

# The Topotactic Reaction of Zinc Hydroxide Nitrate with Aqueous Metal Chloride Solutions

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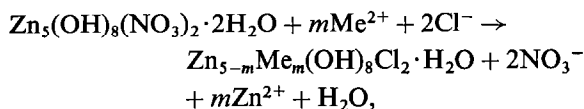
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The topotactic reaction of zinc hydroxide nitrate with aqueous solutions of  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{ZnCl}_2$  yields perfect pseudomorphs of  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  after zinc hydroxide nitrate. With  $\text{MnCl}_2$  and  $\text{NaCl}$  solutions, the nitrate is exchanged by chloride but neither  $\text{Na}^+$  nor  $\text{Mn}^{2+}$  is built into the lattice of zinc hydroxide chloride. The pseudomorphs give an X-ray diffraction pattern which is, disregarding a certain amount of disorder, identical with the single crystal pattern of zinc hydroxide chloride. The relative orientation of the lattices is given by: (100) zinc hydroxide nitrate is parallel to (001) zinc hydroxide chloride and [010] is parallel to [100]. The optical spectra of the pseudomorphs reveal that  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  occur in tetrahedral and octahedral coordination as well. Therefore, these ions are mainly built into the intermediate layer where they occupy tetrahedral sites, but also into the close packed main layer where they are coordinated by six hydroxide ions. The atomic displacements necessary in the course of the reaction are deduced from the crystal structures of the two compounds. The mechanism of the topotactic reaction is believed to consist in oriented nucleation and crystal growth.

## Introduction

The reaction of zinc hydroxide nitrate with aqueous solutions of cobalt, nickel and zinc chloride, yielding pseudomorphs of zinc hydroxide chloride after zinc hydroxide nitrate, has first been described by Feitknecht (1). Oswald (2) has found the concentration range appropriate for a topotactic reaction with cobalt chloride to be 0.02 to 2 M. Higher concentrations yield products of the  $\beta\text{-Co}_2(\text{OH})_3\text{Cl}$  type. Lower concentrations give products of the  $\text{Zn}_5(\text{OH})_9\text{Cl} \cdot \text{aq}$  type. Oswald compared the green colour of the specimen  $(\text{Zn,Co})_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$  obtained from the topotactic reaction with the pink colour of a preparation of similar composition prepared by coprecipitation of mixed zinc and cobalt chloride solution with aqueous sodium hydroxide. He assumed that the green colour is due to cobalt ions in tetrahedral coordination which should be a consequence of the topotactic reaction.

The present paper reports on a study of the reaction



where  $\text{Me}^{2+}$  is  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $2\text{Na}^+$ . The crystal structure of  $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot$

$2\text{H}_2\text{O}$  has recently been determined by Stählin and Oswald (3); it is monoclinic, space group  $C2/m$ . The crystal structure of  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ , which is the parent compound of  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$  has been described by Nowacki and Silverman (4) in the rhombohedral space group  $R\bar{3}m$ . The structures can be regarded as a variation of a hypothetical  $\text{Zn}(\text{OH})_2$  structure in the  $\text{Mg}(\text{OH})_2$  or  $C6$  type. One quarter of the zinc atoms in octahedral interstices are removed from the close packed layer. Above and below the empty octahedra there are tetrahedrally coordinated zinc atoms in an intermediate layer which further contains the anions and the water molecules.

## The Topotactic Reaction

Zinc hydroxide nitrate either as a microcrystalline substance (crystal diameter 5–10  $\mu\text{m}$ ) or as single crystals ( $0.2 \times 0.2 \times 0.03$  mm) was brought into contact with aqueous solutions of  $\text{MnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$ , and  $\text{NaCl}$ . The reaction was carried out at room temperature. The results can be summarized as follows:

A topotactic reaction takes place with solutions of the following metal chlorides:  $\text{MnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{NaCl}$ . In all these cases nitrate is

substituted by chloride.  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  are built into the lattice of the product yielding a substance of the following general formula:  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ . The reaction with  $\text{CuCl}_2$  is not topotactic and yields  $\beta\text{-Cu}_2(\text{OH})_3\text{Cl}$ , which is an intergrowth of  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$  (Paratacamite) and  $\delta\text{-Cu}_2(\text{OH})_3\text{Cl}$  (Atacamite) (6).

The concentration of Co or Ni in the product does no longer change, when the substitution of the anions, chloride for nitrate, has come to an end. The Co:Zn ratio in  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  reaches a value of 1:5, whereas the Ni:Zn ratio is approximately 1:6.

The reaction rate decreases when the chloride concentration is lowered and depends further on the nature of the cation present.

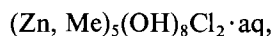
For low concentrations of chloride the reaction yields a product which has the structural type of  $\text{Zn}_5(\text{OH})_9\text{Cl} \cdot \text{aq}$ . This substance is obtained with a maximum concentration of 0.1 *M* for  $\text{CoCl}_2$ , 0.2 *M* for  $\text{NiCl}_2$ , and 1 *M* for  $\text{MnCl}_2$ . It was not possible to isolate a pure  $(\text{Zn, Me})_5(\text{OH})_9\text{Cl} \cdot \text{aq}$  neither with  $\text{NiCl}_2$  nor with  $\text{CoCl}_2$ , as there was always  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  present as well. Therefore, it is not possible to decide whether cobalt or nickel is built into the lattice of  $\text{Zn}_5(\text{OH})_9\text{Cl} \cdot \text{aq}$ . The reaction with manganese chloride yields pure  $\text{Zn}_5(\text{OH})_9\text{Cl} \cdot \text{aq}$  but no manganese can be found in this product.

### Characterization of the Compounds

#### $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$

##### X-Ray Diffraction Investigations

The lattice constants of various



as determined by X-ray powder diffraction, are given in Table I.

The difference between the largest and the smallest value of the lattice constant *a* is 0.54% corresponding to seven times the standard deviation. Therefore, the decrease in *a* for the compound  $(\text{Zn, Ni})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  is significant. On the other hand the values of the lattice constant *c* are within an interval of three times the standard deviation and thus are not significantly different. The amount of the change in the lattice constant *a* with the decreasing ionic radii 0.74 Å for  $\text{Zn}^{2+}$ , 0.72 Å for  $\text{Co}^{2+}$ , and 0.69 Å for  $\text{Ni}^{2+}$  is reasonable.

The orientation of the lattices of zinc hydroxide nitrate and zinc hydroxide chloride, as determined by single-crystal X-ray diffraction, is

$$(100)_{\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}} \parallel (001)_{\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}}, \\ [010] \parallel [100].$$

X-ray diffraction photographs of the layers (*hk*0), (*hk*1), (*hk*2), (*0kl*), (*1kl*), and (*2kl*) can be indexed with the rhombohedral unit cell which has been given by Nowacki and Silverman (4). Photographs of the layers (*0kl*), (*1kl*), and (*2kl*) show that the reflections are sickle shaped and elongated in the hexagonal direction [001]. Some of the reflections in the layers (*hk*0), (*hk*1), and (*hk*2) seem not to fulfill the condition for rhombohedral centering:  $-h + k + l = 3n$ . But it can be shown that all these reflections are due to lattice spikes centered on reciprocal lattice points allowed by the above mentioned condition. This interpretation is further confirmed by the fact that most of the "forbidden" reflections are doubled. In this case two sickles are responsible for the "forbidden" reflection, e.g. "(020)" is due to the (021) and (02 $\bar{2}$ ) reflections.

The sickle shape of the reflections is caused by a misalignment of the numerous small crystallites, which build up the pseudomorph. These are very thin and tilted in respect to (001). On the other hand,

TABLE I  
HEXAGONAL UNIT CELL DIMENSIONS OF VARIOUS  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$

Sample	<i>a</i>	<i>c</i>	Reference
$\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$	6.34 ± 0.01	23.64 ± 0.02	(4)
$\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$	6.34	23.66	(5)
$\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}^a$	6.344 (4)	23.66 (2)	
$\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ [1] <sup>b</sup>	6.344 (4)	23.68 (2)	
$(\text{Zn, Co})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ [2]	6.330 (4)	23.70 (2)	
$(\text{Zn, Ni})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ [3]	6.310 (4)	23.73 (2)	
$\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ [4]	6.344 (4)	23.66 (2)	
$\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ [5]	6.344 (4)	23.68 (2)	

<sup>a</sup> This product was prepared after Nowacki and Silverman (4).

<sup>b</sup> The number in parentheses, e.g. [1], refers to the sample number [1] in Table IV.

the crystallites are only slightly rotated around [001], therefore, the photographs of the layers ( $hk0$ ), ( $hk1$ ), ( $hk2$ ) show distinct reflections and only strongly overexposed photographs do show traces of Debye-Scherrer rings. The relative intensities of the reflections of  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  are within the experimental error equal to the ones measured on a crystal of pure  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$  prepared after Nowacki and Silverman (4).

The disorder in the pseudomorphs obtained by reaction of zinc hydroxide nitrate with  $\text{MnCl}_2$  or  $\text{CoCl}_2$  or  $\text{ZnCl}_2$  or  $\text{NaCl}$  solution is approximately the same. A higher degree of disorder can be found in the products  $(\text{Zn, Ni})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ , an observation which can also be made on the X-ray powder diagrams, where  $(\text{Zn, Ni})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  shows the strongest line-broadening within the series. This can be explained by comparing the ionic radii:  $\text{Ni}^{2+}$  has the smallest ionic radius of the ions built into the lattice of  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ , therefore, the degree of distortion of the lattice is the highest.

#### Spectroscopic Investigations

Electronic spectra of  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  were recorded to settle the question of coordination of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  in the lattice of  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ . For comparison spectra of  $\beta\text{-Co}_2(\text{OH})_3\text{Cl}$  and  $\text{CoCl}_2 \cdot 9\text{Co}(\text{OH})_2 \cdot \text{aq}$  were measured. The first compound, which is pink, has a crystal structure where all cobalt ions are octahedrally coordinated (7). Feitknecht and Lotmar (8) have determined the

crystal structure of  $\text{CoCl}_2 \cdot 9\text{Co}(\text{OH})_2 \cdot \text{aq}$  and have found that three out of five cobalt ions are octahedrally and the others tetrahedrally coordinated. In addition to the spectra of  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ , the product of the topotactic reaction, we measured the spectra of the isostructural compounds of analogous composition but prepared by precipitation of mixed  $\text{MeCl}_2$  and  $\text{ZnCl}_2$  solutions after Oswald (6).

Table II gives the electronic spectra of the following compounds:

- (1)  $\text{Zn}_{4.18}\text{Co}_{0.82}(\text{OH})_{8.24}\text{Cl}_{1.76} \cdot 1.18\text{H}_2\text{O}$ ,  
colour, green;
- (2)  $\text{Zn}_{2.86}\text{Co}_{2.14}(\text{OH})_{8.14}\text{Cl}_{1.86} \cdot 3.16\text{H}_2\text{O}$ ,  
colour, pink;
- (3)  $\text{Zn}_{2.35}\text{Co}_{2.65}(\text{OH})_{8.10}\text{Cl}_{1.90} \cdot 2.85\text{H}_2\text{O}$ ,  
colour, greenish grey;
- (4)  $\beta\text{-Co}_2(\text{OH})_3\text{Cl}$ , colour, pink;
- (5)  $\text{CoCl}_2 \cdot 9\text{Co}(\text{OH})_2 \cdot \text{aq}$ ,  
colour, green.

Preparation (1) was obtained by topotactic reaction from  $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , whereas preparations (2) and (3) are coprecipitations of mixed  $\text{CoCl}_2$  and  $\text{ZnCl}_2$  solutions.

Preparations (1) to (3) show an additional band at 7.09 kK which is not due to an electronic transition because it is also found in pure  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ . It is the overtone of the strong  $\nu\text{OH}$  vibration at 3.505 kK. The spectra numbers (1) and (3) are superpositions of the spectra (4) and (5). As the

TABLE II  
ELECTRONIC SPECTRA OF VARIOUS COBALT-ZINC HYDROXIDE CHLORIDES  
(Wavenumbers in kK)

(1)	(2)	Preparations (3)	(4)	(5)
—	—	—	24.2 m	21.8 st, <sup>a</sup> sho <sup>b</sup>
20.7 m <sup>c</sup>	20.7 st, sho	20.7 st, sho	20.4 m, sho	—
18.6 w, <sup>d</sup> sho	—	18.8 st	18.6 st	—
—	18.4 w, sho	—	18.4 w, sho	—
17.0 sho	—	17.1 sho	—	16.8 w, sho
16.2 m	16.0 sho	16.3 m	15.9 w	16.1 m
15.2 st	15.2 st	15.4 st	—	15.2 st
9.1–6.3 st	9.1–6.3 st	9.6–6.3 st	8.47 st	8.33–6.25
			7.53 w	
			7.13 w	

<sup>a</sup> st = strong.  
<sup>b</sup> sho = shoulder.  
<sup>c</sup> m = medium.  
<sup>d</sup> w = weak.

compound (4) contains cobalt in octahedral and the compound (5) in tetrahedral and octahedral sites, the cobalt ions in  $(\text{Zn}, \text{Co})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  must be octahedrally and tetrahedrally coordinated.

This is further corroborated by the band assignment which is based on the Tanabe-Sugano diagram for  $3d^7$  systems and is proposed, according to Pappalardo et al. (9), to be:

$\text{Co}^{2+}$  octahedral coordination:

$$8.1 \text{ kK } {}^4\text{T}_2({}^4\text{F}) \leftarrow {}^4\text{T}_1({}^4\text{F}),$$

16.2 kK (partially obscured by a band of  $\text{Co}_{\text{tet.}}$ ),

$${}^4\text{A}_2({}^4\text{F}) \leftarrow {}^4\text{T}_1({}^4\text{F}),$$

$$18.6; 20.7 \text{ kK } {}^4\text{T}_1({}^4\text{P}) \leftarrow {}^4\text{T}_1({}^4\text{F}).$$

$\text{Co}^{2+}$  tetrahedral coordination:

$$6.5 \text{ kK } {}^4\text{T}_1({}^4\text{F}) \leftarrow {}^4\text{A}_2({}^4\text{F}),$$

$$15.2 \text{ kK } {}^4\text{T}_1({}^4\text{P}) \leftarrow {}^4\text{A}_2({}^4\text{F}),$$

$$16.2\text{--}17.0 \text{ kK } {}^2\text{T}_2, {}^2\text{A}_1 \leftarrow {}^4\text{A}_2({}^4\text{F}).$$

There is a remarkable difference between the preparation obtained by topotactic reaction and the one obtained by coprecipitation of mixed cobalt and zinc chloride solutions. The cobalt ions in the latter compound predominantly occupy octahedral sites and only with high cobalt content also tetrahedral ones, whereas in the first compound the cobalt ions are mainly tetrahedrally but also octahedrally coordinated, although the cobalt content is relatively low.

A similar procedure was followed with the  $(\text{Zn}, \text{Ni})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  preparations. Electronic spectra of (1)  $\text{Zn}_{4.33}\text{Ni}_{0.67}(\text{OH})_{8.15}\text{Cl}_{1.85} \cdot 1.15\text{H}_2\text{O}$  and (2)  $\text{Zn}_{2.73}\text{Ni}_{2.27}(\text{OH})_{8.21}\text{Cl}_{1.79} \cdot 3.58\text{H}_2\text{O}$  were

recorded. The sample (2) is a product obtained by precipitation of mixed  $\text{NiCl}_2$  and  $\text{ZnCl}_2$  solutions. Table III gives the spectra of compounds (1) and (2). The additional band at 7.1 kK is the overtone of the  $\nu\text{OH}$  vibration as explained above.

The bands in spectra of  $(\text{Zn}, \text{Ni})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  are broad, and therefore, the assignment with respect to octahedral and tetrahedral coordination of  $\text{Ni}^{2+}$  cannot be made convincingly. But the investigations on  $(\text{Zn}, \text{Co})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  have shown that the  $\text{Co}^{2+}$  is partially octahedrally but mainly tetrahedrally coordinated and the assumption is reasonable that the same is valid for the  $\text{Ni}^{2+}$  ions.

#### Electron Microscopic Characterisation of $(\text{Zn}, \text{Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$

The product of the topotactic reaction is a perfect pseudomorph of  $(\text{Zn}, \text{Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  after zinc hydroxide nitrate as shown by the electron micrographs (Fig. 1 and 2). The faces ( $hk0$ ) of the hexagonal zinc hydroxide chloride are corrugated, showing the small crystallites building up the pseudomorph. The plane (001), which corresponds to the (100) face of the initial crystals, seems not to be altered, indicating that the metal chloride solution attacks the planes ( $0kl$ ), that means: The reaction proceeds parallel to the plane (100) of zinc hydroxide nitrate.

Selected area electron diffraction photographs of  $(\text{Zn}, \text{Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  (Fig. 3) can be indexed with the trigonal-rhombohedral unit cell (Nowacki and Silverman (4)). The electron diffraction pattern of the layer ( $hk0$ ) contains additional reflections belonging to the layers ( $hk1$ ) and ( $hk\bar{1}$ ), a feature which had already been observed on the single-crystal X-ray diffraction photographs.

If the electron diffraction pictures are taken without an object cooling device and with heavy irradiation, the crystal is heated and slowly decomposes yielding zinc oxide in the orientation  $(001)_{\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}} \parallel (001)_{\text{ZnO}}$  and  $[100] \parallel [100]$ .

#### The Mechanism of the Topotactic Reaction of Zinc Hydroxide Nitrate with Solutions of Metal Chlorides

##### Comparison of the Crystal Structures of Zinc Hydroxide Nitrate and Zinc Hydroxide Chloride

Projections of the crystal structures of the two compounds are shown in Figs. 4 and 5. The relative orientation of the crystallographic axes is the one determined by single-crystal X-ray diffraction. Both

TABLE III

ELECTRONIC SPECTRA OF NICKEL-ZINC HYDROXIDE CHLORIDES (Wavenumbers in kK).

Preparations	
(1)	(2)
26.1 m <sup>a</sup>	25.9 m
24.3 sho <sup>b</sup>	
15.2 st <sup>c</sup>	15.4 st, bd
14.3 st, sho	
10.5–7.4 st	10.5–7.14 st
<sup>a</sup> m = medium.	
<sup>b</sup> sho = shoulder.	
<sup>c</sup> st = strong.	
<sup>d</sup> b = broad.	

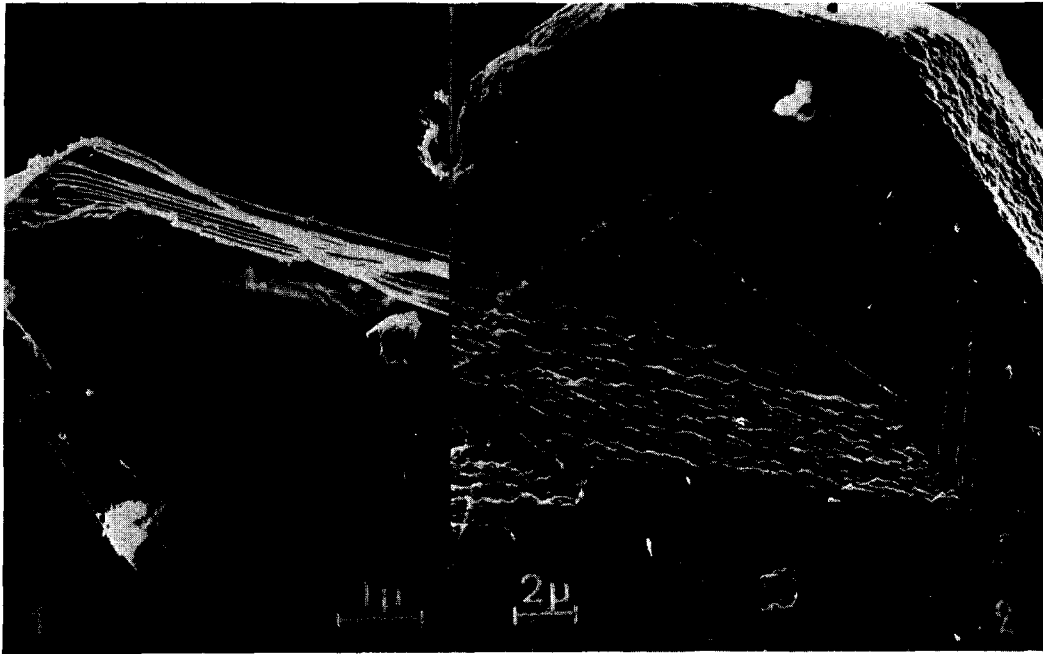


FIG. 1 and 2. Comparison between fracture surfaces of a crystal of the starting material (Fig. 1) and a pseudomorph obtained by reaction of zinc hydroxide nitrate with 0.2 *M*-CoCl<sub>2</sub> solution (Fig. 2).

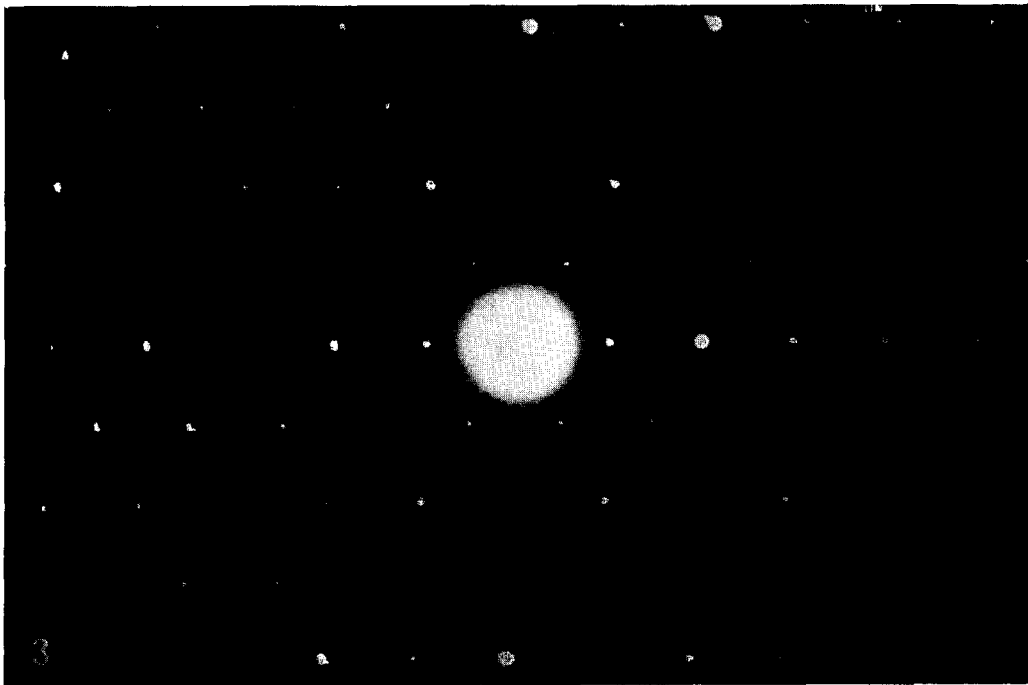


FIG. 3. Selected area electron diffraction photograph of  $(\text{Zn, Co})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  in the (001) orientation.

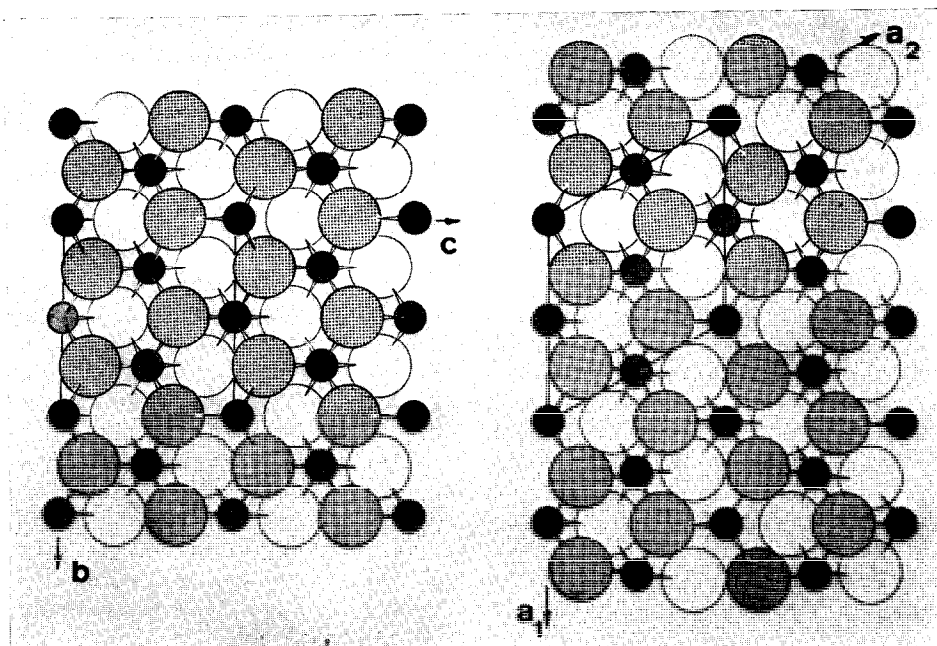


FIG. 4

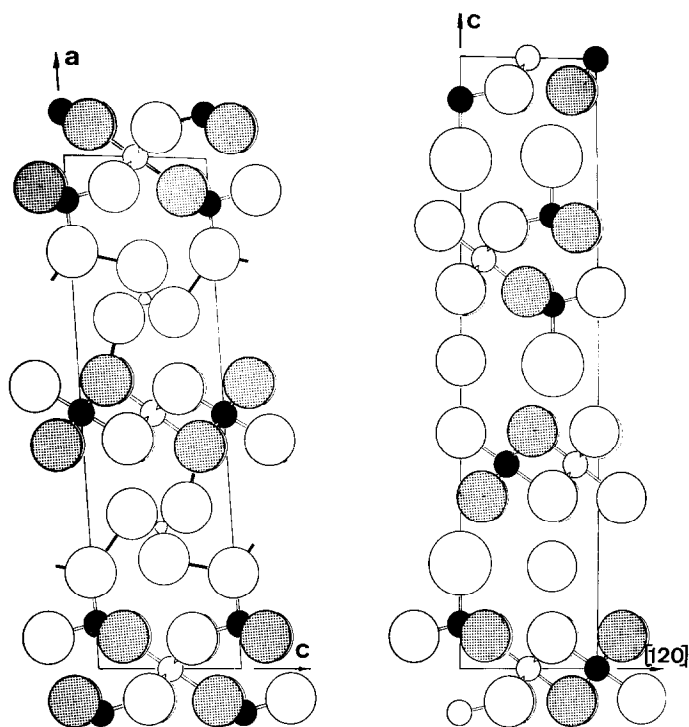


FIG. 5

FIGS. 4 and 5. Comparison of the structures of zinc hydroxide nitrate and zinc hydroxide chloride. Partial projection on the plane ( $b, c$ ) of zinc hydroxide nitrate and ( $a_1, a_2$ ) of zinc hydroxide chloride (Fig. 4). Partial projections along  $b$  of zinc hydroxide nitrate and along  $a_1$  of zinc hydroxide chloride (Fig. 5). The smallest circles represent nitrogen, the small ones zinc, the medium ones oxygen, and the biggest circles chlorine atoms. Shaded circles lie above, empty ones below the plane of the drawing.

structures have similar arrangement of hydroxide ions within one layer: the plane close packing. The main difference in the two structures lies in the position of the tetrahedrally coordinated zinc atoms. In zinc hydroxide nitrate, these atoms are placed following a rectangular net of  $6.238 \times 5.517 \text{ \AA}$ , whereas in zinc hydroxide chloride a hexagonal net of  $6.344 \text{ \AA}$  is realized.

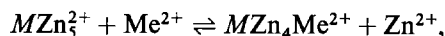
The rectangular net for the tetrahedral atoms cannot be preserved since this would lead to inequalities in the intensities of reflections which are equal in the rhombohedral lattice, e.g. (110) should differ in intensity from  $(\bar{2}10)$ , a feature which has not been detectable. Therefore, the metal atoms have to adopt the order characteristic for pure  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ , that means: One-half of the tetrahedrally and one-sixth of the octahedrally coordinated metal atoms have to leave their positions. As the octahedrally coordinated metal atoms are situated within the close packed layer of hydroxide ions, it appears improbable first, that they should be directly involved in the reaction. Yet the spectroscopic investigations have proved the occurrence of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  in octahedral coordination. Octahedral sites can only be reached by penetrating into the close packed layer. The occurrence of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  in octahedral and tetrahedral coordination thus proves that the above mentioned rearrangement of metal atoms is possible.

The distance between the OH, Zn, OH layers decreases in the course of the reaction from  $a/2 \cdot \sin \beta = 9.73 \text{ \AA}$  to  $c/3 = 7.88 \text{ \AA}$ , reduction of 19%. The pseudomorphs, therefore, consist of thin crystallites piled up along  $c$  alternating with flat holes. In zinc hydroxide nitrate, the layers of hydroxide ions are stacked according to AB AB AB, disregarding a shift of  $a/2 \sin(\beta - 90^\circ) = 0.589 \text{ \AA}$ . But in zinc hydroxide chloride, the stacking sequence is AB BC CA. For the realisation of the latter sequence, a shift of the hydroxide ions of 0.6 to 2.3  $\text{ \AA}$  is needed. The longest diffusion paths have to be covered by the nitrate and zinc ions leaving the crystal and the  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions which are built into the lattice. This mass transport from the faces of the crystal to its centre has to take place mainly within the pores of the pseudomorph, otherwise the relatively high reaction rates cannot be explained.

### Discussion of the Topotactic Reaction

In this paragraph we should like to comment on the dependence of the reaction rate on the concentration and the nature of the metal chloride solution. For this purpose we propose the following

model: At the end of the reaction a stationary state in the crystal is reached,



(where  $M$  means the lattice of the anions).

On this reaction, the mass action law can be applied

$$\frac{[\text{Zn}^{2+}] \cdot [M\text{Zn}_4\text{Me}^{2+}]}{[M\text{Zn}_5^{2+}] \cdot [\text{Me}^{2+}]} = K.$$

$[\text{Zn}^{2+}]$  and  $[\text{Me}^{2+}]$  are the activities of the ions on interstitial positions and  $[M\text{Zn}_4\text{Me}^{2+}]$  and  $[M\text{Zn}_5^{2+}]$  are the activities of the substituted and nonsubstituted hydroxide chloride in the lattice of the reacting crystal. As the constant  $K$  will have characteristic values for different ions  $\text{Me}^{2+}$ , the ratios  $[\text{Zn}]:[\text{Co}] = 5:1$  and  $[\text{Zn}]:[\text{Ni}] = 6:1$  observed in the crystal in equilibrium are merely determined by the value of  $K$ . When a stationary state is reached no change in the  $[\text{Zn}]:[\text{Me}]$  ratio will be observed if the reaction time is increased. Neither  $\text{Na}^+$  nor  $\text{Mn}^{2+}$  ions enter the lattice because these ions are too large:  $r(\text{Na}^+) = 0.97 \text{ \AA}$ ,  $r(\text{Mn}^{2+}) = 0.80 \text{ \AA}$  in comparison to  $r(\text{Zn}^{2+}) = 0.74 \text{ \AA}$ .

The observed decrease in the reaction rate on lowering the chloride concentration must be explained as follows: Prior to the reaction, the chloride ions are adsorbed on the outer and inner surfaces of the reacting crystal. The amount of chloride adsorbed is higher for higher chloride concentrations. Furthermore, the reaction rate depends on the nature of the metal ion present in solution. The reason for such a dependence is not obvious. The end of the reaction is found by powder X-ray diffraction which only indicates the completion of the anion exchange. The metal ion present must influence the chloride activity and thereby the reaction rate. Two possibilities for this can be imagined, (1) the activity of the chloride ions is decreased by complex formation with the cation yielding ions like  $\text{MeCl}^+$ , etc.; and (2) the metal ions are strongly adsorbed to the surface of the crystal thus lowering the concentration of the chloride ions directly adsorbed on the crystal surface.

The first influence alone cannot be responsible for the observed decrease in the reaction rate because the activities of the chloride ions in  $\text{NiCl}_2$  or  $\text{CoCl}_2$  solutions are only lowered by 20 to 30% compared to a  $\text{NaCl}$  solution of the same chloride concentration. Therefore both effects, perhaps together with others, must be responsible for the observed influence of the metal ions on the reaction rate.

In the preceding discussion of the topotactic reaction we have pointed out that the necessary displacements of the atoms in the crystal are rather

big, nevertheless the degree of order in the pseudomorph is high. This may be due to oriented nucleation of the product on inner lattice planes of the reacting crystal. As can be seen in Fig. 4, there are three of four chains of octahedra within the plane ( $b, c$ ) of zinc hydroxide nitrate or ( $a_1, a_2$ ) of zinc hydroxide chloride which are identical in both structures. The fourth is shifted by an amount of  $a_1/2$ . The chains of octahedra which are preserved during the reaction are the starting points for the oriented nucleation of the new phase.

The fact that an only limited, one- or two-dimensional crystal structural relationship between starting crystals and reaction product may be responsible for an astonishingly high degree of topotaxy and the formation of very perfect pseudomorphs was encountered frequently during recent investigations of topotactic reactions [e.g., Oswald and Brunner (10), Günter and Oswald (11–13), Günter (14)]. Thus it seems not to be necessary that the structures involved in a topotactic reaction always bear a close three-dimensional similarity, and the phenomena may at least very often be explained in terms of oriented nucleation and growth of small product crystallites. These nuclei may consist of very small parts of a reacting educt crystal or they may be formed by epitaxy on inner lattice planes.

### Experimental

The reaction of zinc hydroxide nitrate with the metal chloride solutions (0.01–2  $M$ ) took place at

room temperature in air (exception: manganese chloride solutions were handled in purified nitrogen to avoid oxidation). The preparations were either powders (diameter of the crystals 5–10  $\mu\text{m}$ ) or single crystals ( $0.2 \times 0.2 \times 0.03$  mm). Table IV gives the experimental conditions and the results of the reaction of a zinc hydroxide sample of an average crystal size of  $0.2 \times 0.2 \times 0.03$  mm.

In addition to the samples  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$  obtained by the topotactic reaction, products of similar composition were prepared by precipitation of mixed zinc chloride and cobalt or nickel chloride solutions with sodium hydroxide after Oswald (2).  $\beta\text{-Co}_2(\text{OH})_3\text{Cl}$  was prepared after Oswald (6) by reaction of Co metal with  $\text{CoCl}_2$  solution.  $\text{CoCl}_2 \cdot 9\text{Co}(\text{OH})_2 \cdot \text{aq}$  was obtained by precipitation of  $\text{CoCl}_2$  solution with aqueous sodium hydroxide (Feitknecht and Fischer (15)). The compounds were analyzed for zinc, cobalt and nickel by atomic absorption spectroscopy and for chloride by potentiometric titration.

The experimental conditions for X-ray diffraction, infrared spectroscopy and thermal analysis have been described in a previous paper (Stählin and Oswald (16)).

Optical spectra were recorded on a Beckman DK-2 spectrophotometer with reflectance attachment from 6 to 26 kK. Reagent grade  $\text{BaSO}_4$  was used as a standard. The samples were mixtures of 10 to 50% hydroxide chloride with  $\text{BaSO}_4$ .

The electron microscopic investigations were performed with a Hitachi HU 125-S microscope.

TABLE IV

EXPERIMENTAL CONDITIONS FOR THE REACTION OF ZINC HYDROXIDE NITRATE WITH VARIOUS METAL CHLORIDE SOLUTIONS

Conc	Time (hr)	Colour	Product
2 $M$ $\text{Co}^{2+}$	4	Grey-green	$\text{Zn}_{4.16}\text{Co}_{0.84}(\text{OH})_{8.10}\text{Cl}_{1.90} \cdot 1.10 \text{H}_2\text{O}$
1 $M$ $\text{Co}^{2+}$	6	Grey-green	[2] $\text{Zn}_{4.20}\text{Co}_{0.80}(\text{OH})_{8.03}\text{Cl}_{1.97} \cdot 1.04 \text{H}_2\text{O}$
0.5 $M$ $\text{Co}^{2+}$	8	Grey-green	$\text{Zn}_{4.18}\text{Co}_{0.82}(\text{OH})_{8.24}\text{Cl}_{1.76} \cdot 1.18 \text{H}_2\text{O}$
0.02 $M$ $\text{Co}^{2+}$	24	Grey-green	ca. 30% II, 70% III <sup>a</sup>
1 $M$ $\text{Ni}^{2+}$	16	Green	[3] $\text{Zn}_{4.29}\text{Ni}_{0.71}(\text{OH})_{8.01}\text{Cl}_{1.99} \cdot 1.02 \text{H}_2\text{O}$
0.5 $M$ $\text{Ni}^{2+}$	20	Green	$\text{Zn}_{4.33}\text{Ni}_{0.67}(\text{OH})_{8.15}\text{Cl}_{1.85} \cdot 1.15 \text{H}_2\text{O}$
0.1 $M$ $\text{Ni}^{2+}$	60	Green	ca. 30% II, 70% III
1 $M$ $\text{Mn}^{2+}$	7	Colourless	[1] $\text{Zn}_5(\text{OH})_{8.14}\text{Cl}_{1.86} \cdot 1.05 \text{H}_2\text{O}$
0.2 $M$ $\text{Mn}^{2+}$	15	Colourless	ca. 40% II, 60% III
0.1 $M$ $\text{Mn}^{2+}$	28	Colourless	III
1 $M$ $\text{Zn}^{2+}$	5	Colourless	[4] $\text{Zn}_5(\text{OH})_{8.02}\text{Cl}_{1.98} \cdot 1.24 \text{H}_2\text{O}$
2 $M$ $\text{Na}^+$	4	Colourless	[5] $\text{Zn}_5(\text{OH})_{8.01}\text{Cl}_{1.99} \cdot 1.50 \text{H}_2\text{O}$

<sup>a</sup> II =  $(\text{Zn, Me})_5(\text{OH})_8\text{Cl}_2 \cdot \text{aq}$ ; III =  $(\text{Zn, Me})_5(\text{OH})_9\text{Cl} \cdot \text{aq}$ .



The substances were either prepared from suspensions in acetone or water and were observed with a cooling device to prevent decomposition, or carbon replicas shadowed with chromium vapour were used.

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