

Anion-Exchange Reactions of Hydroxy Double Salts

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Hydroxy double salts (HDS's) comprise a class of layered materials which are similar to layered double hydroxides (LDH's) and show a comparable intracrystalline reactivity. All samples described in this paper were prepared by reacting a solid oxide MeO with a solution of a nitrate $M(\text{NO}_3)_2$: ZnO with solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; NiO with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; and CuO with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Typical compositions of HDS's are $[(\text{Me},\text{M})_2(\text{OH},\text{NO}_3)_4]$ and $[(\text{Me},\text{M})_5(\text{OH})_8](\text{NO}_3)_2$. The hydroxy double salts easily exchange anionic surfactants for the interlayer nitrate anions. Toward short-chain acid anions the HDS's are less reactive than the LDH's. The anion exchange capacity is due to the exchange of anions incorporated in the hydroxide layer (as in the basic copper nitrate $[\text{Cu}_2(\text{OH})_3\text{NO}_3]$) or of anions bound as gegenions of the positively charged hydroxide layer. The positive charge originates from an excess of the divalent metal ions as in basic zinc salts $[\text{Zn}_5(\text{OH})_8](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ or $[\text{Zn}_5(\text{OH})_8]\text{Cl}_2 \cdot \text{H}_2\text{O}$. The arrangement of long-chain alkyl sulfate ions in the interlayer space is deduced from basal spacing measurements. In many HDS's the surfactant anions are largely tilted to the hydroxide layers and are aggregated in bilayers. Technical secondary alkanesulfonates which are mixtures of isomers are arranged in the bimolecular film in a way that a constant interlamellar separation is attained. The organic derivatives of the HDS's adsorb neutral molecules between the layers. Typical is the interlamellar adsorption of primary 1-alkanols such as hexanol, octanol, and decanol by the alkyl sulfate derivatives.

Introduction

Reacting a solid oxide with an aqueous solution of a metal salt provides a general procedure to prepare layered double hydroxides, hydroxy double salts, and hydroxy (basic) chlorides and nitrates:

(i) Combination of an oxide MeO with solutions containing Me^{3+} ions produces layered double hydroxides (LDH's), a group of compounds which presently attracts great interest of several research groups. The general formula is $[\text{Me}^{II}_{1-x}\text{Me}^{III}_x(\text{OH})_2]^{x+} \cdot y\text{H}_2\text{O}$.

(ii) Hydroxy double salts (HDS's) form when an oxide MeO is combined with other divalent metal ions M^{2+} . Typical (idealized) compositions are $[(\text{Me},\text{M})_2(\text{OH})_3\text{NO}_3]$ and $[(\text{Me},\text{M})_5(\text{OH})_8](\text{NO}_3)_2$.

(iii) An oxide MeO may also be reacted with a salt solution containing the same divalent cation. For instance, reacting ZnO with a solution of ZnCl_2 gives the hydroxyzinc chloride $[\text{Zn}_5(\text{OH})_8]\text{Cl}_2 \cdot \text{H}_2\text{O}$.

The ionic radii of the metal ions ($\text{Me}^{2+}, \text{M}^{2+}$) in hydroxy double salts do not differ by more than 0.05 Å. Larger differences of the Me^{2+} and M^{3+} ionic radii are tolerated in the layered double hydroxides (Table I).

Conversion of an oxide into a layered double hydroxide was first described by Boehm et al.¹ They prepared zinc chromium hydroxide $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ by reacting ZnO with solutions of $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. This procedure was initiated by the observation that ZnO takes a violet color when impregnated with an ethanolic solution of chromium nitrate.²

The reaction of a solid oxide with aqueous metal salt solutions has been known for a long time. Sabatier,³ Recoura,⁴ and Mailhe⁵ described formation of hydroxy double salts by reacting CuO (or copper and oxygen) with solutions of Ni^{2+} , Co^{2+} , Zn^{2+} , and Cd^{2+}

Table I. Ionic Radii of Metal Ions in Layered Double Hydroxides (LDH's) and Hydroxy Double Salts (HDS's)

layered double hydroxides			hydroxy double salts		
cations	radii (Å)	diff (Å)	cations	radii (Å)	diff (Å)
$\text{Li}^+, \text{Al}^{3+}$	0.68, 0.51	0.17	$\text{Zn}^{2+}, \text{Co}^{2+}$	0.74, 0.72	0.02
$\text{Zn}^{2+}, \text{Cr}^{3+}$	0.74, 0.63	0.11	$\text{Zn}^{2+}, \text{Ni}^{2+}$	0.74, 0.69	0.05
$\text{Cu}^{2+}, \text{Cr}^{3+}$	0.72, 0.63	0.09	$\text{Zn}^{2+}, \text{Cu}^{2+}$	0.74, 0.72	0.02
$\text{Cu}^{2+}, \text{Al}^{3+}$	0.72, 0.51	0.21	$\text{Ni}^{2+}, \text{Cu}^{2+}$	0.69, 0.72	0.03
$\text{Zn}^{2+}, \text{Al}^{3+}$	0.74, 0.51	0.23	$\text{Cu}^{2+}, \text{Co}^{2+}$	0.72, 0.72	0.00
$\text{Mg}^{2+}, \text{Al}^{3+}$	0.66, 0.51	0.15			
$\text{Ni}^{2+}, \text{Al}^{3+}$	0.69, 0.51	0.18			
$\text{Ca}^{2+}, \text{Al}^{3+}$	0.99, 0.51	0.48			

salts. Structural studies of hydroxy double salts were reported by Feitknecht and Maget,⁶ who prepared hydroxy double salts from CuO and NiCl_2 , CoCl_2 , ZnCl_2 , CdCl_2 , and MgCl_2 solutions.

The structural principle of LDH's is the substitution of Me^{2+} ions by other metal ions (M^{3+} or M^{2+}) in brucite type hydroxide layers. Substitution of Me^{2+} by M^{3+} ions (compounds $[\text{Me}^{2+}_{1-x}\text{Me}^{3+}_x(\text{OH})_2]^{x+}$) produces positively charged layers, and anions and water molecules are bound between the layers. In many cases the interlayer anions can be exchanged by other anions.^{7,8} Substitution of Me^{2+} by M^{2+} (HDS's) should not result in charged layers, and anion exchange reactions are not expected to occur. However, many hydroxy double salts do exchange anions and, in particular, are very reactive toward organic anions and anionic surfactants.

Materials and Methods

A hydroxy double nitrate prepared from the solid oxide MeO and a solution of $\text{M}(\text{NO}_3)_2$ will be designed as $(\text{Me}^{2+}, \text{M}^{2+})$ HDS. For instance, $(\text{Ni}^{2+}, \text{Cu}^{2+})$ HDS is obtained from NiO dispersed in $\text{Cu}(\text{NO}_3)_2$ solution, and $(\text{Cu}^{2+}, \text{Ni}^{2+})$ HDS is prepared from CuO dispersed in $\text{Ni}(\text{NO}_3)_2$ solution.

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(Zn²⁺,Co²⁺) and (Zn²⁺,Ni²⁺) Hydroxy Nitrate. A volume of 60 mL of 1 M Co(NO₃)₂ or Ni(NO₃)₂ solution (=0.06 mol) was added to 9.8 g of ZnO (0.12 mol) dispersed in a few milliliters of water. The dispersion was allowed to stand 6 days at 65 °C. The solution still retained the color of Ni²⁺ and Co²⁺ ions. The solid material was isolated, washed, and dried at 65 °C. Identical compounds were produced from the same dispersions standing 5 months at room temperature. The X-ray powder diagram did not show the reflections of ZnO.

(Zn²⁺,Cu²⁺) Hydroxy Nitrate. This compound was prepared from a mixture of 9.8 g of ZnO (0.12 mol) and 100 mL of 1 M Cu(NO₃)₂ solution. After 3 days at 65 °C, the colorless supernatant was poured off and replaced by 30 mL of the Cu(NO₃)₂ solution. Three days later, the solid was separated from the solution, which now had the color of Cu²⁺ ions.

(Cu²⁺,Ni²⁺) Hydroxy Nitrate. An amount of 16 g of CuO (0.2 mol) was added to 58 g of Ni(NO₃)₂·6H₂O (0.2 mol) in 250 mL of water. After 6 days at room temperature, the reflections of CuO were still visible in the X-ray powder diagram, but disappeared a few days later. After standing 4 months at room temperature, the solid was separated from the solution, washed, and air-dried.

(Ni²⁺,Cu²⁺) Hydroxy Nitrate. An amount of 14.9 g of NiO (0.2 mol) was dispersed in a solution of 60.4 g of Cu(NO₃)₂·3H₂O (0.25 mol) in 200 mL of water. After 22 days at room temperature, the solid residue was isolated, washed, and air-dried.

(Cu²⁺,Zn²⁺) Hydroxy Nitrate. An amount of 2 g of CuO (0.025 mol) was dispersed in a solution of 8.9 g of Zn(NO₃)₂·6H₂O (0.03 mol) in 70 mL of water. The dispersion was allowed to stand 3 months at room temperature. After this period, the X-ray reflections of CuO were no longer observed and the solid was isolated, washed, and air-dried.

(Cu²⁺,Co²⁺) Hydroxy Nitrate. This nitrate was prepared from 16 g of CuO (0.2 mol) dispersed in a solution of 72.8 g of Co(NO₃)₂·6H₂O (0.25 mol) in 250 mL water. After 6 days at room temperature, the solid was isolated, washed, and dried at 70 °C.

(Cu²⁺,Cu²⁺) Hydroxy Nitrate. The basic copper nitrate was prepared from 15.9 g of CuO (0.2 mol) in a solution of 60.4 g of Cu(NO₃)₂·3H₂O (0.25 mol) in 200 mL of water at pH = 4. The hydroxy double nitrate was formed after 6 days. The solid residue was separated from the mother liquid after 7 weeks, washed, and air-dried.

(Please note that the long periods for which the samples were allowed to stand may not necessarily be required to obtain the HDS's.)

Analytical Methods. The hydroxy double salts were dissolved in concentrated hydrochloric acid (Ni²⁺,Cu²⁺ hydroxy salts in 65% HNO₃), and the metal ion concentrations were measured by complexometry. The N content was determined by combustion. The amount of hydroxyl ions was obtained as the difference of the equivalents of cations and nitrate ions. The content of interlamellar water was derived from the weight loss after drying the samples for 5 days over P₄O₁₀.

Anion Exchange. The interlayer nitrate ions can be replaced by various short-chain and long-chain anions such as fatty acid anions, alkyl sulfates, and alkanesulfonates.

To prepare the alkyl sulfate derivatives, 100–150-mg amounts of the hydroxy double salt were dispersed in 4–5 mL of the sodium alkyl sulfate solution. The concentration of the alkyl sulfate C_nH_{2n+1}SO₄Na⁺ was 0.1 M in water (for n = 4–12), 0.07 M for n = 14 in H₂O/10% ethanol, and 0.025 M for n = 16, 18 in H₂O/10% ethanol. The dispersions were allowed to stand 2 days at 65 °C. The supernatant solution was removed by centrifugation or decantation, and the solid was again dispersed in a fresh surfactant solution. The samples were occasionally shaken during these periods. After 4 days, the solid was washed six times with 8 mL of water (ethanol/water (1:1) for n ≥ 14) and dried at 65 °C in air and then under high vacuum (< 1 Pa) for 24 h. The X-ray powder diagrams were made from samples in contact with the equilibrium solution ("under mother liquor"), after washing and air-drying at 65 °C and after drying in vacuum at 65 °C.

In a similar way, the hydroxy salts were reacted with carboxylic acid anions and with secondary alkanesulfonates. In most cases, the concentration of the organic anion was 0.1 M in water.

The secondary alkanesulfonates are mixtures of isomers differing by the position of the sulfonate group. Predominant are isomers with the sulfonate group attached to the middle part of the chains. The chains are unbranched.

X-ray Powder Diagrams. The diagrams of the hydroxy double salts were obtained in a powder diffractometer (Siemens Kristalloflex 810, Cu Kα). In all cases, reflections of the starting solid oxide could not be detected. This does not negate the fact that minor amounts of these

Table II. Basal Spacing d_L of Air-Dried Precipitated Dodecyl Sulfates

cation	d_L (Å)	cation	d_L (Å)
K ⁺	33.9	Cr ³⁺	30.0
Cs ⁺	21.1	Fe ³⁺	23.1
Mg ²⁺	20.9	Ni ²⁺	29.5
Ca ²⁺	30.0	Co ²⁺	20.8
Ba ²⁺	33.3	Cu ²⁺	25.2
Al ³⁺	31.6	Zn ²⁺	21.0 + 31.3

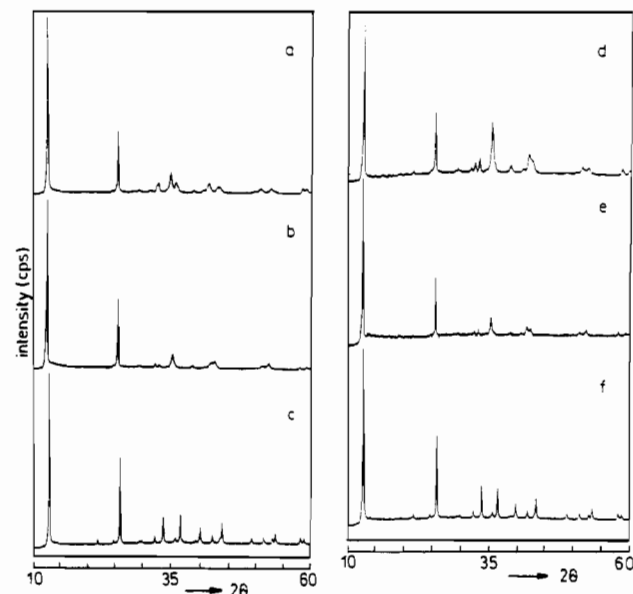


Figure 1. X-ray powder diffraction diagrams of hydroxy double salts (maximum intensity 11 000 counts/s (d, e), 18 000 counts/s (f), 22 000 counts/s (a–c); Cu Kα): (a) (Zn²⁺,Cu²⁺), from ZnO in Cu(NO₃)₂ solution; (b) (Cu²⁺,Zn²⁺), from CuO in Zn(NO₃)₂ solution; (c) (Ni²⁺,Cu²⁺), from NiO in Cu(NO₃)₂ solution; (d) (Cu²⁺,Ni²⁺), from CuO in Ni(NO₃)₂ solution; (e) (Cu²⁺,Co²⁺), from CuO in Co(NO₃)₂ solution; (f) (Cu²⁺,Cu²⁺), from CuO in Cu(NO₃)₂ solution (= copper hydroxy nitrate [Cu₂(OH)₃]NO₃).

oxides were still present in the hydroxy double nitrates, so that the analytical compositions mentioned below should be considered as being approximate.

The organic derivatives ("under mother liquor", air-dried at 65 °C, and dried at 65 °C in vacuum (< 1 Pa)) were studied in Lindemann glass tubes (diameters 0.3–0.5 mm) inserted into Debye-Scherrer cameras (radius 5.73 cm, Cu Kα, Ni filter). For vacuum-drying, the Lindemann glass tubes containing the powdered sample were dried in a vacuum device, immediately sealed after removal, and X-rayed. To measure the basal spacing of samples in contact with the equilibrium solution, the dispersion was sucked into Lindemann glass tubes (diameter 0.5 mm) along with a small excess of the solution.

The basal spacing d_L was derived from several orders of basal reflections ((00l) reflections): $d_L = l d_{001}$.

When hydroxy double salts are reacted with alkyl sulfates and similar surfactants, it should be considered that the surfactant anions and divalent and trivalent metal ions form crystalline precipitates, the (001) reflections of which often lie in the same range as the corresponding derivatives of the hydroxy double salts (Table II). Careful inspection of the X-ray powder diagrams clearly revealed that the hydroxy salts are not decomposed by the surfactants by formation of metal surfactant precipitates.

Results

Hydroxy Double Salts. The topic of this paper concerns the reactivity of hydroxy double salts with organic anions and the arrangement of these anions in the interlayer space. Therefore, we report only briefly a few data concerning the hydroxy double salts themselves.

The analytical composition, in particular the Me²⁺:M²⁺ molar ratio, depends not only on the method of preparation but also on

Table III. Basal Spacing ($d_L = d_{001}$) of Hydroxy Double Salts

hydroxy double salt ^a	color	basal spacing (Å)				
		b	c	d	e	f
(Zn ²⁺ ,Ni ²⁺)	light green	9.68	9.68	8.97	8.92	9.66
(Zn ²⁺ ,Co ²⁺)	rose	9.68	9.68	8.97	8.92	9.68
(Zn ²⁺ ,Cu ²⁺)	light blue	6.96	6.96	6.94	6.94	6.94
(Cu ²⁺ ,Zn ²⁺)	gray-black	6.96	6.97	6.94	6.94	6.94
(Cu ²⁺ ,Ni ²⁺)	black	6.90	6.91	6.90	6.91	6.90
(Ni ²⁺ ,Cu ²⁺)	blue-green	6.90	6.91	6.90	6.91	6.90
(Cu ²⁺ ,Co ²⁺)	black	6.96	6.96	6.94	6.94	6.94
(Cu ²⁺ ,Cu ²⁺) ^g	grayish green	6.91	6.91	6.91	6.91	6.90

^a The notation (Ni²⁺,Cu²⁺) indicates that the salt is prepared from NiO in Cu²⁺ solution; (Cu²⁺,Ni²⁺) is obtained from CuO in Ni²⁺ solution. ^b Under mother liquor. ^c Washed and air-dried at 65 °C (24 h). ^d Washed and air-dried at 100 °C (24 h). ^e Washed, air-dried (65 °C), and dried in vacuum (<1 Pa) at 65 °C (24 h). ^f Sample described in footnote e, rehydrated in water. ^g Copper hydroxy nitrate, [Cu₂(OH)₃NO₃].

Table IV. X-Ray Powder Data for Hydroxy Double Salts^a

d (Å)	I	d (Å)	I	d (Å)	I
(Zn ²⁺ ,Ni ²⁺)					
9.684	100	3.300	15	2.428	10
4.838	35	3.113	14	2.338	15
4.478	8	2.703	35	2.050	8
3.538	10	2.588	37	1.56	b
(Zn ²⁺ ,Co ²⁺)					
9.684	100	3.293	22	2.711	9
4.844	35	3.112	7	2.592	15
3.753	8	2.968	5	2.533	8
3.537	13	2.866	6	2.458	5
3.405	5	2.760	7		
(Zn ²⁺ ,Cu ²⁺)					
6.961	100	2.567	11	1.80 ^b	(2)
3.478	34	2.506	6	1.74 ^b	(3)
3.044	2	2.23 ^b	(2)	1.58 ^b	(2)
2.748	4	2.18 ^b	(5)	1.56 ^b	(2)
2.726	3	2.10 ^b	(3)		
(Cu ²⁺ ,Zn ²⁺)					
6.969	100	2.540	8	2.12 ^b	(4)
3.484	36	2.321	2	1.78 ^b	(2)
2.769	2	2.16 ^b	(4)	1.742	3
2.707	2				
(Ni ²⁺ ,Cu ²⁺)					
6.906	100	2.523	3	1.779	4
4.109	2	2.459	18	1.727	3
3.625	2	2.262	10	1.711	7
3.453	48	2.154	5	1.587	4
2.789	5	2.074	12	1.571	4
2.666	18	1.850	4		
(Cu ²⁺ ,Ni ²⁺)					
6.911	100	2.682	9	2.11 ^b	(7)
4.092	2	2.520	31	1.77 ^b	(4)
3.469	38	2.31 ^b	(4)	1.74 ^b	(4)
2.753	5	2.144 ^b	11		
(Cu ²⁺ ,Co ²⁺)					
6.960	100	2.760	3	2.12 ^b	(4)
3.481	34	2.541	12	1.78 ^b	(3)
2.767	2	2.16 ^b	(5)	1.74 ^b	(4)

^a Siemens Kristalloflex, monochromator, Cu K α ; intensities estimated from peak heights; samples air-dried at 65 °C. ^b Broadened reflection (or band).

the metal ions themselves. For instance, ZnO dispersed in Ni(NO₃)₂ solution transforms into ZnNi_{0.56}(NO₃)_{0.53}(OH)_{2.59}; in Co(NO₃)₂ and Cu(NO₃)₂ solutions hydroxy double salts with the composition ZnCo_{0.39}(NO₃)_{0.44}(OH)_{2.33} and ZnCu_{1.5}(NO₃)_{1.13}(OH)_{3.88} are obtained.

The X-ray powder diagrams show strong and sharp (00l) reflections and a few other lines (Figure 1; Tables III and IV). The reaction of ZnO with Cu²⁺ solution produces a (Zn²⁺,Cu²⁺) HDS different from that obtained by reacting CuO with Zn²⁺ solution. The diagrams (Figure 1) are not too different but the

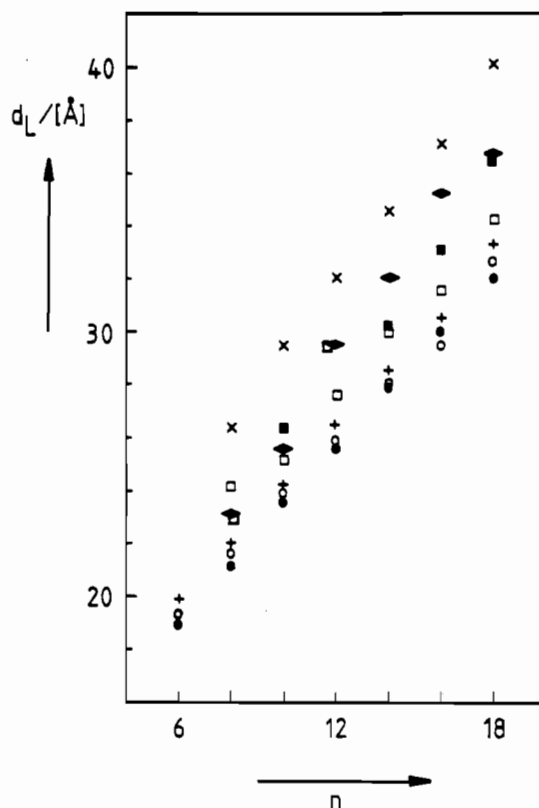


Figure 2. Basal spacings of the alkyl sulfate derivatives of hydroxy double nitrates (HDS's) and layered double hydroxides (LDH's) in equilibrium with surfactant solution. n is the number of carbon atoms in the alkyl chain. HDS: \times (Zn²⁺,Co²⁺); \blacklozenge (Cu²⁺,Co²⁺); \blacksquare (Ni²⁺,Cu²⁺); \square (Zn²⁺,Ni²⁺). LDH: $+$ (Li⁺,Al³⁺); \circ (Zn²⁺,Al³⁺); \bullet (Cu²⁺,Cr³⁺).

(Zn²⁺,Cu²⁺) salt is blue and the (Cu²⁺,Zn²⁺) salt is nearly black. A similar observation was made for (Ni²⁺,Cu²⁺) HDS from NiO and Cu(NO₃)₂ solution (blue-green) and (Cu²⁺,Ni²⁺) HDS from CuO and Ni(NO₃)₂ solution (black).

The basal spacings of the hydroxy salts before washing and drying ("under mother liquor") are 6.9 and 9.7 Å (Table III). Drying at 65 or 100 °C did not change the spacing of the 6.9-Å compounds. Under the same conditions the spacing of the (Zn²⁺,Ni²⁺) and (Zn²⁺,Co²⁺) hydroxy salts decreases to 8.9 Å; in water, the 8.9-Å samples rehydrate to 9.7-Å compounds.

Alkyl Sulfate Derivatives. Alkyl sulfate anions C_{*n*}H_{2*n*+1}SO₄⁻ react easily with hydroxy double nitrates and replace quantitatively the nitrate ions. The amount of surfactant anions bound (from C analysis after washing and drying) can even be larger than the NO₃⁻ content, indicating that hydroxyl ions are also bound as gegenions (see below). The X-ray powder diagrams of the exchanged samples show sharp basal reflections of several orders. The spacings increase linearly or nearly linearly with the alkyl chain length (Figure 2). They are distinctly higher than the spacings of typical LDH derivatives. Washing and vacuum-drying at 65 °C reduce the spacings of the (Zn²⁺,Ni²⁺) and (Zn²⁺,Co²⁺) HDS by about 2 and 3.6 Å (on an average). The changes are moderate (mostly <1 Å) for the other hydroxides (Table V).

The arrangement of the alkyl sulfate ions between the layers of double hydroxides was discussed in some detail.⁹ When the derivatives are in equilibrium with the surfactant solution, the alkyl chains are aggregated in monolayers and tilted at angles $\alpha \approx 60^\circ$ (α = angle between the chain length axis and the surface of the layer). Probably, a water monolayer is inserted between the nonpolar chain ends and the layer.^{7,10} By drying (65 °C,

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Table V. Basal Spacing of the Alkyl Sulfate Hydroxy Double Salts (Alkyl Sulfate = $C_nH_{2n+1}SO_4^-$)

<i>n</i>	(Zn ²⁺ ,Ni ²⁺) basal spacing (Å)			(Zn ²⁺ ,Co ²⁺) basal spacing (Å)			(Zn ²⁺ ,Cu ²⁺) basal spacing (Å)			(Ni ²⁺ ,Cu ²⁺) basal spacing (Å)		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
8	24.2	22.9	21.3	26.4	23.3	20.8	23.0	22.8	22.8	23.1	23.0	22.4
10	25.2	24.5	23.9	29.5	27.6	25.2	26.0	25.9	25.9	26.4	26.2	25.4
12	27.6	26.9	25.6	32.1	30.6	29.0	29.0	28.8	28.8	29.5	29.2	28.2
14	30.0	29.2	27.6	34.6	32.7	31.0	31.6	31.0	31.0	30.2	30.0	29.7
16	31.6	31.3	30.0	37.2	36.1	36.1	34.6	34.0	34.0	33.1	32.5	32.5
18	34.3	34.1	32.1	40.2	39.0	36.8	37.2	37.2	37.2	36.6	35.8	35.6

^a In equilibrium with the surfactant solution. ^b Washed and air-dried at 65 °C (24 h). ^c Sample described in footnote *b*, dried in vacuum at 65 °C (24 h).

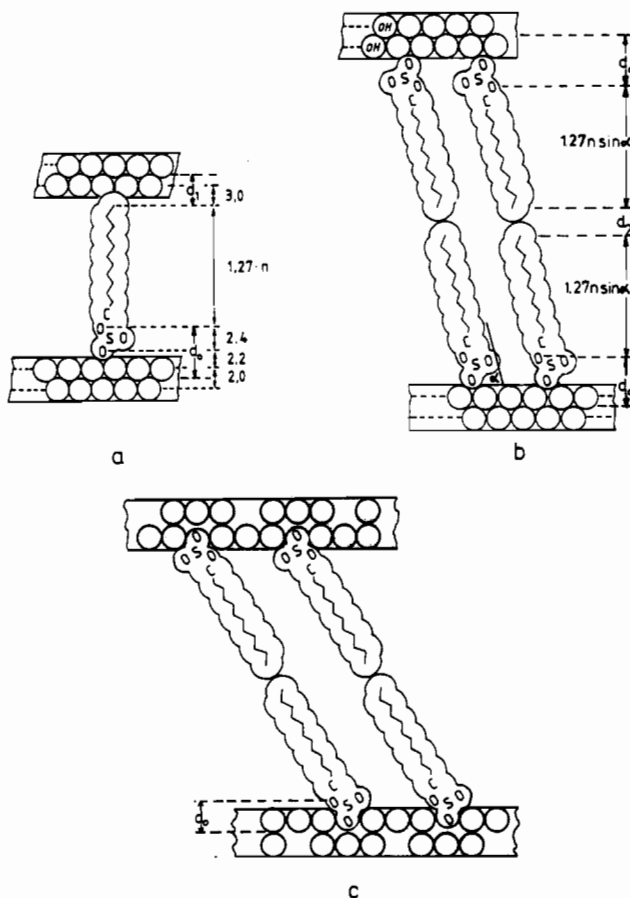


Figure 3. Interlamellar orientation of surfactant anions (alkyl sulfates): (a) monolayers, chains perpendicular; (b) bilayers, chains tilted, α = angle of tilt (between the chain length axis and the layer); (c) bilayers, chains tilted. The sulfate ions replace OH groups of the layer. The structure of the layer is that of $[Cu_2(OH)_3NO_3]^{16}$ with $C_nH_{2n+1}SO_4^-$ replacing NO_3^- (cf. Figure 6a).

vacuum), the compounds lose these additive water molecules and the orientation of the chains changes. In certain double hydroxides (for instance (Zn^{2+},Cr^{3+}) LDH), the chains move into a more perpendicular orientation; in other cases, the angle of tilt decreases slightly ((Li^+,Al^{3+}) and (Cu^{2+},Cr^{3+}) LDH,¹⁰ (Zn^{2+},Cr^{3+}) LDH⁹).

The basal spacings of alkyl sulfate hydroxy double salts indicate bilayers of alkyl sulfate ions between the hydroxide layers. The spacings are calculated by the equations (cf. Figure 3a,b)

$$\text{monolayers: } d_L = d_0 + 1.27n \sin \alpha + d_1 \quad (1)$$

$$\text{bilayers: } d_L = 2d_0 + 2.54n \sin \alpha + d_2 \quad (2)$$

The additive terms are d_0 = distance between the center of the layer and the sulfate oxygen ion, d_1 = distance of the terminal methyl group from the center of the layer, and d_2 = distance between the chain ends in the bimolecular structure (≈ 3 Å).

The (Zn^{2+},Ni^{2+}) and (Zn^{2+},Co^{2+}) hydroxy salts in the dried state have a basal spacing of 8.9 Å, identical to that of the (Zn^{2+},Cr^{3+}) double hydroxide. One may assume that the thickness of the layer and the distance of the end groups of the surfactant anions from the center of the layers are as in the layered double hydroxides. In this case, $d_0 \approx 5.6$ Å, $d_1 \approx 4$ Å (Figure 3a,b), and the spacings are

$$\text{monolayers: } d_L = 9.6 + 1.27n \sin \alpha \quad (\text{Å}) \quad (1a)$$

$$\text{bilayers: } d_L = 14.2 + 2.54n \sin \alpha \quad (\text{Å}) \quad (2a)$$

The basal spacings of the dried derivatives of the (Zn^{2+},Ni^{2+}) hydroxy salt with $n = 14, 16, 18$ correspond to monolayers of perpendicular chains. When n is smaller, the experimental spacings are 1.6 Å higher than calculated. Therefore, it is more likely that the surfactant anions are arranged in bilayers. Good agreement is attained for $\alpha = 22^\circ$ (Figure 4a). In equilibrium with the surfactant solution, additional water molecules and pairs of surfactant + gegenion are adsorbed between the layers and increase the basal spacing by 1.3–2.9 Å.

The spacings of the (Zn^{2+},Co^{2+}) derivatives are distinctly higher. The angle of tilt is about 36° for the samples in equilibrium with surfactant solution (Figure 4a).

With exception of (Zn^{2+},Ni^{2+}) and (Zn^{2+},Co^{2+}) , the hydroxy double salts listed in Table III have the same basal spacing as $[Cu_2(OH)_3NO_3]$ (≈ 6.9 Å). Therefore, the distance d_1 may be derived from the model that a nitrate group is replaced by a sulfate group and $d_1 \approx 6.9/2 \approx 3.5$ Å (Figures 3c and 6a). The basal spacings for bilayers are then calculated from

$$d_L = 10 + 2.54n \sin \alpha \quad (\text{Å}) \quad (3)$$

Good agreement between observed and calculated spacings is attained for angles of tilt between 35 and 40° (washed and vacuum-dried samples) (Figure 4b). The spacings of samples in equilibrium with the surfactant solution are only slightly larger (Table V), and the angles of tilt are nearly the same.

In most HDS derivatives, the angle of tilt decreases slightly with increasing chain length. When long-chain amines are intercalated into neutral layer compounds, α is constant or, in a few cases, increases.¹² The van der Waals interaction increasing with the chain length attracts a larger number of alkylamines per unit area of the interlayer space, which increases α . When long-chain ions are bound by exchange processes, the number of these organic ions is constant when the degree of exchange is independent of the chain length, and the increased van der Waals interaction between longer chains can decrease the angle of tilt.

The angles of tilt in the bimolecular structures are relatively small. It was argued that such bimolecular structures probably will not contain the chains in an all-trans conformation but in conformations with isolated gauche bonds (or similar conformations like gtg).^{11–14} When the distribution of gauche bonds

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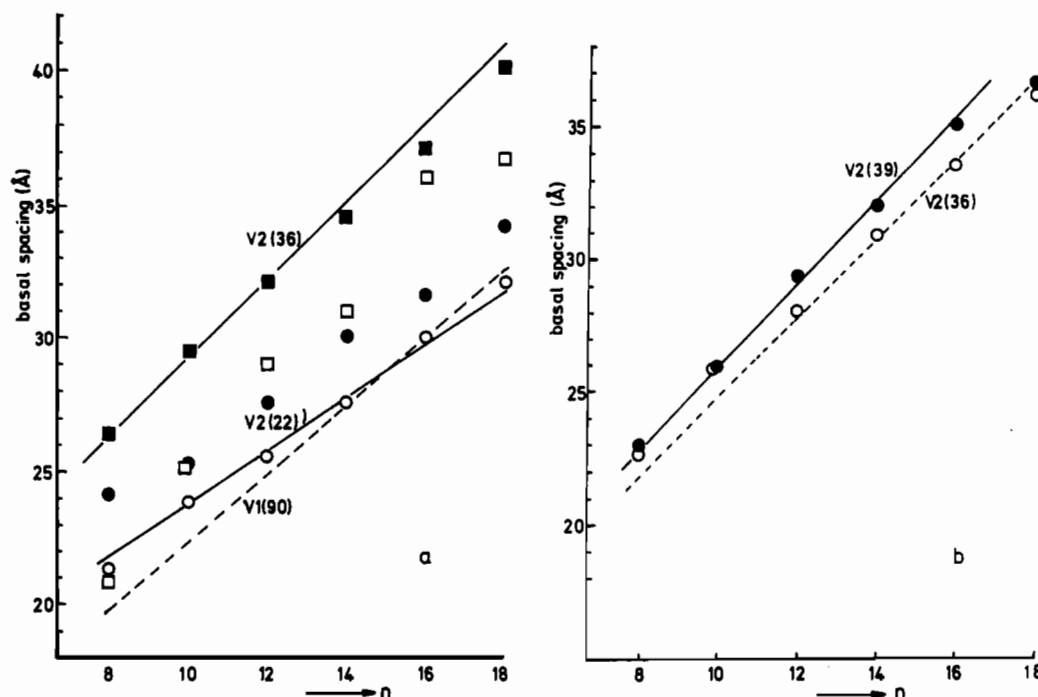


Figure 4. Basal spacings of hydroxy double salts after reaction with alkyl sulfates $C_nH_{2n+1}SO_4^-$. Interlamellar structure: V1(90°) monolayers of perpendicular chains (Figure 3a), basal spacings calculated by eq 1a; V2(α), bilayers of tilted chains (Figure 3b,c), basal spacings calculated (a) by eq 2a and (b) by eq (3). Key: (a) ●, ○ (Zn^{2+}, Ni^{2+}) and ■, □ (Zn^{2+}, Co^{2+}); (b) ○ and □, compounds washed and dried in vacuum at 65 °C (24 h); ● and ■, compounds in equilibrium with surfactant solution.

Table VI. Basal Spacing of Hydroxy Double Salts after Reaction with Secondary Alkanesulfonates (n = Number of Carbon Atoms in the Alkanesulfonate Ion)

n	(Zn^{2+}, Ni^{2+}) basal spacing (Å)		(Zn^{2+}, Co^{2+}) basal spacing (Å)		(Zn^{2+}, Cu^{2+}) basal spacing (Å)		(Cu^{2+}, Co^{2+}) basal spacing (Å)	
	a	b	a	b	a	b	a	b
11	26.4	23.0	26.8	23.6	24.9	21.6	25.2	24.5
12	27.6	24.4	27.6	25.4	26.0	22.3	25.6	21.8
13	28.7	25.6	29.0	26.1	27.2	23.3	26.4	22.2
14	30.3	17.6	30.7	27.8	28.5	24.7	27.6	23.8
15	31.3	28.5	31.6	29.0	29.5	25.8	28.4	24.2
16	32.1	30.0	32.7	30.0	30.5	27.2	29.5	25.2
17	32.9	30.5	33.6	31.6	31.6	28.1	30.2	26.4

^a In equilibrium with surfactant solution. ^b Washed, air-dried, and vacuum-dried at 65 °C (24 h).

follows a certain regular pattern, gauche blocks are formed. However, the spacings cannot be explained by assuming gauche-block aggregations as in Figure 8 in ref 12. Only the model of interpenetrating chains with one or two gauche bonds (as in Figure 4 in ref 15) can be considered as one possibility. In any way, assuming a dense packing of chains at small angles of tilt would be the simplest explanation. One cannot decide between aggregation of all-trans chains and chains containing gauche bonds, as direct proofs of the presence of gauche bonds are difficult to obtain.

Secondary Alkanesulfonates. These surfactants are technical products which consist of mixtures of different isomers. The isomers differ in the position of the sulfonate group. Nevertheless, sharp (00 l) reflections are observed and a high degree of order is attained when these surfactants are reacted with LDH's. The isomers which form U-type anions (the length of the branches depends on the position of the sulfonate group) arrange in the interlayer space in a way that a constant interlayer separation (constant basal spacing) is attained.⁷

The hydroxy double nitrates react in the same way with secondary alkanesulfonates. The spacings (Table VI) lie between the corresponding values of (Zn^{2+}, Cr^{3+}) and (Li^+, Al^{3+}) double hydroxides.^{7,10} Again, relatively sharp (001) reflections of several orders are measured, which indicate the high regularity of the

interlayer separation. The basal spacings are calculated similarly by those for the double hydroxides. (For the 6.9-Å hydroxy double salts, the reduced thickness of the layer must be taken into consideration.)

The basal spacings of the alkanesulfonate derivatives vary with the composition of the layer (Table VI). The principal question arises as to whether these changes are caused by different angles of tilt or by different pairwise combinations of the U-type anions. Mostly, the changes in d_L would correspond to changes in the angle of tilt by no more than $\pm 5^\circ$ (around 55°) or changes in n_1 or n_2 by ± 1 (cf. eqs 1–3 in ref 7). So, it cannot be decided clearly between both possibilities. Only in the case of the extremely high spacings observed for (Zn^{2+}, Co^{2+}) and (Zn^{2+}, Ni^{2+}) hydroxy double alkanesulfonates is an almost perpendicular orientation of the chains the most likely arrangement.

Short-Chain Acid Anions. The reactivity of the hydroxy double nitrates with short-chain acid anions is reduced compared to that of LDH's. For instance, the nitrate ions of most LDH's are displaced by the anions of benzoic acid, aminobenzoic acid, salicylic acid, phthalic acid, terephthalic acid, tartaric acid, succinic acid, etc.,^{7,10} but only a few hydroxy double nitrates react with these anions. The most reactive members among the hydroxy double nitrates are (Zn^{2+}, Co^{2+}) and (Zn^{2+}, Ni^{2+}) hydroxides.

Interlamellar Sorption. The alkyl sulfate derivatives adsorb neutral molecules or ionic pairs in the interlayer space. This is

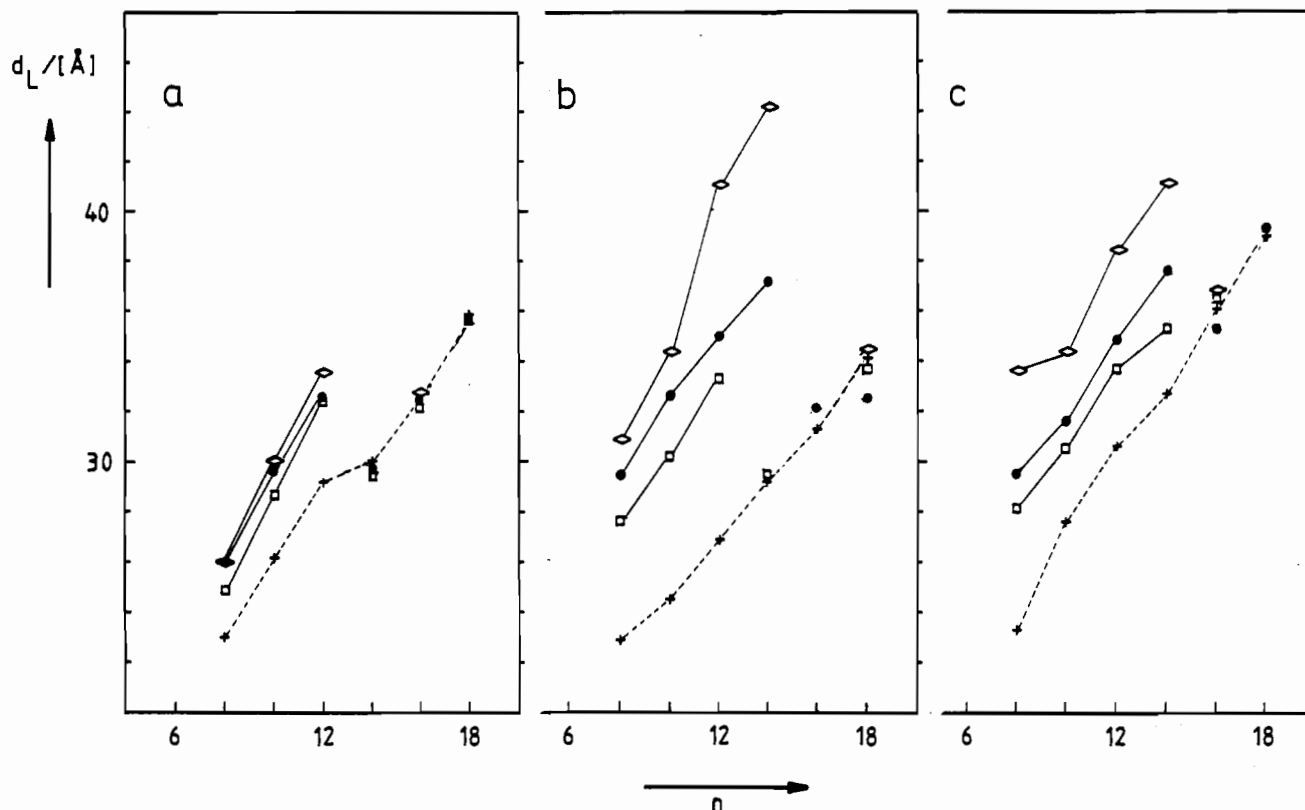


Figure 5. Basal spacings of alkyl sulfate hydroxides after intercalation of alcohols: (a) (Ni^{2+} , Cu^{2+}); (b) (Zn^{2+} , Ni^{2+}); (c) (Zn^{2+} , Co^{2+}). n is the number of carbon atoms in the alkyl sulfate ion. Key: \square , 1-hexanol; \bullet , 1-octanol; \diamond , 1-decanol; broken lines, basal spacings of the alkyl sulfate hydroxy double salts, washed and dried in vacuum at 65°C .

clearly seen by the basal spacings which, in equilibrium with the surfactant solution, are larger than they after washing and drying (Table V, Figure 4). The extents of interlamellar sorption are different for the various hydroxy double salts. The spacings of the (Zn^{2+} , Co^{2+}) derivatives are 3.6 \AA (average value) larger, for the (Zn^{2+} , Ni^{2+}) HDS the average increase is 2.1 \AA , and for the other hydroxides it is $0.6\text{--}0.9\text{ \AA}$ only.

The alkyl sulfates of HDS (after washing and drying) easily adsorb primary 1-alkanols with considerable interlayer expansion, provided the surfactant anions are not too long. For instance, hexanol, octanol, and decanol are adsorbed by derivatives with $n = 6\text{--}14$ for (Zn^{2+} , Ni^{2+}) and (Zn^{2+} , Co^{2+}) HDS and with $n = 6\text{--}12$ for (Ni^{2+} , Cu^{2+}) HDS (Figure 5).

Alcohol adsorption in (Zn^{2+} , Ni^{2+}) and (Zn^{2+} , Co^{2+}) HDS derivatives (Figure 5b,c) causes an interlamellar rearrangement in a way that the chains move into a perpendicular orientation. The spacings are determined by pairs of alkyl sulfate ions and alcohol molecules.⁹ They are calculated by the equation

$$d_L = d_0 + 1.27n_1 + 3.0 + d_3 \quad (4)$$

where $n_1 = n(\text{alkyl sulfate}) + n(\text{alcohol})$, $d_0 = 5.6\text{ \AA}$ (for (Zn^{2+} , Ni^{2+}) and (Zn^{2+} , Co^{2+}) HDS), and d_3 is the distance of the OH group of the alcohol from the center of the layer ($=3.2\text{ \AA}$; cf. Figure 4 in ref 9). With a few exceptions, the observed spacings are $1\text{--}2.3\text{ \AA}$ smaller than calculated, which seems to be a consequence of kink formation (see, for instance, Figure 4b in ref 9). In most cases, the observed spacing decreases somewhat when, at $n_1 = \text{constant}$, $n(\text{alkyl sulfate})$ decreases. This indicates that the interlayer also contains some pairs of two alkyl sulfate ions besides the pairs alkyl sulfate ion + alcohol.

The derivatives of the (Ni^{2+} , Cu^{2+}) HDS assume a different interlamellar structure when alcohols are intercalated. The increase of the spacing is distinctly smaller than for the other hydroxides and not so different for hexanol, octanol, and decanol (Figure 5a). The spacing seems to be determined by pairs of two

surfactant ions (as in the dried samples), but the angle of tilt is increased to 47° (hexanol), 51° (octanol), and 52° (decanol). These results again illustrate the variety of alkyl chain arrangements that form in the interlayer space of hydroxy double salts.

Discussion

A layered hydroxide of type $[(\text{Me}, \text{M})(\text{OH})_2]$ formed by reacting MeO with a M^{2+} solution should not be able to undergo anion-exchange reactions. Simply, a part of the Me^{2+} cations of the brucite layers are replaced by M^{2+} cations. However, a certain modification of the structure can result in anion-exchange behavior.

One group of compounds forms when the second anion is nitrate; the compounds may be derived from $[\text{Cu}_2(\text{OH})_3\text{NO}_3]$ by substituting Cu^{2+} by other divalent metal ions. The structure of $[\text{Cu}_2(\text{OH})_3\text{NO}_3]$ consists of $[\text{Cu}_2(\text{OH})_4]$ layers where 25% of the OH^- ions are replaced by NO_3^- anions.¹⁶ One oxygen ion of the NO_3^- group occupies the position of one hydroxide ion of the layer whereas the two further oxygen ions lie between the hydroxide layers (Figure 6a; cf. also Figure 3c). These oxygen ions of the nitrate groups form single layers between the $[\text{Cu}_2(\text{OH})_3]$ layers. Feitknecht and Maget⁶ and Feitknecht¹⁷ report spacings of $5.4\text{--}5.8\text{ \AA}$ for the double hydroxy chlorides with Cu^{2+} as the main cation. The spacing of the double hydroxy nitrates ($=6.9\text{ \AA}$) is $1.1\text{--}1.5\text{ \AA}$ larger, which corresponds to the difference between the ionic radii of NO_3^- (4.98 \AA) and Cl^- (3.62 \AA).

The basic copper nitrate reacts very easily with alkyl sulfate and alkanesulfonate ions, and the nitrate ions are replaced by the sulfate or sulfonate groups. All hydroxy double nitrates with a basal spacing of 6.9 \AA (Table III) react in the same way.

The chemical composition of the (Ni^{2+} , Cu^{2+}) hydroxy salt deviates from the ideal composition $[(\text{Cu}, \text{Ni})_2(\text{OH})_3\text{NO}_3]$. The

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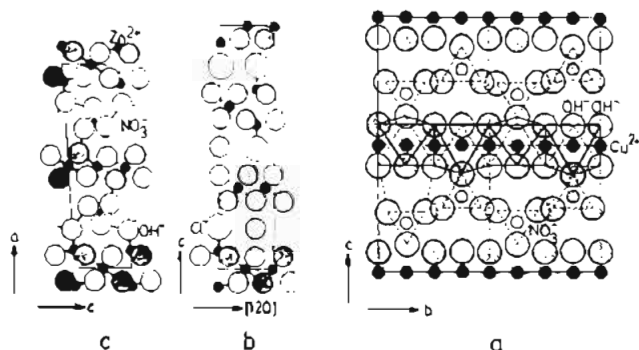
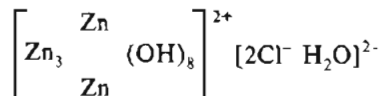


Figure 6. Structures of hydroxy double salts: (a) $[\text{Cu}_2(\text{OH})_3\text{NO}_3]$, \circ and \bullet , OH above and below the plane of projection, respectively;¹⁶ (b) $[\text{Zn}_5(\text{OH})_8]\text{Cl}_2 \cdot \text{H}_2\text{O}$;²¹ (c) $[\text{Zn}_5(\text{OH})_8](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.²¹

analytical composition $[\text{Cu}_{1.91}\text{Ni}_{0.09}(\text{OH})_{3.17}(\text{NO}_3)_{0.83}]$ makes evident that a smaller amount of lattice OH^- groups are substituted by NO_3^- anions.

The second type of anion-exchanging hydroxy double salts is derived from basic zinc hydroxide: $[\text{Zn}_5(\text{OH})_8](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Zn}_5(\text{OH})_8]\text{Cl}_2 \cdot \text{H}_2\text{O}$.¹⁸⁻²¹ The structure consists of brucite-type $[\text{Zn}_3(\text{OH})_8]^{2-}$ layers with 25% of the octahedral positions remaining unoccupied. Above and below the unoccupied octahedral positions, two further zinc ions per formula unit occupy tetrahedral positions (Figure 6b,c). The tetrahedra are completed by water molecules or chloride ions lying between the $[\text{Zn}_5(\text{OH})_8]^{2-}$ layers. In this way, the layers themselves obtain a positive charge.²² Allmann²² proposed to represent the composition by the formula



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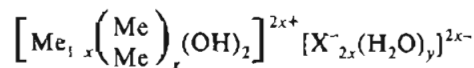
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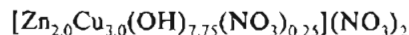
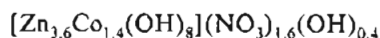
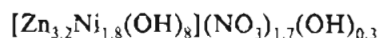
or generally



Stählin and Oswald²³ describe topotactic reactions between $[\text{Zn}_5(\text{OH})_8](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and solutions of MCl_2 . NO_3^- ions are replaced by Cl^- ions and Zn^{2+} ions by Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and even Na^+ . Co^{2+} and Ni^{2+} ions occupy octahedral and tetrahedral positions. (The reaction with Cu^{2+} finally leads to the destruction of the $[\text{Zn}_5(\text{OH})_8]^{2+}$ structure with formation of $\beta\text{-}[\text{Cu}_2(\text{OH})_3\text{Cl}]$.)

The studies of Stählin and Oswald²³ prove that Zn^{2+} ions can be easily substituted by other metal ions, so that it is very likely that products from the reactions between ZnO and $\text{M}(\text{NO}_3)_2$ solutions obtain their positive layer charge similarly to $[\text{Zn}_5(\text{OH})_8](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ or $[\text{Zn}_5(\text{OH})_8]\text{Cl}_2 \cdot \text{H}_2\text{O}$. The basal spacing of the compounds derived from $[\text{Zn}_5(\text{OH})_8](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ typically is 9.8 Å and decreases to 8.9 Å upon drying (Table III).

The products obtained from ZnO and $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, and $\text{Cu}(\text{NO}_3)_2$ are formulated as



The first two formulas make evident that NO_3^- ions in the interlayer space may be replaced by OH^- anions. (This exchange is also typical of layered double hydroxides.) In the $(\text{Zn}^{2+}, \text{Cu}^{2+})$ hydroxide, the NO_3^- content is very high and a certain part of the NO_3^- ions may be incorporated into the $(\text{Zn}^{2+}, \text{Cu}^{2+})$ hydroxide layers similarly to their incorporation in $[\text{Cu}_2(\text{OH})_3\text{NO}_3]$. This also demonstrates the variability of the chemical composition of the hydroxy double salts.

Acknowledgment. We thank Dr. Quack (Hoechst AG) for donation of the secondary alkanesulfonates. We are also grateful to the Fonds der Chemischen Industrie for financial support.

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