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THE ALPHA-FORM OF THE HYDROXIDES OF BIVALENT METALS

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16. Abstract

X-ray analyses were made of the hydroxides of the bivalent metals. The freshly pptd. hydroxide is usually in the α-form, which on standing is converted to another form or other forms. The α and c grating dimensions of the α-form and the C6-type of Co, Zn, Cd, Co-Zn and Ni-Zn hydroxides are tabulated. Ni hydroxide does not exhibit an α-form. α-Co(OH)$_2$, the blue form, is stabilized by sugar or by the higher alcs.: these compounds do not stabilize α-Zn(OH)$_2$.

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88. CONCERNING THE α-FORM OF THE HYDROXIDES OF BIVALENT METALS

W.Feitknecht

1. INTRODUCTION

The most unstable crystalline form of zinc hydroxide, identified by X-ray, first by Fricke, Gottfried and Skaliks,[1] was desginated as α-zinc hydroxide at the time [2]. It shows a very poorly linear X-ray diagram, and the principal lines could be indicated hexagonal as hK0.[3] Later Feitknecht and Lotmar [4] obtained entirely similar X-ray patterns with double hydroxides of cobalt-zinc and nickel-zinc. Finally, Feitknecht and Bedert [5] established that the blue cobalt hydroxide also gave the same X-ray pattern if it was isolated under conditions under which it cannot be transformed into the stable pink form.

All of these compounds appear to possess a very similar structure, which to be sure is very close to the C-6 type of the stable hydroxides, but still represent a special type.

According to Weiser and Milligan [6] one can completely stabilize the blue cobalt hydroxide with high molecular weight polyfunctional alcohols such as mono-, di- and trisaccharides. Blue cobalt hydroxide thus stabilized gives the same X-ray pattern as the unprotected, as established by Bedert**, and therefore possesses the same structure. This gave us the motive to investigate whether, by use of the stabilizing action of sugars on other bivalent metal hydroxides, the α-form could be obtained. Preliminary experiments showed that this is actually the case.

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*Numbers in margin indicate pagination of original foreign text.
**Unpublished experiments.

Since the α-forms give only an imcomplete X-ray pattern, their structure cannot be established from this alone. It is for this reason, which will be shown more precisely below, that the original conclusion concerning the structure of α-zinc hydroxide will be shown to be not entirely correct. For the structure elucidation, other properties also must be considered, above all the chemical behavior. In the following presentation the accumulated material on this α-form of the hydroxides will be brought together and discussed. It is intended to describe the experiments pertaining to the matter.

II. MEANING OF THE X-RAY PATTERNS

Incomplete X-ray patterns of the type outlined above, in which only hKO reflections appear, have also been observed with other substances with layer lattices. [5,6,7,8,9] The orgin of the occurrence of these types of patterns has been discussed at various times, especially exhaustively in a work which appeared recently by U.Hofmann and Wilm. [9] They have shown, as an example, graphite oxide, the hKO reflections patterns of which could be explained as "cross-lattice interferences", that is, as interferences which proceed from an even point lattice. Von Laue [10] has provided /768 a theory of the cross-lattice interferences, from which it is shown that the intensity of the reflections undergoes a gradual decrease with increasing deflection angle. The intensity curve of the reflections observed with graphite oxide actually shows the calculated result according to the theory of von Laue, whereby it is to be concluded that it is really a matter of cross-lattice interference.

From the subjective consideration of the X-ray patterns Lotmar [11] has concluded that the reflections of α-zinc hydroxide are symmetrical. From the photometer curves it is evident that with all these α-hydroxides the intensity of the hKO reflections likewise slowly decreases with increasing deflection angle (compare Figure 1).

It therefore appears correct to explain these reflections as cross-lattice interferences. Therefore these α-hydroxides consist of an aggregate of expanded, ordered layers of molecular thickness.*

As already mentioned, the patterns are indicated to be hexagonal, and from the deflection angle of the reflections it is possible to calculate the interval of the lattice point of the two-dimensional lattice, and thereby the atoms in the layers. These are almost equally as large (compare Table 1), as the interval of the metal ions in the hydroxide layers of the normal C-6 type crystalline hydroxides of these metals. It can be explained that the layers of the α-form have the same structure, that is, that here also hexagonal layers of metal ions cover a layer of hydroxide ions on each side.**

TABLE I. LATTICE DIMENSIONS OF THE C-6 AND THE α-FORM OF THE HYDROXIDES OF IVALENT METALS

Hydroxide	C6-Typ		α-Form	
	a	c	a	c
Co(OH)$_2$	3.173	4.64	3.09	~8
Zn(OH)$_2$	3.19	4.65	3.11	7.8
Cd(OH)$_2$	3.49	4.69	3.36	—
(Co,Zn)(OH)$_2$ . .	3.176	4.64	3.08	~8
(Ni,Zn)(OH)$_2$ . .	3.125	4.605	3.07	8.2

At the outset it is apparent that these layers are not inter- /769 mingled through one another, but that rather a large number are oriented parallel as solid platelets layered together in which the layer separation is not constant, and therefore not suitable for X-ray analysis. In some cases it is true that with suitable preparations there occasionally appear 001 reflections, if only

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* This form is not capable of existence. The dimensions are calculated from the mixed crystals of nickel- and cobalt-zinc hydroxide.

**Mixed crystals with approximately 20 mole % zinc hydroxide.

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indistinctly. From the deflection angle of these reflections the layer separation is found to be approximately 8 Å, approximately 3.4 Å more than in the hydroxide. of the C-6 type. This leads to the assumption of a double layer structure, in which unordered hydroxide layers are inserted between the ordered ones. It is clear that an assumption of a structure of particles of that type and an approximately 8 Å weak layer separation is entirely unsupported by the base reflections.

Related is the fact that the separation of the atoms in the layers is always appreciably smaller than in hydroxides of the C-6 type (compare Table I). Lotmar and Feitnecht [12] have established that this contraction also occurs in the basic salts with double layer lattice and have referred to the effect of the intermediate layer. Hofmann and Wilm [13] have, to be sure, established that also with extremely laminar dispersed graphite the layers are contracted, so that it may not be concluded with certainty that the presence of an intermediate layer is a consequence of such a contraction.

On the other hand, it is possible in some cases to derive the proposed double layer structures of the α-hydroxides from their chemical properties. Furthermore, from that information under certain circumstances it is also possible to show criteria concerning the distribution of hydroxide between the principal and intermediate layers, and thereby the basis for the establishment of a structural formula. This is applicable especially for the blue cobalt hydroxide, and therefore this material will be discussed in detail.

III. THE BLUE OR α-COBALT HYDROXIDE

It is known that by treating a cobalt II salt solution with an equivalent or an excess of strong alkali there is formed at first the blue cobalt hydroxide, which is transformed rather rapidly

into the stable pink form. The question regarding the nature of the blue form has been investigated frequently[14]; here only the last two works which have appeared will be discussed.

Hüttig and Kassler [15] obtained an X-ray diagram for their /770 preparation of the blue hydroxide which differed only in the intensities of the reflections of higher order from those of the pink form. They concluded that the two forms possessed the same structure.

Weiser and Milligan [16], on the other hand, in the case of their preparation of the blue cobalt hydroxide obtained a distinct X-ray pattern and described this as a special modification. Shortly it was shown [3] that the X-ray pattern obtained by Weiser and Milligan was that of the green basic cobalt chloride, and therefore that these research workers had in no way employed blue cobalt hydroxide for X-ray investigation.

Bedert* of this Institute has thoroughly investigated the conversion of blue cobalt hydroxide into the pink form. This work showed that the preparation employed by Hüttig and Kassler must have been composed essentially of converted pink hydroxide. By especially careful operation it was possible to isolate blue hydroxide which was free of the pink form. This gave an X-ray pattern which displayed only three reflections, which could be indicated as hexagonal 100, 110 and 200. An identical pattern is given by a blue hydroxide which is obtained from a solution containing glucose by the method proposed by Weiser and Milligan. The blue cobalt hydroxide therefore actually corresponds to a special modification, and the X-ray pattern has the characteristic which would be specified as typical of the α-form.

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*A detailed publication of the results of this investigation will follow later.

From the deflection angle of the reflections of the X-ray pattern one obtains for $\underline{a}$, that is for the separation of the cobalt atoms in the ordered hydroxide layers, a value of approximately 3.09 Å, therefore 0.08 Å less than in the pink hydroxide. In addition it should be noted that the value is somewhat uncertain, because the blue cobalt hydroxide is oxidized exceptionally easily and therefore the separation of the cobalt atoms in the hydroxide layers is somewhat decreased.

From the mechanism of the formation of the blue hydroxide it now follows that between these layers of ordered hydroxide, some layer must be inserted in a disordered manner. It has recently been shown, [17] by treatment of a cobalt salt solution with lye, that a basic salt is precipitated and this is transformed by further addition of lye into a blue hydroxide. This transformation is frequently characterized by a distinct color change from green to blue. The structure of some of these basic salts can be explained. They possess a double layer lattice with the principal layer having a structure like the pink hydroxide and the intermediate layer composed of disordered basic salt.

Further discussion shall be limited to the precipitation from chloride solution, since here the relationship is especially simple. The initally precipitated basic chloride is green in color and has the formula $9\ Co(OH)_2, 1CoCl_2$, that is, $4\ Co\ (OH)_2, 1\ Co\ (OH)Cl$. The principal layers are separated by 8.2 Å, superimposed rhombohedric, and contain $4\ Co(OH)_2$ per $1\ Co(OH)$ of the intermediate layer.

It appeared desirable to indicate the structure of these compounds by suitable symbols. If one bonds the ordered atoms of the principal layer with a thick line and those in the intermediate layer with a dotted line and writes the entire formula so as to symbolize that it consists of a single solid compound in brackets, then the following formula would be obtained for the green basic chloride.

$$4\,Co(OH)_2 \rightleftharpoons Co(OH)Cl]^{2}).$$

*
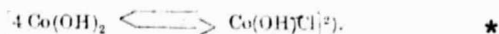
As recently has been shown [19], the structure of this green basic salt is in close agreement with its color. Green or blue colored compounds of divalent cobalt contain homopolar bonded cobalt. With the basic salts with double layer lattice the intercalated cobalt in the intermediate layers is homopolar bonded, while the same in the principal layer is heteropolar bonded and is limited to a red color, if the light absorption in the intermediate layer is not too intense. The color change from green to blue by transformation of the basic salt into the α-hydroxide means that the cobalt of the intermediate layer has undergone only gradual alteration of its bonding characteristics; the absorption spectra of the two are very similar.** Thereby the transformation of the basic chloride into the α-hydroxide follows in the manner that simply the chloride ion of the intermediate ion layer is substituted by hydroxide ion, which can be formulated as follows:

$$4\,Co(OH)_2 \rightleftharpoons Co(OH)Cl] + OH' \rightleftharpoons [4\,Co(OH)_2 \rightleftharpoons Co(OH)_2] + Cl'.$$

With this transformation there is a strong topochemical reaction with the characteristics of a permutoid reaction.*** This is in /772 agreement with the fact that it occurs very rapidly and reversibly.

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* I am indebted to Prof. V. Kohlschütter for suggesting this formulation.

** Compare loc. cit; a publication of the absorption spectra will follow later.

***W. Feitknecht , "Concerning Topochemical Transformation of Solid Materials in Liquids", Progress. Chem. Phys. and Phys. Chem., 21, Vol. 2 (1930).

If one adds chloride ion, for example as ammonium chloride, to glucose-protected α-cobalt hydroxide, then the basic chloride is again formed almost immediately, which is clearly evident by the color change.

Thus it is concluded without further discussion that the ratio of the ordered hydroxide of the principal layer to the disordered of the intermediate layer is 4:1, as expressed in the formula given above.

By X-ray analysis the transition of the basic salt into the α-hydroxide can be seen by the disappearance of the 001 and hKl reflections and the survival of only the hKO reflections. Thus one must consider not only the altered binding relationships in the intermediate layers, but that the bonding between principal and intermediate layers is so strongly weakened that the separation is diminished, and also that the principal layers can be displaced toward one another. However, since the number of molecules in the intermediate layer remains the same, one cannot be in error if one assumes that the layer separation is not significantly altered, and therefore fluctuates around approximately 8 Å.

This conclusion is supported by the behavior of α-cobalt hydroxide, particularly that which has been protected with glucose, in its oxidation with molecular oxygen. Of these reactions studied by Bedert*, only the facts will be referred to for the present which have significance for explaining the structure of the α-cobalt hydroxide.

Glucose-protected α-cobalt hydroxide becomes green and finally brown-green by passing through air or oxygen. The oxygen uptake ceases when approximately 20% of the cobalt has been transformed into the trivalent state. The X-ray pattern changes gradually and finally becomes the same as that of green basic cobalt chloride.

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*Compare loc. cit; a communication on the absorption spectra will appear later.

The two are therefore isomorphous and differ only from one another in that the dimensions of the elementary unit cell of the 20% oxidized form hydroxide are somewhat smaller. This isomorphism is understandable without further explanation, if one assumes that the oxidized contains Co(OH)O in the intermediate layers instead of Co(OH)Cl. The oxidation therefore also takes place strongly topochemically and can be formulated:

$$[4 Co(OH)_2 \longleftrightarrow Co(OH)_2] + \tfrac{1}{2} O_2 \quad 4 Co(OH)_2 \longleftrightarrow Co(OH)O + \tfrac{1}{2} H_2O.$$

Also, from the reaction there is obtained a ratio of ordered to disordered hydroxide of the α-form of 4:1 and a layer separation of approximately 8 Å.

On the basis of this conclusion concerning the structure of the α-cobalt hydroxide a simple explanation is obtained for the spontaneous transformation into the stable form, and the action of higher molecular weight alcohols and sugars in hindering this reaction. The edges of the layers are saturated very little, and therefore crumble easily, and the fragments are deposited together as the stable crystalline form. As a result of the general strong van der Waal's bonding between hydroxyl groups, higher molecular weight alcohols and sugars are easily absorbed, especially on the edges of the layers. As a result, these become saturated and the crumbling is hindered.

One could also conclude that the molecules of the material under discussion penetrate between the layers and thereby bring about a strengthening of the crystal structure. However, its dimensions are so large that this is not a question. On the other hand, it is possible that a single molecule is absorbed on hydroxyl groups of two separate layers, which can bring about an especially strong protective action.

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IV. α-ZINC HYDROXIDE

Work on α-zinc hydroxide has been described at various times. The views concerning the nature of this compound have been somewhat altered in the course of time and some of the older reports need correction. This will be done in connection with some further research.

Preparations which give characteristic X-ray patterns for α-zinc hydroxide are obtained by incomplete precipitation of zinc salt solutions with lye [20], steeping highly dispersed basic zinc chloride or bromide with lye, and in the form of beautiful pseudo-morphs from coarsely crystallized basic iodide and lower basic nitrate [21].

It has been emphasized several times that it is very difficult to obtain α-zinc hydroxide entirely pure, [22] and that it contains mostly zinc salt, apparently in the form of basic salt, and that this is essential for its stability.

On the basis of the X-ray patterns it was concluded [23] that the α-zinc hydroxide is isomorphous with hydroxides of other divalent metals of the C-6 type, to be sure, very incompletely developed.   <u>/774</u> For the dimensions of the elementary unit cell there was found $\underline{a}$ = 3.14 Å and $\underline{c}$ fluctuating around a value of approximately 5 Å. The last value was determined from two weak reflections, which were observed with a pseudomorph from basic iodide, and indicated as 002 and 101.

Later, Lotmar and Feitknecht [24] have calculated the dimensions of the elementary unit cell of the hypothetical zinc hydroxide of the C-6 type from mixed crystals of zinc-cobalt and zinc-nickel hydroxide: $\underline{a}$ = 3.19 Å and $\underline{c}$ = 4.65 Å. However, the $\underline{a}$ of α-zinc hydroxide is, according to more recent determinations, only 3.11 Å, therefore significantly smaller and the layers are accordingly

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contracted. It has already been referred to that one such contraction of the basic salt with double layer lattice is often generally observed and is a result of the intercalation of an intermediate type.

This leads to the conclusion that with α-zinc hydroxide the hydroxide layers likewise are separated from one another, and the disordered material is intercalated between them. Therefore, the α-zinc hydroxide does not correspond to the C-6 type, also not to an extreme laminar dispersed form but to a special structure type and is isomorphous with α-cobalt hydroxide. For the layer separation therefrom is derived likewise a value of approximately 8 Å. The reflections indicated as 002 and 101 by the X-ray pattern from basic zinc iodide, which had led to a layer separation of approximately 5 Å, have another meaning -- that with these preparations one is not dealing with a pure α-zinc hydroxide, as subsequently proved.

With pure α-zinc hydroxide the intermediate layers, similar to cobalt hydroxide, must possess intermediate layers of disordered hydroxide. In the preparations containing zinc salt a portion of the hydroxide ions of the intermediate layer is displaced by other anions, and these obviously act to stabilize the crystal structure.

There is now a question of whether the presence of such foreign anions is indispensable for the possible existence of the α-zinc hydroxide structure, and whether by experiment these could be substituted by hydroxide ions causing the structure to collapse, or whether entirely pure α-zinc hydroxide could be prepared.

According to previous reports [25] practically halogen-free α-zinc hydroxide can be obtained by steeping highly dispersed basic chloride and bromide with lye. These preparations, however, contained carbonate instead; this provided the basis for their apparently

excessive water content. It now appears possible that here the carbonate ions exert a stabilizing action.

To clarify these questions an additional series of experiments was initiated. First of all the precipitate obtained by precipitation of zinc chloride solution was investigated somewhat more closely. With incomplete precipitation there was obtained a very voluminous translucent precipitate, which gave the X-ray pattern of α-zinc hydroxide. The earlier reports about this [26] should be corrected, since α-zinc hydroxide, and not the basic chloride /775 $ZnCl_2,4Zn(OH)_2$, is precipitated from solutions of intermediate concentration. The older erroneous finding may be traced back to the fact that the precipitate was not completely washed, and was thereby enriched with zinc chloride upon drying and caused a transformation into the basic chloride mentioned above.

The composition of the initial precipitated product is still not clearly understood. According to orientation determinations, the chloride content is only rather small; there is one molecule of chloride to approximately 25-30 molecules of hydroxide. This chloride is very difficult to remove by washing. (In order to obtain a chloride-free preparation, washing at least twelve times with a four-fold quantity of water is required.) Although boiled water was employed in the washing, the preparation still contained carbonate. It appears that the very small carbonic acid content of the wash water plays an essential role in that the chloride ion of the intermediate layer is substituted by carbonate anion, which then takes over the stabilizing action.

An experiment to substitute chloride ion by hydroxide ion by further addition of lye as in the preparation of α-cobalt hydroxide, likewise was unsuccessful. There immediately occurred transformation into amorphous hydroxide, and partially oxide also. Also, these reactions cannot be prevented by an addition of glucose, which remarkably exhibits no stabilization in this case.

Since the basic zinc nitrate is less stable than the basic chloride, [27] it was supposed that possibly the nitrate ion would be more easily removed from the intermediate layer. Therefore some experiments were conducted with the precipitated product obtained from nitrate solution. With incomplete precipitation from solutions of intermediate concentration there was likewise obtained essentially the X-ray pattern of α-zinc hydroxide. According to orientation experiments it is relatively nitrate-rich and consists of one molecule of nitrate to approximately 9 molecules of hydroxide.

Likewise, the nitrate is removed only with difficulty with water, and the precipitate absorbs carbon dioxide very easily. From the X-ray pattern of such leached out preparations there appear along with the lines of the α-.ydroxide, also the diffuse blackening of the amphorphous hydroxide (compare Figure 1c). /776

By treatment of the initially precipitated product with lye, likewise it is not possible to obtain pure α-hydroxide. In the product, as the nitrate ions are substituted by hydroxide ions, the X-ray pattern reveals that the reflections of the α-hydroxide disappear at the expense of the amorphous blackening (compare Figure 1c), and with complete substitution of the nitrate ions the precipitate consists entirely of amorphous hydroxide. Also, in this case the α-hydroxide is not stabilized by glucose. /777

According to these experiments it actually appears that the existence of the α-form depends on a certain content of foreign anions in the intermediate layer.

The photometric curve of the X-ray pattern gives only a few additional points concerning the nature of the materials being investigated here. For comparison purposes one such amorphous hydroxide is reproduced in Figure 1. It was obtained from a gelatinous hydroxide which was prepared by addition of sodium hydroxide solution to zinc nitrate solution. Both previous descriptions [28] reveal distinctly broad blackened zones in the photometric curves.
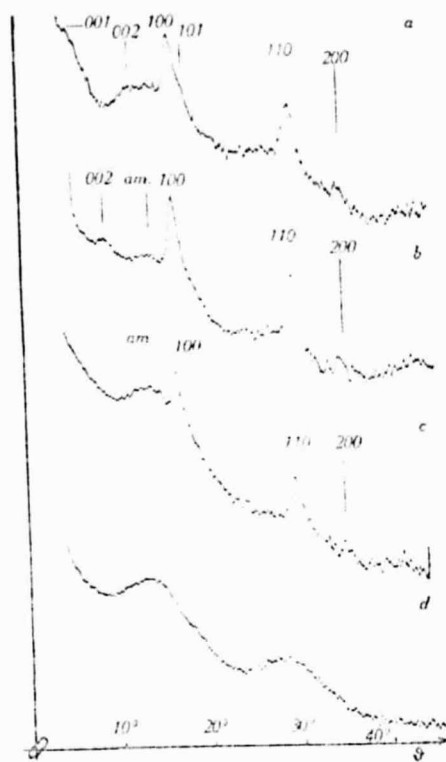
13

Figure 1.

Key: a) zinc hydroxide obtained by incomplete precipitation from zinc chloride solution; 6) precipitation from zinc nitrate solution; c) precipitate (b) washed several times with water; d) amorphous zinc hydroxide.

With the photometric curves of the first precipitated product which was obtained from chloride solution (Figure 1a) there are still a few additional, weak, more diffuse blackenings to be seen, along with the hK0 reflections of the α-zinc·hydroxide, which by subjective consideration of the film do not stand out so distinctly. So one distinguishes one such very near the penetration point and another very broad near 100; the latter appears to consist of two broadened reflections (compare Figure 1a).

The signs β of both innermost reflections are in the ratio
1:2 and can be designated as 001 and 002. From these results a
layer separation of approximately 7.8 Å is deduced, a value which
is to be expected for a double layer lattice. Furthermore, the
falling intensity which follows the larger deflection angle dis-
tinguishes the darkening of a reflection, which with this layer
separation can be identified as 101.

The more strongly diffracted part of the broad zone, along
with the diffused blackening agrees with amorphous hydroxide. Thus,
this initial precipitate from chloride solution is also possibly
admixed with some amorphous hydroxide, by which one can conclude
that by treatment of the chloride solution with lye, localized
regions become strongly supersaturated with hydroxide ions, in
which there exists the possibility of formation of amorphous
hydroxide.

The X-ray pattern of carbonate-containing preparations obtained
by leaching with lye is very similar to the original preparation.
Here also indistinct reflections are present, which can be identified
as 001, 002 and 101 and reveal a layer separation of approximately
7.8 Å and the corresponding amorphous blackening as well.

The photometric curves of the primary precipitate obtained
from nitrate solution show, along with the hKO reflections, likewise
some additional weakly diffuse rings. The first is so close to
the penetration point that it disappears in the general blackening
and cannot be measured. If one designates the second as 002, then <u>/778</u>
one calculates a layer separation of approximately 9.5 Å, which
corresponds with the layer separation of normal basic zinc nitrate
[29] and green basic cobalt nitrate.[30] The layer separation
determined with these products therefore appears to be larger than
that obtained from chloride solution and from the dimensions of
the nitrate anion.

In addition the patterns show a diffuse blackened zone which comes from amorphous hydroxide. This is especially true if it is precipitated from dilute solution. Similar to the chloride, the initially precipitated product from nitrate appears to be not entirely homogeneous, which again can be traced back to localized differences in concentration of the lye during its addition.

By addition of larger amounts of lye the corresponding blackening of the base reflections disappear and the hKO reflections are weaker, while the amorphous zone is intense (compare Figure 1c). Finally, by precipitation with a small excess of lye one obtains only amorphous hydroxide.

On the basis of the photometric evaluation of the X-ray pattern one may conclude that it is not possible to obtain α-zinc hydroxide free of foreign anions. Still, the preparations obtained by precipitation of salt solutions with lye apparently always contain some amorphous hydroxide. Besides, it appears that the layer separation of the precipitate from chloride solution is not as large as that obtained from nitrate solution.

This leads to the question whether these products, which always still contain zinc salts, generally denoted "α-zinc hydroxide", should better be called basic salts. It appears desirable to apply the first expression with those with very small foreign anion content. The α-form is designated as that zinc hydroxide which possesses a double layer structure consisting of a principal layer of the 6C type, a layer separation of approximately 8 Å and a disordered intermediate layer of hydroxide in which a small portion of the hydroxide ions is substituted with foreign anions. The ratio /779 of the number of zinc atoms arranged in the principal and intermediate layers is likewise assumed to be 4:1. This can be concluded from the analogy with the α-cobalt hydroxide and the composition and structure of a series of basic zinc salts. The structural formula for α-zinc hydroxide therefore reads:

$$[4\,Zn(OH)_2 \rightleftharpoons 1\,Zn(OH.X)_4].$$

where X can be a uni- or bivalent anion.

There is a question whether a sharp boundary can be shown between α-zinc hydroxide and basic salts; this requires some further experimental clarification. Still one can, according to the definition given above, denote the product obtained by incomplete precipitation from chloride solution as α-zinc hydroxide, just as that carbonate-containing product resulting by leaching out with water. The one from nitrate solution, on the other hand, which has a higher salt content and greater layer separation, is better described as a basic salt. As with the lower basic nitrate and basic zinc iodide pseudomorphs' behavior, clarification is likewise required.

V. α-CADMIUM HYDROXIDE

Cadmium hydroxide has until now been obtained only in crystalline form [31]. It shows a very good crystallization capability and also preparations obtained immediately after precipitation give X-ray patterns, which only allow small lattice perturbation. Of course, for example, the precipitate obtained from nitrate solution is at first very voluminous and translucent and is dense and chalky white when first isolated; possibly therefore the α-form precipitates out. It was therefore investigated whether this can be protected with glucose similar to the cobalt hydroxide treatment.

Clearly a hydroxy precipitate which is obtained from a glucose-containing cadmium nitrate solution with a small excess of sodium hydroxide solution remains voluminous and translucent for several weeks. Therefore glucose acts as a protective agent here.

The X-ray pattern of an immediately isolated, glucose-protected hydroxide obtained from nitrate solution shows the intense background blackening, especially in the vicinity of the penetration point, and only two strong broad-ended rings, the innermost being intense with a somewhat large deflection angle and designated as the 100 and the second a very weak one at 110 assigned to the normal hydroxide. A glucose-protected hydroxide aged for a long time reveals a background blackening somewhat less broadened and more intense; in addition 200 still appears.

On the other hand, all 001 and hKl reflections are lacking. Also, with this aged and protected hydroxide the reflections are essentially less intense, particularly 110, as with α-zinc and α-cobalt hydroxides. Some additional experiments to obtain preparations which give only hKO reflections, but sharper and more intense, have for the present been unsuccessful.

From the deflection angle of the reflection indicated to be hKO, the glucose-protected one gives for a an average 3.36 Å which is 0.13 Å less than with a normal hydroxide. From that one can conclude that the hydroxide layers of disordered intermediate layers are under divided and that actually the α-form of $Cd(OH)_2$ is present. Of course the layers are, above all, with the fresh precipitate only slightly expanded and possibly still mixed with amorphous material.

VI. NICKEL HYDROXIDE

Nickel hydroxide has until now only been obtained in the C-6 type. Of course, the freshly precipitated product is very highly dispersed and incompletely ordered [32]. From nickel chloride or bromide, similarly to cobalt, there is precipitated by treatment with lye, the complete nickel content as a basic salt, and the hydroxide forms with additional addition of lye only secondarily

from this. This basic nickel halide has a structure similar to the analogous cobalt salt.* It was therefore to be expected that by transformation with lye first an α-nickel hydroxide corresponding to the blue cobalt hydroxide should be produced.

An hydroxide, still containing some chloride ion precipitated from chloride solution with a small excess of lye, gives clearly the pattern of the normal hydroxide, of course with very strong broadened 001 and hKl reflections. An addition of glucose only acts to cause the platelets to become more highly dispersed and more strongly laminar, and the increased coarseness of the platelets is closely related to the aging. It appears questionable whether the α-form of nickel hydroxide can be obtained in other ways.

VII. THE α-FORM OF DOUBLE HYDROXIDES

While therefore the α-form of pure nickel hydroxide has still not been observed, the double hydroxide obtained from nickel salt solutions containing zinc salts possesses this structure type [33]. At an appropriate mixture ratio there appears with old preparations also basic reflections from which a layer separation of 8.2 Å is obtained (Figure 2). This also results with the products with irregular separation to a lowered 8 Å value. The separation a is 3.07 Å, which is therefore as expected (approximately 0.05 A smaller than in pure nickel hydroxide). The disordered material of the intermediate layer is composed of zinc hydroxide, while the ordered principal layer is nickel hydroxide, with which a part of the nickel can be substituted with zinc ions.
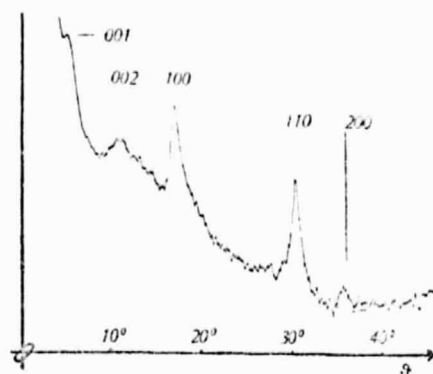
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*According to the unpublished work of A. Collet.

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Figure 2. Aged Nickel-Zinc Double Hydroxide.

From cobalt solution containing zinc ions a blue precipitate
is formed by treatment with excess sodium hydroxide which gives
an X-ray pattern similar to pure α-cobalt hydroxide.[34] This
mixed precipitate becomes pink rather quickly like the pure blue
cobalt hydroxide. With low zinc content, the precipitate becomes
dense and gives an X-ray pattern of the stable α-cobalt hydroxide.
The zinc ions therefore substitute a part of the cobalt ions iso-
morphous in the C-6 lattice. [35] The precipitate with intermediate
zinc content remains voluminous and translucent and the X-ray pattern
is unchanged; therefore it has the α-structure.

On the basis of the briefly communicated summary between structure
and color of the bivalent cobalt compounds, [36] this relationship
can be described as follows. In the initial precipitated product
the intermediate layer consists principally of amorphous cobalt
hydroxide with preponderant homopolar bonding which accounts for
the blue color. The transformation from blue into pink consists
only simply of the cobalt atom of the intermediate layer exchanging
with the zinc atom of the main layer. In pink-colored final product
the intermediate layer contains, as in nickel-zinc double hydroxide,
only zinc hydroxide. The main layer consists of cobalt hydroxide   /782
in which a part of the cobalt ions are substituted by zinc ions.
This compound is pink because the cobalt is predominately heteropolar
bonded.

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In contrast to pure cobalt hydroxide the mixed hydroxide of the blue-pink transformation is not inhibited with glucose, obviously because the reaction takes place in a single phase inside the crystal structure and therefore cannot be influenced by externally adsorbed material.

The blue and pink-colored double hydroxides show only hKO reflections and both give for $\underline{a}$ a value of 3.08 Å, which is 0.09 Å smaller than the pink-colored cobalt hydroxide. Since the zinc and cobalt ions have almost the same radius, the value of $\underline{a}$ is practically independent of the zinc ion content of the main layer. Since the basic reflections are always lacking, it can only be concluded, by analogy with α-cobalt hydroxide and nickel-zinc double hydroxide, that the layer separation decreases to approximately 8 Å.

From the analogy with the basic salts and from the chemical behavior of the nickel zinc double hydroxide it was concluded that the ratio of the metal ions in the principal and intermediate layers is 4:1. [37] This assumption was supported by our experience with the blue cobalt hydroxide. Thereby the following formulas are given for these double hydroxides:

1. Nickel-zinc double hydroxide = $[4\,(Ni,\,Zn)(OH)_2 \Longleftrightarrow 1\,Zn(OH)_2]$

2. Blue zinc-cobalt double hydroxide = $[4\,(Zn,\,Co)(OH)_2 \Longleftrightarrow 1\,Co(OH)_2]$

3. Pink cobalt-zinc double hydroxide = $[4\,(Co,\,Zn)(OH)_2 \Longleftrightarrow 1\,Zn(OH)_2].$

Until now only the two systems referred to have proved close to the possibility of formation of double hydroxides with the α-form structure. It appears quite evident that the same type of

double hydroxide is also precipitated out of other binary salt solutions. Apparently the zinc hydroxide is especially suited as a component for the intermediate layer.

VIII. CONCLUSIONS

1. Hydroxides of some bivalent metals which have been freshly precipitated from salt solutions with lye show very similar X-ray patterns, which give only hK0, under certain conditions only weak and broadened 001 reflections. It is a matter of a special structure type which shall be designated the α-form of these hydroxides.

2. The blue cobalt hydroxide possesses this structure type. It is concluded on the basis of the X-ray pattern, and especially on the basis of chemical behavior, that in this case the principal layers (of the same structure as in the pink hydroxide, that is of the C-6 type, but somewhat contracted) are divided between intermediate layers of disordered hydroxide. The chemical facts which lead to this structure are above all the exchangeability of half of the hydroxide ions of the intermediate layers by chloride ion and the behavior of the blue cobalt hydroxide on oxidation. The ordered layers are nearly parallel, but lie displaced with respect to one another, arranged in an approximately 8 Å restricted separation from one another. Of four molecules of ordered hydroxide there is only one disordered molecule. The cobalt in the disordered intermediate layer is bonded predominately homopolar and has the blue color of this modification of the cobalt hydroxide.

The blue cobalt hydroxide can be protected by high molecular weight alcohols or sugars, whereby the originally obtained structure is retained. The protective action of compounds with several hydroxyl groups is traced back to the fact that these groups exert large van der Waals forces as result of the action between strongly absorbed hydroxyl groups which thereby saturate the layer edges.

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3. The previously described α-zinc hydroxide does not have, as originally assumed, an incompletely formed lattice of the C-6 type, but has the same structure as the blue cobalt hydroxide. It is only capable of existence when a part of the hydroxide ions of the intermediate layer are substituted by other anions. If these foreign anions are exchanged by hydroxide ions, then the principal layers lose their order and the α-zinc hydroxide becomes amorphous. This transformation cannot be prevented by addition of high molecular weight alcohols or sugars. With the previously described preparations of α-zinc hydroxide, which were obtained from highly dispersed basic halides by leaching out, there is found instead the substitution of the halide ion by carbonate ions from the carbonic acid present in the water.

4. The initially precipitated hydroxide obtained from cadmium nitrate solution appears from the X-ray pattern to have the same structure as the α-form of cobalt and zinc hydroxide.

5. With nickel hydroxide the α-form has not yet been obtained.

6. The previously described nickel-zinc and cobalt zinc double hydroxides possess the same structure type as the α-form of pure hydroxide. With nickel-zinc double hydroxide, the intermediate layer consists of disordered zinc hydroxide. The freshly precipitated blue cobalt-zinc double hydroxide, containing disordered cobalt hydroxide in the intermediate layer, is found on aging to exchange the cobalt of the intermediate layer with zinc of the principal layer, which is characterized by a color change to pink; the aged cobalt zinc double hydroxide contains only zinc hydroxide in the intermediate layer.

7. It has been proposed that the structure of these solid compounds with double layer structure be represented by a simple formula.

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