

## Anion-Exchange Reactions of Layered Double Hydroxides

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Received February 27, 1990

Layered double hydroxides are antitypes of 2/1 clay minerals. In spite of a high surface charge density, as in micas, they react easily with various types of organic anions. Short- and long-chain anions are rapidly exchanged for the inorganic interlayer anions, and high degrees of reaction are attained. The pronounced preference of primary long-chain compounds as typical of the more highly charged clay minerals is not observed. The small equivalent area forces the alkyl chain compounds (fatty acid anions, dicarboxylates, alkyl sulfates) to point away from the interlamellar surfaces and to form monomolecular films of high regularity. However, the linear carboxylate derivatives are greatly disordered along the stacking direction by mild drying. Secondary alkanesulfonates and technical anionic surfactants, which are mixtures of isomers and of compounds with different chain lengths, aggregate in the interlayer spaces forming bimolecular films of constant thickness, and well-ordered organo-double hydroxides are formed, which produce integral series of basal reflections in the X-ray diagrams.

## Introduction

An increasing interest exists in layered double-metal hydroxides, which are or may be used in the production of catalysts, sorbents, and bonding materials. Thermal decomposition of certain synthetic materials containing carbonate as the exchangeable anion results in a useful catalyst for vapor-phase aldol condensations and a number of peripheral base-catalyzed reactions.<sup>1-3</sup> Magnesium-aluminum oxides obtained by calcination of hydrotalcite-like compounds in the temperature range from 450 to 900 °C adsorb various anions under reconstruction of the hydrotalcite structure.<sup>3-5</sup> For this reason, heated double hydroxides are used as halogen scavengers in polyolefin production. A further practical application may be found in the production of ceramic aluminum nitride from hydrotalcite poly(acrylonitrile) complexes.<sup>6</sup>

A widespread application of layered double hydroxides (LDHs) is anticipated by reason of the pronounced anion-exchange capacity toward inorganic<sup>7-14</sup> and organic anions. Even halide-exchange processes between the halide ions X<sup>-</sup> in [Zn<sub>2</sub>Cr(OH)<sub>6</sub>]X·2H<sub>2</sub>O and alkyl halides in toluene or in the vapor phase can proceed to high reaction yields.<sup>16</sup> The interlayer halide anions are capable of migrating to external edge surfaces for reaction with the substrate. To make the interlamellar space itself accessible to simple organic substrates, pillared double hydroxides can be obtained, for instance by interlamellar binding of polyoxocations like V<sub>10</sub>O<sub>28</sub><sup>6-</sup>.<sup>15</sup>

Exchange of interlamellar anions by organic ions (dicarboxylic acid anions) was first reported by Miyata and Kumura.<sup>17</sup> Zinc chromium hydroxide, [Zn<sub>2</sub>Cr(OH)<sub>6</sub>]NO<sub>3</sub>·2H<sub>2</sub>O, easily exchanges

Table I. Layered Double Hydroxides [M<sub>1-x</sub>M<sup>III</sup>(OH)<sub>2</sub>]<sup>ξ+</sup>X<sup>n-</sup>·nH<sub>2</sub>O

	M-M <sup>III</sup>				
	Zn-Cr	Zn-Al	Mg-Al	Ca-Al	Li-Al
x	0.333	0.333	0.250	0.333	0.667
X <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>
basal spacing, Å <sup>a</sup>					
"under soln"	8.9 <sup>7</sup>	8.9	7.8	10.4	8.9
24 h, 100 °C	8.9 <sup>7</sup>	8.8	7.3	7.3	8.8
24 h, 65 °C		8.7	7.4	7.3	9.0
rehydrated	8.9	9.0	7.8	10.4	9.0
a, Å <sup>b</sup>	3.09 <sup>7</sup>	3.08 <sup>20</sup>	3.06 <sup>20</sup>	3.32 <sup>20</sup>	3.07 <sup>20</sup>
equiv area, Å <sup>2</sup> /charge	24.8	24.6	32.4	28.6	24.5
charge density, (m <sup>-2</sup> )	0.32	0.33	0.25	0.28	0.33

<sup>a</sup> Basal spacings of the double hydroxides in solution after precipitation and alteration ("under solution"), air-drying at 100 °C, drying in vacuo at 65 °C, and rehydration under water. <sup>b</sup> a = lattice parameter of the hexagonal subcell that contains two OH groups: a = a<sub>0</sub> (Zn-Cr, Zn-Al, Mg-Al) or a = a<sub>0</sub>/√3 (Ca-Al, Li-Al).<sup>20</sup>

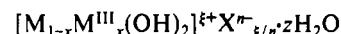
short- and long-chain alkyl sulfate ions.<sup>7</sup> The interlayer arrangement of anionic surfactants (alkyl sulfate and dodecyl glycol ether sulfate anions) has been studied extensively.<sup>18</sup>

Organic gegenions can be bound directly during coprecipitation of the hydroxides. Subsequent exchange of these anions, for instance terephthalate dianions, by polyoxometalate ions (Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup>, V<sub>10</sub>O<sub>28</sub><sup>6-</sup>) provides a simple way to produce pillared hydrotalcites on a large scale.<sup>19</sup>

The exchange reactions described in the literature produce the impression that layered double hydroxides react easily with various types of organic anions. The following study confirms the high intracrystalline reactivity.

## Structure and Synthesis

The layered double hydroxides consist of positively charged layers separated by the anionic gegenions X<sup>-</sup> and water molecules (Figure 1). The general composition may be written as

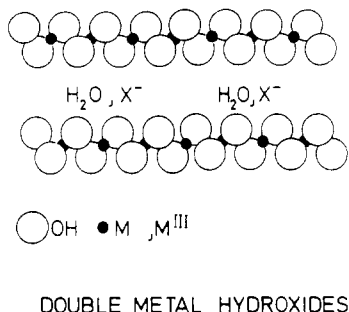


with M = divalent cation (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>, but also Li<sup>+</sup>); M<sup>III</sup> = trivalent cation (Al<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Co<sup>3+</sup>, Ni<sup>3+</sup>, Mn<sup>3+</sup>), and X = interlayer anion (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and many other inorganic anions). The layer charge is ξ = x for M = divalent cation and ξ = 2x - 1 for M = monovalent cation.

The layers are 4.8–4.9 Å thick; the distance in the c direction between the hydroxyl groups within one layer is 2.04 Å (2.00 Å for calcium aluminum hydroxide).<sup>20</sup> The layers are stacked with

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**Figure 1.** Layer structure of double hydroxides:  $M = \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Mn}^{2+}, \text{Li}^+$ ;  $M^{\text{III}} = \text{Al}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}, \text{Co}^{3+}, \text{Ni}^{3+}, \text{Mn}^{3+}$ ;  $X^- = \text{interlayer anion } \text{Cl}^-, \text{NO}_3^-, \text{ClO}_4^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{etc.}$

two layers per unit cell (rhombohedral symmetry) or in less symmetrical arrangements.<sup>20–22</sup> Hydrotalcite,  $[\text{Mg}_3\text{Al}(\text{OH})_8]_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ , crystallizes in rhombohedral symmetry (pyroaurite group). Manasseite has the same chemical composition but hexagonal symmetry (sjögrenite group).

The interlayer water molecules, at least in  $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]\text{NO}_3 \cdot n\text{H}_2\text{O}$  ( $x = 0.20, 0.25, 0.30$ ) are partially oriented, retaining activated motional freedom around the  $C_{2v}$  symmetry axis. This orientation and the barrier to free rotation are a consequence of the formation of hydrogen bonds to and from the hydroxyl groups of the layers.<sup>23</sup>

Most of the hydroxides are synthesized by coprecipitation of the two hydroxides or from gels at mild hydrothermal conditions.<sup>7,9,12,21,24,25</sup> A rational method of synthesizing double hydroxides as suitable precursors for catalysts and with controlled surface area has been described by Reichle<sup>1</sup> and Nunan et al.<sup>3</sup>

### Experimental Section

**Preparation of Double Hydroxides.** Five double hydroxides have been selected for anion-exchange studies (Table I):  $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Zn}_2\text{Al}(\text{OH})_8]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Mg}_3\text{Al}(\text{OH})_8]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ,  $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$ . Nitrate was selected as the gegenion since carbonate anions are often difficult to be exchanged, for instance in magnesium, calcium, and nickel aluminum hydroxides (see also ref 20).

Zinc chromium hydroxide has been prepared by reacting solid ZnO with a solution of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .<sup>7,18</sup> Zinc aluminum hydroxide was prepared in a similar manner. An amount of 5 g of ZnO was mixed with small amounts of water, producing a pasty material, before 30 mL of an aqueous 1 M  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution was added. (Slight stirring can produce a gel-like consistency. Addition of a few milliliters of water and further stirring destroy the gel, and a fluid dispersion is obtained.) The dispersion was allowed to stand (with occasional shaking) for a period of 3 months at room temperature. The precipitate was separated by centrifugation, washed, and dried at 55 °C.

The magnesium aluminum hydroxide was prepared by a procedure similar to the methods of Miyata<sup>17</sup> and Reichle.<sup>1</sup> A solution of 32 g of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.125 mol) and 23.4 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.0625 mol) in 125 mL of water was added dropwise within 1 hour to a solution of 12.5 g of NaOH (0.31 mol) and 18.2 g of  $\text{NaNO}_3$  (0.21 mol) in 145 mL of water. The mixture was held at 65 °C for a period of 16 days. The precipitate was separated by centrifugation, washed, and dried at 40 °C.

The calcium aluminum hydroxide was prepared in a similar way from a solution of 68.1 g of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.288 mol) and 46.8 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.125 mol) in 325 mL of water and a solution of 25 g of NaOH (0.63 mol) and 36.4 g of  $\text{NaNO}_3$  (0.43 mol) in 175 mL of water.

The synthesis of  $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$  has been described by Serna et al.,<sup>24</sup> Schutz and Biloen,<sup>26</sup> and Ulibarri et al.<sup>27</sup> Aluminum hydroxide

was precipitated by addition of a diluted NaOH solution (about 2 M) to a solution of 20 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.053 mol) in 225 mL of water. Then 17 g of  $\text{LiNO}_3$  (0.25 mol) in 50 mL of water was added during stirring. The dispersion was held at room temperature for 25 days with occasional shaking. The precipitate was washed until pH = 7 was reached and dried at 65 °C.

**Organic Acid Salts.** Most of the sodium salts were prepared by neutralization of the organic acids (obtained from Fluka Chemie AG, Buchs, Switzerland, and E. Merck, Darmstadt, FRG).

The series of secondary alkanesulfonates were obtained from Hoechst AG (Frankfurt, FRG). They were pure compounds in reference to the alkyl chain length but mixtures of isomers due to the position of the sulfonate group. Technical alkanesulfonates (Marlon PS 65, Hüls AG, Marl, FRG; Hostapur SAS 93, Hoechst AG) also contain alkyl chains of different lengths, usually in the range from  $C_{13}$  to  $C_{18}$ . Marlon A 350 and 375 (Hüls AG) are sodium alkylbenzenesulfonates with a chain length distribution of  $C_{10} \approx 5\text{--}10$ ,  $C_{11} \approx 40\text{--}45$ ,  $C_{12} \approx 35\text{--}40$ ,  $C_{13} \approx 10\text{--}15$ , and  $C_{14} < 1\%$  (wt/wt). Marlinat 242/70, the sodium salt of a fatty alcohol ( $C_{12}\text{--}C_{14}$ ) ethylene ether sulfate (mainly with two ethoxy groups), was obtained from Hüls AG.

**Anion Exchange.** About 100 mg of the double hydroxide was dispersed in 4–5 mL of the aqueous solution of organic acid salt (concentration about 0.1 M; technical products, 2.5%) and allowed to react for 2 days at 65 °C. The supernatant solution was decanted, and the solid material was again reacted with a fresh salt solution for 2 days at 65 °C. The samples were occasionally shaken during these periods. The organic derivatives were washed six times with 8 mL of water or water/ethanol (1:1), dried at room temperature and in vacuo ( $< 1$  Pa) at 65 °C.

The X-ray diagrams were obtained by the Debye–Scherrer technique by cameras with diameters of 11.4 cm and Cu K $\alpha$  radiation. The basal spacings,  $d_L$ , were measured at different conditions: in contact with the equilibrium solution (“under solution”), after washing and air-drying (25, 65 °C), and after drying in vacuo ( $p \leq 0.1$  Pa) at 65 °C. Generally, several orders of the basal reflections ((001) reflections) were observed.

The degree of exchange was obtained from C analysis (by combustion) of the washed and air-dried organo-double hydroxides and, in some cases, from determination of the amounts of displaced anions.

### Results

The basal spacings of the five selected double hydroxides vary between 7.8 and 10.4 Å (Table I). Excepting the calcium aluminum hydroxide, the spacings change only slightly during drying, as the interlamellar monolayer of the water molecules is not desorbed under these conditions. The calcium aluminum hydroxide adsorbs reversibly a second layer of water molecules, and the spacings change between 7.3 and 10.4 Å.

The interlayer ions are easily exchanged by fatty acid anions. The basal spacing of the formate derivative is 11.2 Å (zinc chromium hydroxide, Table II) and then increases linearly with the chain length ( $\Delta d_L = 1.19 \text{ \AA}/-\text{CH}_2-$ ). For anions longer than undecanoic acid anions, the mean increase is slightly smaller; the nonadecanoic acid anion expands the structure to  $d_L = 31.6 \text{ \AA}$ . These basal spacings refer to samples in equilibrium with the salt solution (“under solution”). Even mild drying (30–65 °C) reduces the structural order along the stacking direction. The intensity of the (001) reflections is strongly reduced, and the shape of the peaks becomes very strange (Figure 2b,c). The position of the first peak centered around  $d$  values of 9 and 11 Å reveals that most of the fatty acid anions (Figure 2b) or nearly all anions (Figure 2c) are displaced from the interlayer spaces. Probably, disordering is promoted by noticeable decarboxylation of the carboxylate anions.

The spacing of zinc chromium hydroxide changes to 9.9 Å when oxalate ions are exchanged for the interlayer nitrate ions. Again, the spacings of the dicarboxylic derivatives increase linearly with the chain length (mean increase  $\Delta d_L = 1.01 \text{ \AA}/-\text{CH}_2-$  from oxalic acid to sebacic acid (decanedioic acid)). The spacings of the alkanedioic acid derivatives are about 3–4 Å smaller and increase more slowly with the chain length than those of the alkanedioic acid double hydroxides ( $\Delta d_L = 1.19 \text{ \AA}/-\text{CH}_2-$ ).<sup>28</sup>

In Table II are also listed the spacings of double hydroxides with a number of various aliphatic and aromatic acid salts. Tartrate and citrate anions do not react as easily as other acid anions. With zinc, calcium, and lithium aluminum hydroxides,

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**Table II.** Basal Spacings ("under Solution" in Angstroms) of Double Hydroxides with Carboxylic Acid Anions Exchanged for the Inorganic Interlayer Anions

anion	Zn-Cr <sup>a</sup>	Zn-Al	Mg-Al	Ca-Al	Li-Al
carboxylate C <sub>n</sub> H <sub>2n+1</sub> CO <sub>2</sub> <sup>-</sup>					
<i>n</i> = 0	11.2		<i>b</i>		
<i>n</i> = 10	23.6		23.0		
<i>n</i> = 18	31.6		31.6		
dicarboxylate C <sub>n</sub> H <sub>2n</sub> (CO <sub>2</sub> <sup>-</sup> ) <sub>2</sub>					
<i>n</i> = 0	9.9	9.9	<i>b</i>		
<i>n</i> = 2	12.2	12.0	12.1		
<i>n</i> = 8	18.0	18.2	18.2		
succinate	12.2	12.0	12.1		
tartrate	12.1	12.2	12.2	<i>b</i>	<i>b</i>
citrate	12.1	12.1	12.2	12.1	12.1 <sup>c</sup>
diglycolate	12.2	12.2	12.2	11.9	12.2
maleate	13.2	13.0	13.0	<i>b</i>	13.2
benzoate	15.5	15.4	15.4	<i>b</i>	15.2 <sup>c</sup>
phthalate	15.0	14.9	15.0	14.7	14.9
salicylate	15.4	17.4	<i>b</i>	<i>b</i>	14.1/17.7
anthranilate	15.5	13.3	15.4	<i>b</i>	14.4 <sup>c</sup>
terephthalate	14.0	14.1	14.3	13.2	14.1

<sup>a</sup>See Table I. <sup>b</sup>No reaction observed within several days at 65 °C. <sup>c</sup>Broadened basal reflections.

**Table III.** Layered Double Hydroxides after Reaction with Various Sodium Arenesulfonates (Basal Spacings "under Solution", in Angstroms)

anion	Zn-Cr	Zn-Al	Mg-Al	Ca-Al	Li-Al
benzenesulfonate	15.7	15.7	15.9	15.7	15.5
<i>p</i> -toluenesulfonate	17.5	17.0	17.3	17.2	17.2
sulfanilate	16.4	16.2	16.8	15.4	16.5
vinylbenzenesulfonate	18.0	18.0	18.2	18.4	18.2
naphthalene-1-sulfonate	16.5	16.5	16.8	16.5	16.5
naphthalene-2-sulfonate	17.9	17.9	18.0	18.0	17.9
naphthalene-1,5-disulfonate	15.2	15.1	15.1	15.6	15.3
dodecylbenzenesulfonate	30.0	30.2	29.5	28.5	30.7

the degree of exchange is low or the (001) reflections are somewhat broadened. Almost identical spacings are observed for the double hydroxides with interlayer succinate, tartrate, citrate, and diglycolic acid anions.

The benzoate derivative may be compared with the butyrate derivative. In fact, similar spacings are observed ( $d_L = 15.5$  Å for benzoate,  $d_L = 15.0$  Å for butyrate). Terephthalate anions increase the spacing to 14.0 Å, which corresponds to the spacing in the presence of adipate anions ( $d_L = 14.4$  Å). Phthalate, salicylate, and anthranilate anions assume the same interlayer orientation as benzoate anions and expand the structure to 15.0–15.5 Å.

Simple arenesulfonates (benzenesulfonate, toluenesulfonate, vinylbenzenesulfonate, and *p*-aminobenzenesulfonate (sulfanilate) and naphthalene sulfonates (Table III)) expand the interlayer space to basal spacings between 15.5 and 18.0 Å. The spacings of the different double hydroxides are very similar; even the calcium aluminum hydroxide makes no exception. The derivatives are stable against washing and drying at 65 °C in vacuo; this procedure decreases the spacings by no more than 3 Å, mainly due to desorption of interlamellar water.

Among long-chain sulfates or sulfonates only the primary alkyl sulfates and secondary alkanesulfonates were available. Typically, the spacings ("under solution") of the alkyl sulfate derivatives increase linearly from 19.2 Å (hexyl sulfate) to 33 Å (octadecyl sulfate) for zinc chromium hydroxide<sup>18</sup> and several other hydroxides.<sup>28</sup>

The basal spacings of the secondary alkanesulfonates with 11–17 carbon atoms in the alkyl chain increase from 23.7 to 30.3 Å (zinc chromium hydroxide, Table IV). Similar spacings are observed for the zinc aluminum and magnesium aluminum hydroxides. Calcium aluminum hydroxide gives slightly smaller and lithium aluminum hydroxide slightly larger spacings. Washing and drying reduce the spacing by 2 Å for zinc chromium and zinc aluminum hydroxides, and the spacing is reduced more strongly by 4–5 Å for calcium aluminum hydroxide (Table VI). The spacings of the derivatives of lithium aluminum hydroxide increase by 1–2 Å during drying in vacuo.

**Table IV.** Layered Double Hydroxides after Reaction with Secondary Alkanesulfonates (Basal Spacings "under Solution", in Angstroms)

<i>n</i> <sup>a</sup>	Zn-Cr	Zn-Al	Mg-Al	Ca-Al	Li-Al
11	23.7	23.9	23.6	22.2	24.9
12	24.8	24.0	24.5	23.8	26.2
13	25.9	25.6	25.4	24.7	27.2
14	27.2	26.5	26.7	25.6	28.5
15	28.2	28.1	27.2	27.1	29.8
16	29.5	29.0	29.5	28.1	31.0
17	30.3	29.5	30.2	29.3	32.1

<sup>a</sup>Number of carbon atoms in the alkyl chain.

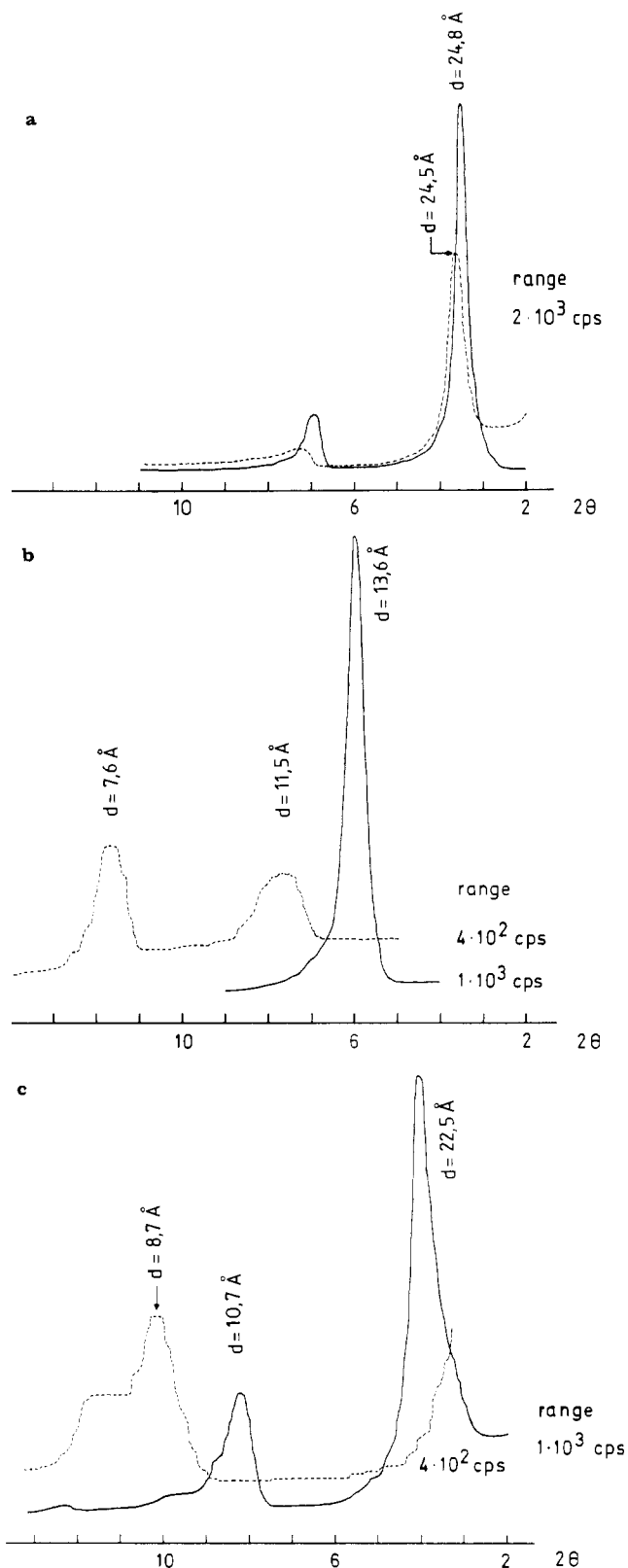
**Table V.** Layered Double Hydroxides after Reaction with Technical Surfactants (Basal Spacings in Angstroms)

surfactant	Zn-Cr	Zn-Al	Mg-Al	Ca-Al	Li-Al
Secondary Alkanesulfonates					
Maronil A	29.0	29.5	29.5	30.0	<i>a</i>
Marlon PS 65	27.8	27.6	27.6	27.0	30.0
Hostapur SAS 93	28.1	28.2	28.4	27.2	30.0
Alkylbenzenesulfonates					
Marlon A 350	28.3	29.6	28.5	27.6	30.7
Marlon A 375	29.8	29.5	29.5	30.3	30.5
Ether Sulfate					
Marlinat 242/70	32.3	32.1	31.0	32.3	30.0

<sup>a</sup>No reaction at 65 °C within several days.

The technical secondary alkanesulfonates (Marlon PS 65 and Hostapur SAS 93, Table V) expand the Zn-Cr, Zn-Al, and Mg-Al hydroxides to about 28 Å. A similar spacing is shown by the hydroxide with pure secondary alkanesulfonate ions containing 14–15 carbon atoms. In Hostapur the chain length varies between 13 and 18 carbon atoms.

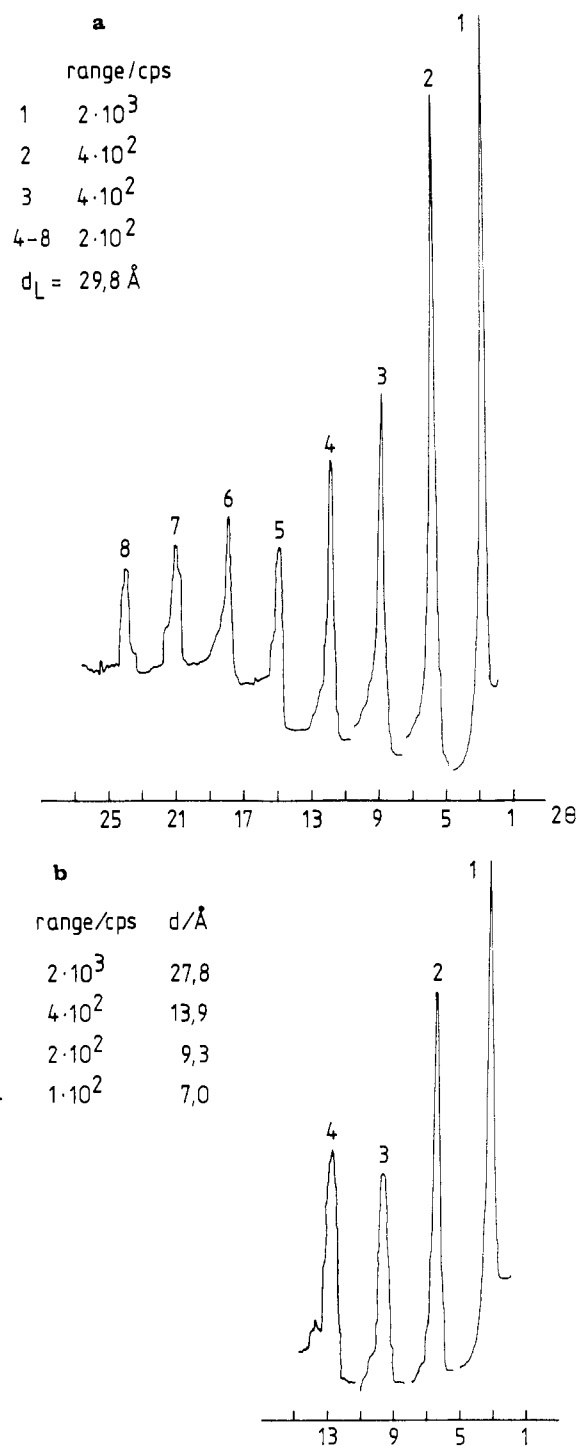
Marlon A 350 and A 375, technical alkylbenzenesulfonates, give spacings of 28–30 Å (table V). As expected from the chain length distribution in Marlon A 350, these spacings correspond



**Figure 2.** Influence of drying on the shape and intensity of the (001) reflection: (—) under equilibrium solution; (---) dried at 65 °C, 24 h; (a) zinc chromium hydroxide with dodecylsulfate ions; (b) zinc chromium hydroxide with butanoate ions; (c) zinc chromium hydroxide with decanoate ions. Note that the intensity of the peaks of the dried samples in b and c are recorded with increased sensitivity.

to the spacing for dodecylbenzenesulfonate.

Marlinat 242/70 is a technical alkyl ( $C_{12}$ – $C_{14}$ ) ethoxy sulfate with about two ethoxy groups. The spacings of 30–32 Å (Table V) are comparable to the spacings of the pure dodecyl ethoxy sulfate with one (31.6 Å) and two ethoxy groups (34.1 Å).<sup>18</sup>



**Figure 3.** X-ray powder patterns of zinc chromium hydroxide reacted with technical surface active agents: (a) with Marlon A 375 (an alkylbenzenesulfonate), under equilibrium solution; (b) with Marlon PS 65 (a secondary alkanesulfonate), washed and dried at 65 °C.

Surprisingly, reaction with technical surface-active anions (Table V) leads to highly ordered derivatives with an integral series of (001) reflections (Figure 3).

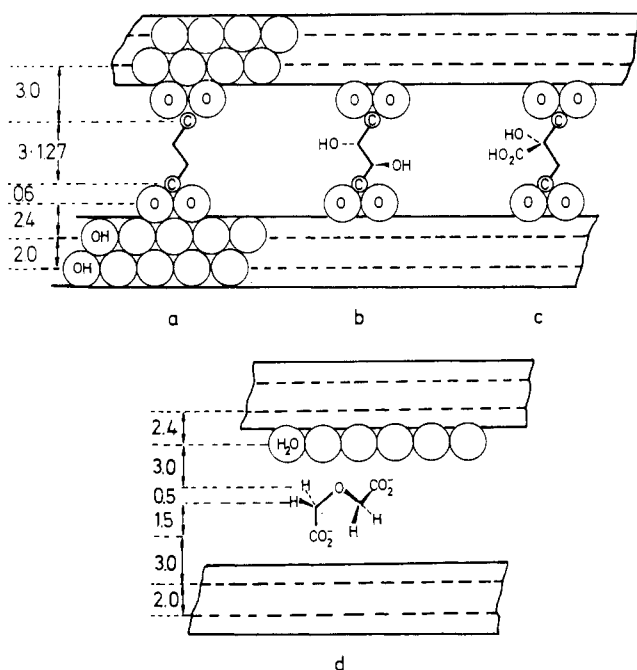
#### Discussion

The interlamellar arrangement depends strongly on the area available to each interlayer anion. As the hexagonal subcell with  $a = 3.05$ – $3.32 \text{ \AA}$  (Table I) contains two OH groups and  $\xi$  positive charges, the area per charge (equivalent area) is  $a^2\sqrt{3}/2\xi$ . The equivalent area is in the range from 24.5 to 32.4 Å<sup>2</sup>/charge, which corresponds to surface charge densities of 0.33–0.25 C m<sup>-2</sup> (Table I). This is a density as high as that in micas (0.32–0.34 C m<sup>-2</sup>). Increasing charge density in three-layer clay minerals (smectites

**Table VI.** Basal Spacing Changes of Ca-Al and Li-Al Double Hydroxide Derivatives by Drying at 65 °C in Vacuo

	Ca-Al		Li-Al	
	$d_L^a$	$d_L^b$	$d_L^a$	$d_L^b$
Arenesulfonates				
benzenesulfonate	15.7	11.8	15.5	13.1
<i>p</i> -toluenesulfonate	17.2	14.3	17.2	14.1
vinylbenzenesulfonate	18.4	14.3	18.1	15.1
naphthalene-1-sulfonate	16.5	13.8	16.5	16.2
naphthalene-2-sulfonate	18.0	14.1	17.9	15.8
dodecylbenzenesulfonate	28.5	25.4	30.7	28.1
Marlon A 350	27.6	24.4	30.7	28.5
Secondary Alkanesulfonates				
11 <sup>c</sup>	22.5	18.6	24.9	27.2
12	23.8	19.7	26.2	28.0
13	24.7	20.4	27.2	29.5
14	25.6	21.3	28.5	30.1
15	27.1	22.2	29.8	31.0
16	28.1	23.6	31.0	32.1
17	29.3	24.2	32.1	34.0

<sup>a</sup>Basal spacing (Å) "under solution". <sup>b</sup>Basal spacing (Å) of the washed and dried organo double hydroxides. <sup>c</sup>Numbers in this column are the number of carbon atoms in each alkyl chain.

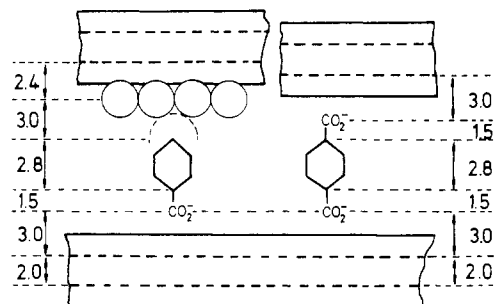


**Figure 4.** Interlamellar arrangement of dicarboxylic acid anions: (a) succinate; (b) tartrate; (c) citrate; (d) diglycolate. Calculated basal spacings (a-c)  $d_L = 11.8$  Å; (d) 12.4 Å.

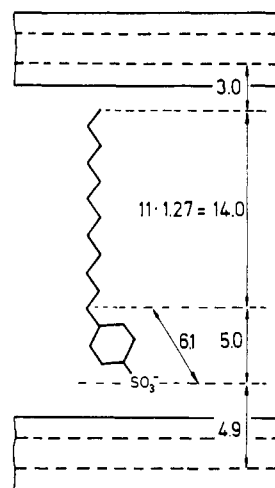
→ vermiculites → micas) decreases the capability of these minerals to exchange the interlayer gegenions by organic cations, in particular by secondary, ternary, and quaternary alkylammonium ions.

The most remarkable behavior of the layered double hydroxides as antitypes of the clay minerals is the high reactivity toward various types of organic anions. The reaction is fast, and a high degree of exchange is generally attained. About 80–100% of the interlayer cations are exchanged by most of the anions listed in this paper. Also, the rate and degree of reaction are not as strongly dependent on the alkyl chain length as they are on clay minerals.

Because of the smaller equivalent area, longer chain molecules are not lying flat on the interlamellar surfaces but point away from them and form mono- or bimolecular films. In contact with equilibrium solution, alkyl sulfate ions are oriented perpendicular in the interlayer space of zinc chromium hydroxide. Desorption of water during drying decreases the spacings by 3–5 Å, and the alkyl chains are tilted at an angle of 56° to the surface of the hydroxide layers.<sup>18</sup> The perpendicular orientation is also observed



**Figure 5.** Interlamellar arrangement of benzoic acid anions (calculated basal spacing  $d_L = 14.7$  Å) and terephthalic acid anions ( $d_L = 13.8$  Å).



**Figure 6.** Dodecylbenzenesulfonic acid anions between double hydroxide layers. Calculated basal spacing: 26.9 Å.

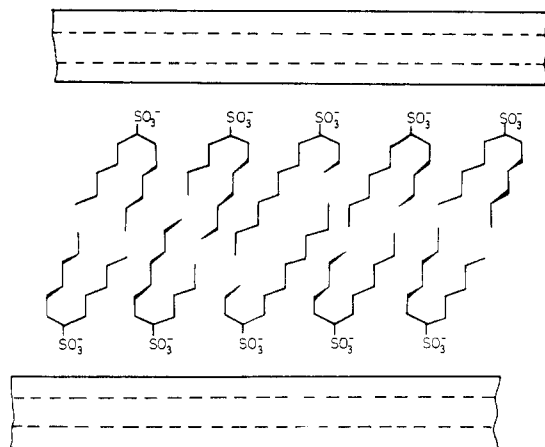
for fatty acid and dicarboxylic acid anions. For very long anions (dodecanoic acid salt and longer compounds) the alkyl chains are probably shortened by one or two kinks or are no longer in perpendicular orientation.<sup>28</sup>

The identical spacings observed with succinate, tartrate, and citrate are in agreement with an almost perpendicular interlayer orientation (Figure 4). Diglycolic acid seems to adopt a conformation with the C–O bond in gauche position, so that the ether oxygen atoms can accept hydrogen bonds from water molecules or OH groups (Figure 4). As in the carboxylic acid derivatives, water molecules are retained between the anion and the surface.

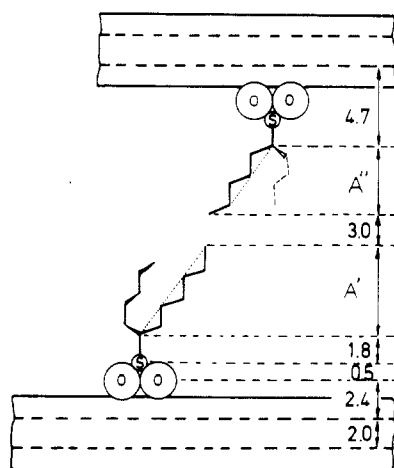
The distance of the carbon atom of the –COOH group from the carbon atom in the para position in benzoic acid (4.3 Å) nearly corresponds to the length of three carbon–carbon bonds in an alkyl chain (3.8 Å). Therefore, benzoate, phthalate, salicylate, and anthranilate anions expand the lattice to the same extent ( $d_L = 15.0$ – $15.5$  Å) as butyrate ( $d_L = 15.0$  Å). The theoretical spacing for the benzoate derivative is 14.7 Å when, as in the fatty acid derivatives,<sup>28</sup> water molecules are retained between the benzene ring and the surface oxygen atoms (Figure 5). Terephthalate anions ( $d_L = 14.1$ – $14.3$  Å) give spacings similar to those of adipate anions ( $d_L = 14.0$ – $14.4$  Å). The theoretical spacing for perpendicular terephthalate anions is 13.8 Å (Figure 5).

Dodecylbenzenesulfonate anions (Figure 6) orient the alkyl chain into the perpendicular position. The benzene ring is tilted toward the layer (calculated spacing: 26.9 Å). When water molecules remain adsorbed between the methyl end group and the hydroxyl layer, the spacing is 29.7 Å. Observed spacings are 26.8 Å (dried) and 30.0 Å ("under solution").

Of particular interest are the results with secondary alkanesulfonates. At first sight the similarity of the spacings of these alkanesulfonates and the alkyl sulfates<sup>18</sup> may indicate the same interlayer arrangement. However, the absolute values of the spacings (after drying) could only be attained by perpendicular alkanesulfonate anions with the sulfonate group attached to carbon atom 2. In reality, the sulfonate group is distributed over the whole



**Figure 7.** Formation of bilayers consisting of isomers of secondary alkanesulfonates between the double hydroxide layers.



**Figure 8.** Calculation of the basal spacing of double hydroxide layers separated by bimolecular layers of secondary alkanesulfonates. Note that the contribution of the alkyl chains is different for even- and odd-numbered chains (eqs 2 and 3).

length of the chain with some preference to the middle part. This leads to the conclusion that the interlamellar structure must be essentially bimolecular.

The secondary alkanesulfonates assume a V-like shape when all C-C bonds are in the trans conformation. As proposed for dimethyldialkylammonium ions,<sup>29</sup> U-shaped conformations are more likely when the surfactant ions are packed to form mono- or bimolecular films. Such conformations are formed when gauche bonds<sup>30-32</sup> occur near the secondary carbon atom (Figures 7 and 8).

An important observation is that sharp X-ray diffraction diagrams with several orders of (001) reflections are obtained, though the secondary alkanesulfonates are mixtures of isomers, which differ in the position of the sulfonate group. The bimolecular films built up between the hydroxide layers must be of constant thickness in spite of the fact that they contain differently shaped surfactant ions. According to the position of the sulfonate group, alkyl chains of different lengths constitute the branches of the U. These ions can easily aggregate to form bimolecular films of constant thickness when they join to pairs of the same length (Figure 7). The theoretical spacing is then (Figure 8)

$$\begin{aligned} d_L (\text{\AA}) &= 6.7 + A' + 3 + A'' + 4.7 \\ &= 14.4 + A' + A'' \end{aligned} \quad (1)$$

where  $A'$  and  $A''$  are the contributions of the alkyl chain sections

**Table VII.** Basal Spacings for Secondary Alkanesulfonates Calculated by Eq 1-3 and Spacings Observed for Zinc Aluminum Hydroxide (Dried at 65 °C in Vacuo)

	observed		calculated	
	$n_C$	$d_L, \text{\AA}$	$d_L, \text{\AA}$	$n_C'$
11	22.1	21.7	4	6
12	23.0	22.8	5	5
		23.3	5	6
13	24.5	23.8	6	6
		24.8	5	7
14	25.6	25.4	6	7
		25.9	6	8
15	26.4	26.9	7	7
		27.5	7	8
16	27.2	27.5	7	8
		28.0	8	8

with  $n_C'$  and  $n_C''$  carbon atoms. When  $n_C'$  or  $n_C''$  is odd ( $=n_1$ ),  $A'$  or  $A''$  is

$$A' \text{ or } A'' (\text{\AA}) = (n_1 - 1)1.27 \sin 55^\circ \quad (2)$$

For  $n_C'$  or  $n_C'' = \text{even} (=n_2)$  the length is

$$A' \text{ or } A'' (\text{\AA}) = (n_2 - 2)1.27 \sin 55^\circ + 0.53 \quad (3)$$

As shown in Table VII, good agreement between calculated and observed spacings is attained for pairs with the sulfonate group distributed around the middle position.

The fit of the "right" surfactant molecules to pairs of the same length may be accompanied by changes in the ratio of the isomers in the interlayer space and the equilibrium solution. Reliable experimental data could not be attained. However, selective adsorption of only one or two isomers can be excluded.

The constant film thickness is maintained by two further properties: the high conformational freedom of the aggregating U-shaped surfactants and the fact that bimolecular films can bear considerable amounts of holes,<sup>30</sup> which may be formed between alkanesulfonate ions not exactly fitting one to another.

The derivatives of calcium aluminum hydroxide show spacings distinctly smaller (after washing and drying, Tables VI and VII) than those of the other hydroxides. Due to the larger equivalent areas, the pairs of surfactant ions (as shown in Figures 7 and 8) are no longer close-packed. Closer packing could be attained by increasing the chain tilt, which, however, requires reorientation of the  $\text{SO}_3$  group so that only two oxygen atoms remain in contact with the surface oxygen atoms. Insertion of additional gauche bonds also increases the chain-packing density, but it would be too speculative to outline a special model.

The spacings of the lithium aluminum hydroxide derivatives (in contact with the equilibrium solution, Table IV) are slightly higher than for the other derivatives. This is easily explained by preference of pairs with somewhat longer chain sections  $A'$  and  $A''$  (Figure 8). The unusual effect, however, is that the basal spacing increases during drying. Conformational changes in the alkyl chains only decrease the length of the pairs. The spacing increases when the S-C bond is tilted. In fact, the theoretical spacings agree with the observed values when the pairs are tilted in a way that the chain sections  $A'$  and  $A''$ , which determine the spacing, assume a perpendicular orientation. The decline of the S-C bond could be a consequence of the different charge distributions of the  $\text{Li}^+ - \text{Al}^{3+}$  hydroxide compared to the  $\text{M}^{2+} - \text{M}^{3+}$  hydroxides. The reorientation of the  $\text{SO}_3$  group is promoted when hydroxyl groups (such as water) are desorbed from the layer.

The bilayer model of Figure 7 even explains why double hydroxides with technical alkanesulfonates show sharp (001) reflections. The technical sulfonates not only contain the sulfonate group at different positions but are also composed of alkanesulfonates with different alkyl chain lengths. The molecules of different lengths can aggregate to form films of constant thickness similarly to the different isomers.

The driving forces for formation of the interlayer films of constant thickness originate from the rigidity of the hydroxide layers, which promotes the adsorption of surfactant pairs of similar

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length, and the large mixing and conformational entropy in the interlayer space. The large mixing entropy impedes demixing of the surfactant anions to form films of different thicknesses.

**Acknowledgment.** Martina Meyn is grateful to Fonds der

Chemischen Industrie for a fellowship. We also thank Dr. Quack (Hoechst AG, FRG) for donation of the secondary alkane-sulfonates and several technical surfactants. The technical surfactants Marlinat and Marlon were obtained from Hüls AG, and Maranil was obtained from Henkel KGaA (FRG).

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## Spin Coupling in Ferric Porphyrin and Chlorin $\pi$ -Cation-Radical Complexes

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Received February 27, 1990

The ferric porphyrin  $\pi$ -cation-radical complexes (OEP\*)Fe<sup>III</sup>(ClO<sub>4</sub>)<sub>2</sub> (1) (OEP\* = monoanion of octaethylporphyrin) and (OEP\*)Fe<sup>III</sup>Cl[SbCl<sub>6</sub>] (2) and the ferric chlorin  $\pi$ -cation-radical complexes (OEC\*)Fe<sup>III</sup>(ClO<sub>4</sub>)<sub>2</sub> (3) (OEC\* = monoanion of octaethylchlorin), (OEC\*)Fe<sup>III</sup>Cl[SbCl<sub>6</sub>] (4), and (TPC\*)Fe<sup>III</sup>Cl[SbCl<sub>6</sub>] (5) (TPC\* = monoanion of tetraphenylchlorin) were examined in microcrystalline form by magnetic susceptometry over a range of 1.6 K to room temperature at an applied field. The effective magnetic moments of the two six-coordinate complexes, 1 and 3, were in reasonable agreement with simulation in which an  $S = 5/2$  iron ion antiferromagnetically couples with an  $s = 1/2$  porphyrin (or chlorin)  $\pi$  radical by weak exchange interaction. In the five-coordinate complexes, 2, 4, and 5, the results of the magnetic susceptibility measurements are consistent with the calculations based on the model that the  $S = 5/2$  iron ion antiferromagnetically couples with the  $s = 1/2$   $\pi$  radical with energies of  $-8$  cm<sup>-1</sup> for 2,  $-20$  cm<sup>-1</sup> for 4, and  $-85$  cm<sup>-1</sup> for 5. Thus the ground states of all these complexes measured are of total spin  $S_T = 2$ . The difference in the magnitude of the antiferromagnetic coupling between the five-coordinate complexes and the six-coordinate complexes is reasonably explained by the difference of the symmetry of the radical orbitals: A<sub>1g</sub> symmetry of OEP, OEC, and TPC complexes. From these results A<sub>1g</sub> symmetry for the radical orbitals in horseradish peroxidase compound I (HRP compound I) and myeloperoxidase compound I (MPO compound I) is proposed.

### Introduction

In recent years a number of heme and non-heme enzymes that exhibit intramolecular spin-coupling phenomena have been explored.<sup>3-5</sup> For example, it has been suggested that in HRP (horseradish peroxidase) compound I, the  $S = 1$  spin of the central Fe(IV) ion weakly couples antiferromagnetically with an  $s = 1/2$  porphyrin  $\pi$ -cation-radical spin to produce a spin system with an overall  $S = 1/2$ .<sup>6-10</sup> These states in the native enzymes have received continuous interest, since they might be closely related to chemical and biological functions.

Since the success of chemical oxidation of synthesized iron(III) porphyrin complexes,<sup>11-15</sup> various oxidative states of metallo-

porphyrins have been examined as model complexes for these heme enzymes.<sup>16-23</sup> So it has become increasingly important to recognize the coupling behavior between the central iron ion and the ligand  $\pi$  radical, whether the coupling mode is ferromagnetic, antiferromagnetic, or virtually absent. Furthermore, when each of these three situations is known, a qualitative understanding of the circumstances under which each will occur becomes the next problem.

Gans et al.<sup>24</sup> have proposed a theory to account for the notable difference in coupling of the metal ion and the ligand spin between (TPP\*)Fe<sup>III</sup>(ClO<sub>4</sub>)<sub>2</sub> and (TPP\*)Fe<sup>III</sup>Cl[SbCl<sub>6</sub>] (TPP\* = monoanion of tetraphenylporphyrin). Spin coupling in the former compound is ferromagnetic, while that in the latter is antiferromagnetic. Their theory is based on the occupations and symmetries of a radical orbital that is related to magnetic coupling. They have reported that in the TPP system the  $\pi$  radical orbital has A<sub>2u</sub> symmetry, which leads to ferromagnetic coupling in D<sub>4h</sub> symmetry and to antiferromagnetic coupling in lower C<sub>2v</sub> symmetry.

In this paper we wish to report the magnetic properties of spin coupling in Fe(III) complexes with OEP, OEC, and TPC  $\pi$  cation

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