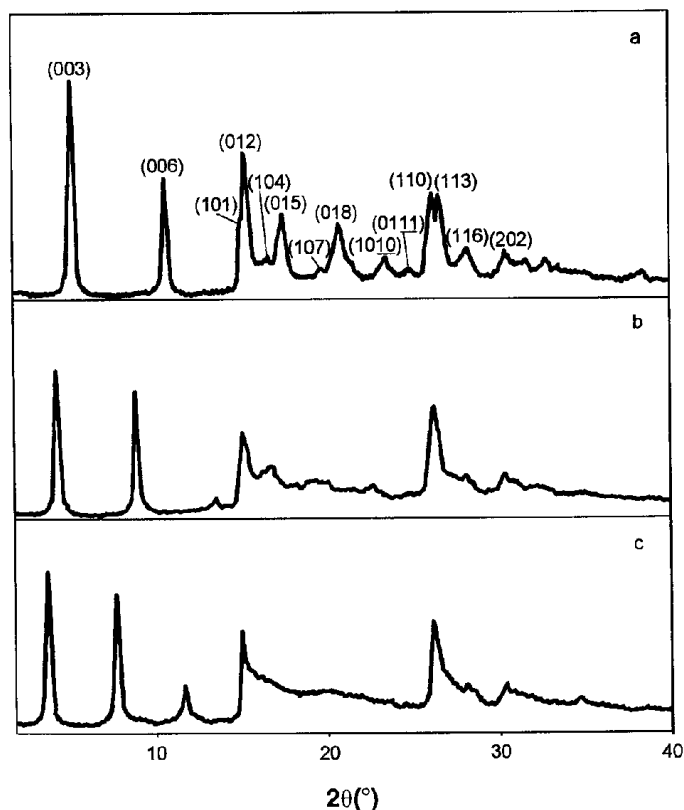


FIG. 1. Powder diffractograms of selected $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{X}\cdot n\text{H}_2\text{O}$ (MoK_α radiation). (a) $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{F}\cdot 2\text{H}_2\text{O}$, (b) $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{NO}_3\cdot 2\text{H}_2\text{O}$, and (c) $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{cis-}[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}$.

In the range of $2\theta \geq 15^\circ$ the diffraction peaks have the following shape: relatively sharp onset at low 2θ and a tail toward higher 2θ . This feature becomes more distinct the greater the basal spacing. The differences between CO_3^{2-} and NO_3^- , particularly the different basal spacings, are caused by varying arrangement in the interlayer, CO_3^{2-} parallel and NO_3^- slantwise to the hydroxide layers (25, 26).

IR Measurements

The results of the FTIR spectroscopy in the range of O—H stretching vibrations is shown in Fig. 2 and Table 2. Due to the position of the absorption of O—H stretching vibrations, significantly different H-bonded hydroxyl groups can be recognized: (i) some forming H-bonds with the interlayer water ($\nu_{\text{OH}} \geq 3490 \text{ cm}^{-1}$) and (ii) some forming H-bonds with the anions ($3320 \text{ cm}^{-1} \leq \nu_{\text{OH}} \leq 3430 \text{ cm}^{-1}$). The separation of the two bands in the spectrum is especially obvious in the cases of the intercalated anionic complexes $\text{cis-}[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$ and $[\text{Cr}(\text{mal})_3]^{3-}$. This is definitely a consequence of the large space required by these anions. In the case of NO_3^- , a reversed sequence of the band assignment is also possible because nitrate is

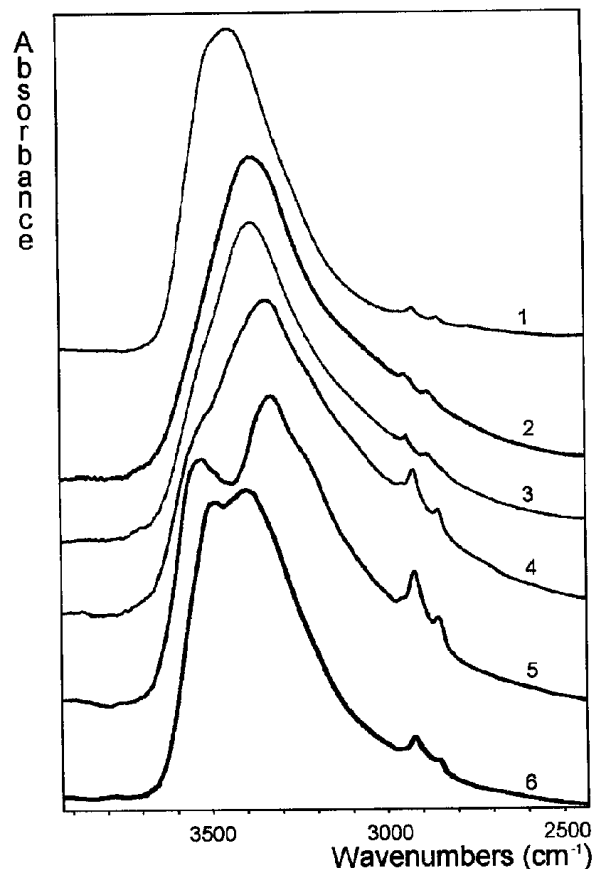


FIG. 2. Infrared absorption spectra in the $4000\text{--}2400 \text{ cm}^{-1}$ range of the studied $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{X}\cdot n\text{H}_2\text{O}$, with $\text{X}^- = \text{NO}_3^-$ (1), $\frac{1}{2} \text{CO}_3^{2-}$ (2), F^- (3), $\frac{1}{2} \text{mal}^{2-}$ (4), $\text{cis-}[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$ (5), and $\frac{1}{3} [\text{Cr}(\text{mal})_3]^{3-}$ (6).

considered as a worse proton acceptor than water (27). An assignment of bands concerning the H-bonding between water and anions which are generally found in the range of about $3000\text{--}3200 \text{ cm}^{-1}$ (28) cannot be made by these spectra. Particularly for many of the LDHs with an interca-

TABLE 2
Band Positions in the Region of OH Stretching Vibrations and Estimated O—H...O Distances of Applied $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{X}\cdot \text{H}_2\text{O}$

X^-	Band A (cm^{-1})	d_A [OH...O] (nm)	Band B (cm^{-1})	d_B [OH...O] (nm)
NO_3^-	3490(sh) ^b	~0.286	3430	~0.280
$\frac{1}{2} \text{CO}_3^{2-}$			3360	~0.278
F^-			3370	~0.272 ^a
$\frac{1}{2} \text{mal}^{2-}$	3520(sh) ^b	~0.287	3330	~0.276
$\text{cis-}[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$	3520	~0.287	3320	~0.275
$\frac{1}{3} [\text{Cr}(\text{mal})_3]^{3-}$	3490	~0.286	3390	~0.279

^a In fact, this is an OH...F distance estimated by powder data and from the OH...OH distance of a hydroxide layer perpendicular to the (001) plane of $d' = 0.204 \text{ nm}$ (12) by assuming that the fluoride ion lies exactly on the connecting line between OH-groups facing each other in the c direction.

^b sh denotes shoulder.

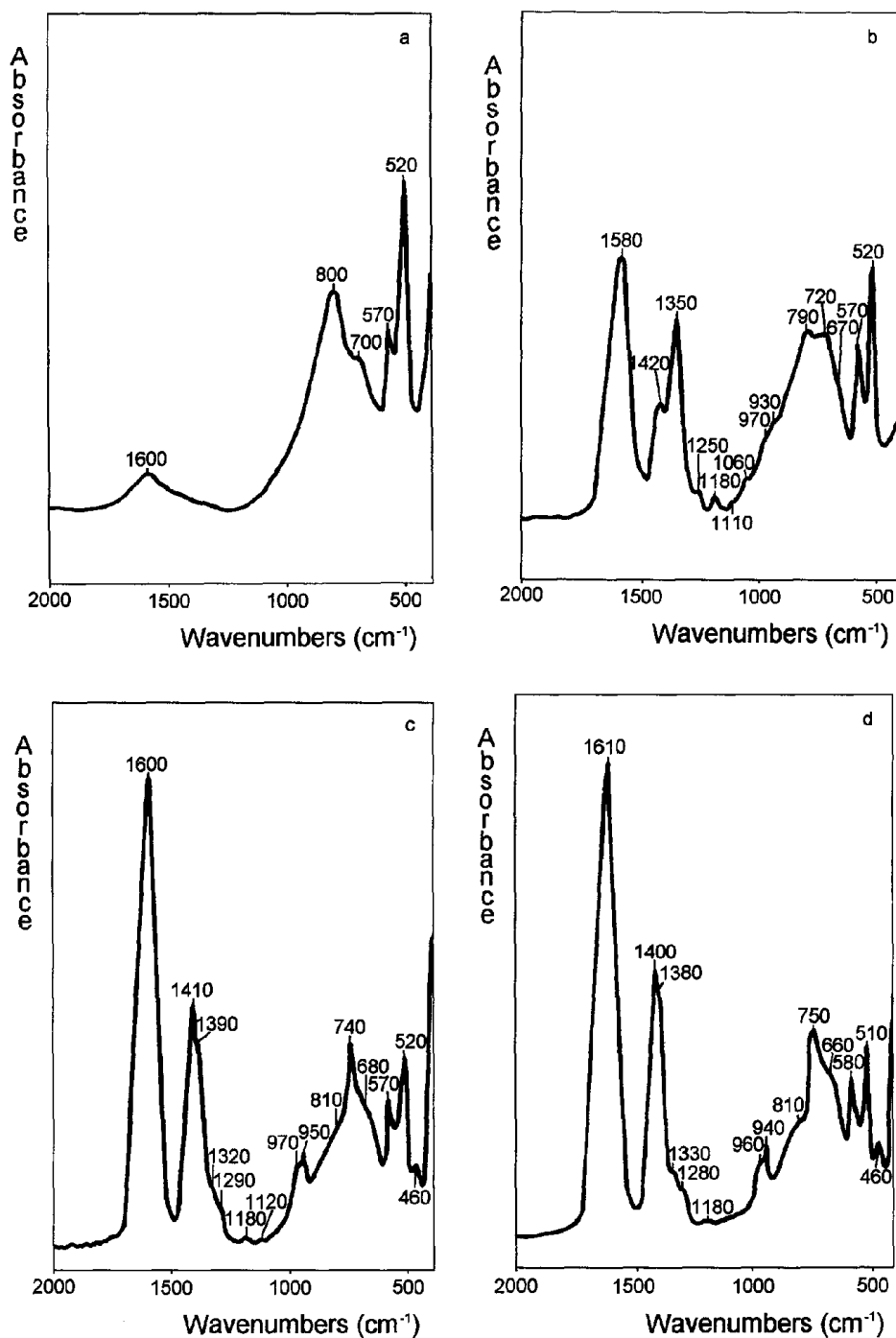


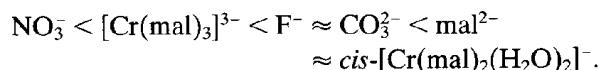
FIG. 3. Infrared absorption spectra in the 2000–400 cm^{-1} range of (a) $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{F}\cdot 2\text{H}_2\text{O}$, (b) $[\text{Zn}_2\text{Cr}(\text{OH})_6](\text{mal})_{0.5}\cdot 2\text{H}_2\text{O}$, (c) $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{cis-}[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}$, and (d) $[\text{Zn}_2\text{Cr}(\text{OH})_6][\text{Cr}(\text{mal})_3]_{0.33}\cdot \text{H}_2\text{O}$.

lated carbonate ion a broad absorption at 3100 cm^{-1} is known (26, 29, 30). For the coordinatively bonded water of $\text{cis-}[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$ it is also not possible to make an assignment of bands. Definitely it is involved in the formation of H-bonds. However, in both the aquo ligands, because of their binding to the central ion, and the OH-

groups of the brucite-like layers being subject to a polarization dominates the ability as H-bond donor. The position of the ν_{OH} band of such water is determined by a "synergistic" effect of two interactions: (i) the interaction metal ion–water and (ii) the interaction proton acceptor/anion–water (27, 31). In comparison, for the analogous compound K

cis-[Cr(mal)₂(H₂O)₂] · 3H₂O this band lies at about 3050 cm⁻¹ (32) which gives evidence of a considerably greater weakening of O-H bonds than in the corresponding LDH.

According to the first band position (band A in Table 2) a general O-H ··· O distance of 0.287 nm for the interaction OH-H₂O in compliance with correlations described by Schwarzmann (33) can be estimated. Analogously the second band position (band B in Table 2) gives O-H ··· O distances in the range of 0.275–0.280 nm for H-bonds between OH-groups and anions. Furthermore, the position of the latter band allows the development of a sequence of intercalated anions describing their ability as H-bond acceptors:



An analogy to the Brønsted basicity in an aqueous solution of the simple ions ($\text{p}K_a(\text{HNO}_3) = -1.32$, $\text{p}K_a(\text{HCO}_3^-) = 10.40$, $\text{p}K_a(\text{HF}) = 3.14$, and $\text{p}K_a(\text{Hmal}^-) = 5.29$ (34)) is only apparently limited; the carbonate ion noticeably falls out. The relatively drastic difference between both of the anionic complexes must be judged as a steric effect, but not as an electronic one: The substitution of a malonate ligand by two aquo ligands makes the anion less bulky. This confirms also the smaller basal spacing (Table 1).

The IR absorption spectra of [Zn₂Cr(OH)₆]X · nH₂O with X⁻ = 1/2 mal²⁻, *cis*-[Cr(mal)₂(H₂O)₂]⁻, 1/3 [Cr(mal)₃]³⁻, and F⁻ (for comparison) in the 2000–400 cm⁻¹ range is shown in Fig. 3. The band positions of the metal oxygen stretching vibrations 570 and 520 cm⁻¹ ($\nu(\text{ZnO})$ and $\nu(\text{CrO})$ of the hydroxide layers, respectively) are relatively consistent in all spectra. The absorptions of the bending vibrations of crystal and surface water at about 1600 cm⁻¹ are only seen in the case of the hydroxy fluoride and obscured in the other cases. Two bending vibrations assignable to several OH-groups are found in the region of 850–660 cm⁻¹.

An assignment of all recorded bands of the malonate containing LDHs is given in Table 3. The interpretation of the bands caused by malonate vibrations is more complex. This is not only the case because a greater number of vibrational bands can be expected due to a large number of atoms in the regarding ions (3N-6 = 21 normal vibrations should occur). It is noticeable that the different bonding characters (mal²⁻-ionic, *cis*-[Cr(mal)₂(H₂O)₂]⁻ and [Cr(mal)₃]³⁻—coordinative) cause no clear differences on the band position of the C-O stretching vibrations. Due to the coordinative bonding on a central ion one would expect a $\nu(\text{C}=\text{O})$ and a $\nu(\text{C}-\text{O})$ stretching vibration corresponding to the bonding arrangement Cr-O-C=O which should differ clearly in the band positions like the carbonic acid esters. Instead, in both cases, malonate nonbonded as well as bonded on a Cr(III) central ion, we only find

TABLE 3

IR Wavenumbers (in cm⁻¹) and Band Assignments in the 2000–400 cm⁻¹ Region for [Zn₂Cr(OH)₆]X · nH₂O with X⁻ = 1/2 mal²⁻, *cis*-[Cr(mal)₂(H₂O)₂]⁻, and 1/3 [Cr(mal)₃]³⁻

X ⁻ = 1/2 mal ²⁻	X ⁻ = <i>cis</i> - [Cr(mal) ₂ (H ₂ O) ₂] ⁻	X ⁻ = 1/3 [Cr(mal) ₃] ³⁻	Assignment
1580	1600	1610	} $\nu_{\text{as}}(\text{COO})$ $\delta(\text{H}_2\text{O})^a$
1420	1410	1400	
1350	1390}	1380}	} $\nu_s(\text{COO})$
	1320}	1320}	
1250	1290	1280	$\omega(\text{CH}_2)$
1180}	1180}	1180	} $\nu_{\text{as}}(\text{CC})$
1110}	1120}		
1060}			} $\nu_s(\text{CC})$
970}	970	960	
930	950	940	$\rho(\text{CH}_2)$
790	810	810	$\delta(\text{OH})$
720	740	750	$\delta(\text{OCO})$
670	680	660	} $\gamma(\text{OH})$
570}	570}	580}	
520}	520}	510}	
	460}	460}	$\nu(\text{MO})^b$

Note. ν_s , ν_{as} symmetrical and asymmetrical stretching vibrations, respectively; δ , γ bending vibrations; ω wagging vibrations; ρ rocking vibrations.

^a Bending vibrations of both the crystal water and the ligand water (*cis*-[Cr(mal)₂(H₂O)₂]⁻).

^b Metal-oxygen stretching vibrations.

differences between the two C-O stretching vibration bands being very similar to salt-like compounds (36). Similar cases are known for other malonate compounds from the literature (35). In an analogy to monodentately coordinated acetate-metal complexes (37) it is assumed that as a result of H-bonds on the noncoordinating carboxylate oxygen of the more complex anions a tendency toward the adjustment of both of the C-O bonds takes place. Thus, their band positions can hardly ever be distinguished. Consequently it appears more useful to speak of $\nu_{\text{as}}(\text{COO})$ and $\nu_s(\text{COO})$ vibrations. In the case of the noncoordinated malonate ion it was suggested that the interaction of the carboxylate groups with the hydroxide layers is a bridging one (36), i.e., each oxygen atom is involved in H-bonding.

Propositions for Anion Arrangements in the Interlayer

For long chain organic molecule anions a perpendicular orientation of the carbon chain to the (001) plane should be assumed because of the small area per cationic charge (equivalent area) of [Zn₂Cr(OH)₆]⁺ by formation of H-bonds via the acceptor atoms of the functional groups (12, 13). Resulting from the hexagonal subcell of the OH-groups [Zn_{2/3}Cr_{1/3}(OH)₂]^{1/3+} the equivalent area is $a^2\sqrt{3}/(2z_+) = 0.251 \text{ nm}^2$ (z_+ is the cationic charge number, $z_+ = 1/3$) (12). In general, a high variability of the malonate conformation in solids is known (38). This fact makes it difficult to reach firm conclusions. By the intercalation of the malonate ion into the interlayer the formation of H-bonds with the neighboring hydroxide layers can be

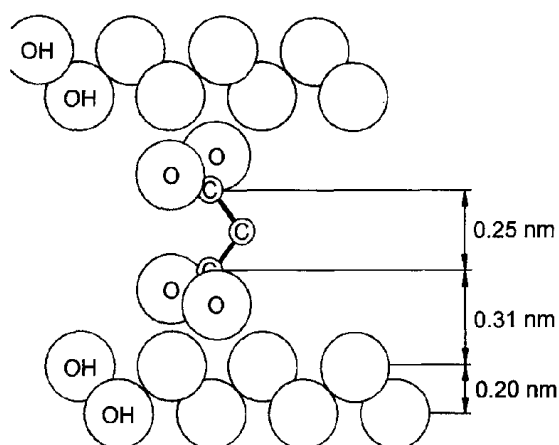


FIG. 4. Arrangement of a malonate ion in the interlayer.

assumed as the dominating factor for its conformation. The resulting conformer should have the following shape: The O-C-O planes are turned out of the C-C-C plane. That gives a favored O...O separation between the two carboxylate groups so that the internal strain caused by O...O repulsion is minimized and the C-C-C angle is close to the tetrahedral value (39, 40). The resulting distance between the two carboxylate C-atoms is 0.25 nm (Fig. 4). The twisting of the two O-C-O planes out of the C-C-C plane should have opposite sense so that at least C_2 symmetry arises (40). Based on the determined basal spacing $c' = 1.074$ nm and the O-H...O distance for H-bonding between carboxylate and hydroxyl groups of 0.276 nm, it can be concluded that either the carbon chain is oriented perpendicularly to the hydroxide layers and one O-atom per carboxylate group is situated in a triangular

interstice of this layer with the other one outside or the carbon chain is adjusted slantwise and the two O-atoms per carboxylate group lie parallel to these layers. Figure 4 shows the first structure proposition. This proposition does not seem to be unlikely since such a form of interaction between hydroxide layers and interlayer anions has been found for intercalated polyoxometalates (17) and for the following intercalated malonatochromates(III). Stronger interactions in terms of shorter H-bonds for dicarboxylic acid anions were already described elsewhere (10, 13). These authors report hydrogen bonding distances of about 0.24 nm. This value is in contrast to that found by us. It seems that there are nonlinear H-bonds. Consequently, a shortened distance perpendicular to the plane of OH close packing results.

The malonate conformation within the intercalated anionic complexes are fixed chiefly by its six-membered ring coordination on the chromium central ion and to a lesser extent by the H-bonds with the hydroxyl groups. The most widespread and possibly also the most stable conformation for six-membered malonate chelates is the so-called boat conformation (41, 42). Here a malonate ligand has C_s symmetry. Corresponding to the X-ray powder data the arrangement of the C_3 -axis of the $[\text{Cr}(\text{mal})_3]^{3-}$ anion (Fig. 5) perpendicular to the hydroxide layers can be assumed. An analogous arrangement is also known for the anionic complexes $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{4-}$ which belong to the point group O_h (43). As a result, the edges of the pseudooctahedra supplied with malonate ligands form an angle of 54.75° with the brucite-like layers. By the underlying boat conformation all four oxygen atoms of any malonate ligand and the Cr^{3+} central ion lie nearly in the same plane (Fig. 6). For the two noncoordinating O-atoms per ligand the average O...O separation is 0.435 nm (41, 42).

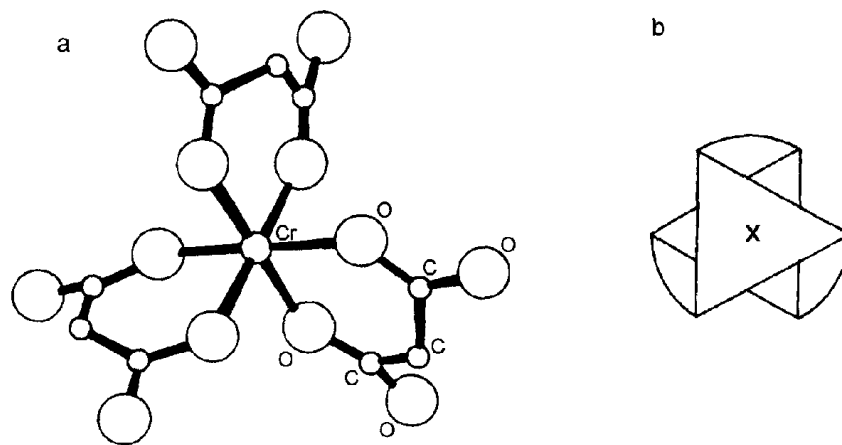


FIG. 5. (a) View of a $[\text{Cr}(\text{mal})_3]^{3-}$ ion. The hydrogen atoms are neglected. (b) Strong simplification of this view. The continuously drawn triangle lies above and the uncontinuously drawn one below the plane of paper. The metal ion is located in the plane of paper (x); the ligands are symbolized by arcs of a circle.

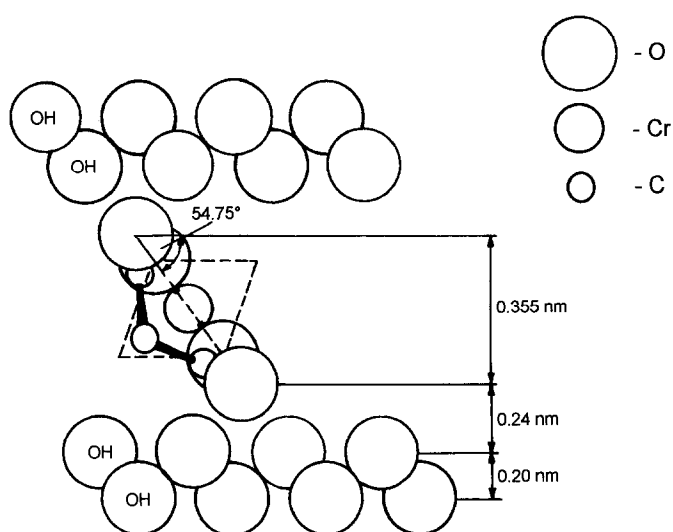


FIG. 6. Arrangement of the pseudooctahedral anionic complexes cis - $[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$ and $[\text{Cr}(\text{mal})_3]^{3-}$ in the interlayer. The figure shows only one malonate ligand; the others are neglected for better clarity.

By using the spacing between these O-atoms of $0.435 \text{ nm} \cdot \sin 54.75^\circ = 0.355 \text{ nm}$ and the spacing between two OH-groups within the same layer of 0.204 nm (12) (perpendicular to the plane of OH close packing in both the cases) the calculation provides a perpendicular O(OH)–O($[\text{Cr}(\text{mal})_3]$) spacing of nearly 0.240 nm . This value is far from that of 0.279 nm determined for the H-bond length by IR spectroscopy. Therefore we conclude that the interaction between the hydroxide layers and anionic complex is more intense, i.e., the above noncoordinating malonate O-atoms are inserted into triangular holes of the hydroxide layers. Perhaps the O–H \cdots O bonds are also not linear. A triple of these O-atoms which is situated parallelly to the plane of OH close packing forms a triangle with equal edge length of about 0.56 nm (41). This value is of an order of magnitude comparable to both the distances between two holes in a closely packed OH-layer of $2a = 0.620 \text{ nm}$ (triangle II in Fig. 7) and $a\sqrt{3} = 0.538 \text{ nm}$ (triangle I in

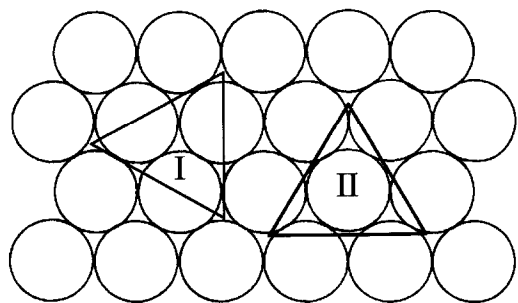


FIG. 7. Projection perpendicular to a layer of closely packed OH-groups (strongly simplified). The triangles symbolize variations of $[\text{Cr}(\text{mal})_3]^{3-}$ arrangement (explanations in the text).

Fig. 7). If, for instance, a $[\text{Cr}(\text{mal})_3]^{3-}$ O-triple is inserted into three holes with the distance $a\sqrt{3}$ then each O-atom is shifted out of the hole centers by $\sim 0.03 \text{ nm}$ and the above O(OH)–O($[\text{Cr}(\text{mal})_3]$) spacing of nearly 0.240 nm can be obtained.

The situation in the case of intercalated cis - $[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$ ion is a similar one. This anion has a C_2 symmetry. Consequently the C_2 -axis is oriented parallelly to the hydroxide layers since the malonate ligands form the equal angle with the plane of OH close packing like in the case of intercalated $[\text{Cr}(\text{mal})_3]^{3+}$. However, this anionic complex is less bulky. The substitution of one malonate ligand by two aquo ligands allows a deeper insertion into the hydroxide layer holes since one of the three malonate "anchors" is no longer effective. Therefore this results in smaller basal spacing and shorter H-bonds.

REFERENCES

1. R. Allmann, *Chimia* **24**, 99 (1970).
2. H. F. W. Taylor, *Mineralog. Mag.* **39**, 377 (1973).
3. S. J. Ahmed and H. F. W. Taylor, *Nature* **215**, 622 (1967).
4. R. Allmann, *N. Jahrb. Mineral., Monatsh.* **140** (1968).
5. N. Gutmann and B. Müller, in preparation.
6. W. T. Reichle, *Solid State Ionics* **22**, 135 (1986).
7. K. A. Corrado, A. Kostapapas, and S. L. Suib, *Solid State Ionics* **26**, 77 (1988).
8. S. Miyata, *Clays Clay Miner.* **31**, 305 (1983).
9. A. Mendiboure and R. Schöllhorn, *Rev. Chim. Miner.* **23**, 819 (1986).
10. K. El Malki, M. Guenane, C. Forano, A. de Roy, and J. P. Besse, *Mater. Sci. Forum* **91–93**, 171 (1992).
11. S. Miyata and T. Kumura, *Chem. Lett.* 843 (1973).
12. H. Kopka, K. Beneke, and G. Lagaly, *J. Colloid Interface Sci.* **123**, 427 (1988).
13. M. Meyn, K. Beneke, and G. Lagaly, *Inorg. Chem.* **29**, 5201 (1990).
14. A. Clearfield, M. Kieke, J. Kwan, J. L. Colon, and R.-C. Wang, *J. Includ. Phenom. Mol. Recognit. Chem.* **11**, 362 (1991).
15. M. A. Drezdson, *Inorg. Chem.* **27**, 4628 (1988).
16. E. D. Dimotakis and T. J. Pinnavaia, *Inorg. Chem.* **29**, 2393 (1990).
17. J. Wang, Y. Tian, R.-C. Wang, and A. Clearfield, *Chem. Mater.* **4**, 1276 (1992).
18. R. S. Weber, P. Gallezot, F. Lefebvre, and S. L. Suib, *Microporous Mater.* **1**, 223 (1993).
19. A. Clearfield, M. Kuchenmeister, J. Wang, and K. Wade, *Stud. Surf. Sci. Catal.* **69**, 485 (1991).
20. J. C. Chang, *Inorg. Synth.* **16**, 80 (1976).
21. H. P. Boehm, I. Steinle, and C. Vieweger, *Angew. Chem.* **89**, 259 (1977).
22. M. Casula, G. Illuminati, and G. Ortaggi, *Inorg. Chem.* **11**, 1062 (1972).
23. H. Stünzi and W. Marty, *Inorg. Chem.* **22**, 2143 (1983).
24. K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.* **75**, 1460 (1953).
25. A. de Roy and J. P. Besse, *Solid State Ionics* **46**, 95 (1991).
26. E. C. Kruissink, L. L. van Reijen, and J. R. H. Ross, *J. Chem. Soc., Faraday Trans. 1* **77**, 649 (1981).
27. H. D. Lutz, *Struct. Bonding (Berlin)* **69**, 97 (1988).
28. S. Miyata, *Clays Clay Miner.* **23**, 369 (1975).
29. P. G. Rouxhet and H. F. E. Taylor, *Chimia* **23**, 480 (1969).
30. G. J. Ross and H. Kodama, *Am. Mineral.* **52**, 1036 (1967).
31. G. Zundel, *Angew. Chem.* **81**, 504 (1969).
32. N. Gutmann, unpublished results.

33. E. Schwarzmann, *Z. Anorg. Allg. Chem.* **317**, 176 (1962).
34. E.-G. Jäger, K. Schöne, and G. Werner, "Elektrolytgleichgewichte und Elektrochemie." Arbeitsbuch 5, Deutscher Verlag für Grundstoffindustrie, 1985; N. Yasuda, K. Yamasahi, and H. Othaki, *Bull. Chem. Soc. Jpn.* **33**, 1067 (1960).
35. M. J. Schmelz, I. Nakagawa, S.-I. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.* **81**, 287 (1959); B. S. Azikov, S. E. Kharaseyeva, Z. A. Grankina, and V. V. Serebrennikov, *Zh. Neorg. Khim.* **13**, 1831 (1968).
36. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds." p. 231. Wiley, New York, 1986.
37. R. C. Mehrota and R. Bohra, "Metal Carboxylates." p. 47. Academic Press, San Diego, 1987; G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.* **33**, 227 (1980).
38. A. Karapides, J. Ault, and A. T. Reed, *Inorg. Chem.* **16**, 3299 (1977).
39. J. A. Goedkoop and C. H. McGillivray, *Acta Crystallogr.* **10**, 125 (1957).
40. B. Briggmann and Å. Oskarsson, *Acta Crystallogr. B* **33**, 1900 (1977).
41. K. R. Butler and M. R. Snow, *J. Chem. Soc., Dalton Trans.* 251 (1976).
42. R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.* **16**, 1600 (1977).
43. K. Itaya, H.-C. Chang, and I. Uchida, *Inorg. Chem.* **26**, 624 (1987).