

## Kurze Mitteilungen

Bis am 15. des Monats bei der Redaktion eingehende Kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht. Es werden auch Manuskripte aus dem Ausland angenommen. Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen)

# Chromium(III)hydroxide hydrate—a new hydroxide structure type with cross-linked hydrogen bonding\*

### Summary

Precipitation of hexaquo chromium(III) solutions with  $\text{OH}^-$  ions yields a hydroxide with analytical composition  $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$  of the anti-bayerite type. The lattice constants of the pseudo-hexagonal unit cell are  $a_0 = 5,047$  and  $c_0 = 4,73$  Å. This lattice has vacancies where bayerite would have occupied octahedral sites, and *vice versa*, in a hexagonal closest arrangement of  $\text{OH}^-$  and  $\text{H}_2\text{O}$ . It consists of layers of isolated  $[\text{Cr}(\text{OH}_2)_3(\text{OH})_3]$  units. These are held together by a network of two kinds of hydrogen bonds. IR evidence gives O...HO distances of 2,7 and 2,9 Å, respectively. Precipitation experiments with  $\text{H}_2^{18}\text{O}$  enriched solvent could be explained by a simple and fast deprotonation mechanism where the inner coordination sphere of the hexaquo chromium (III) ion remains unaltered. Upon ageing an amorphous phase of undefined composition is formed, where corner and/or edge sharing of hexaquo chromium (III) octahedra occurs. The solubility rate of this aged product in acids is distinctly lower, as the inner coordination sphere of the  $\text{Cr}^{3+}$  has to be attacked.

### 1. Introduction

As known since the investigations of FRICKE<sup>1</sup> and HANTZSCH and TORKE<sup>2</sup> the precipitation of hexaquo chromium (III) solutions with hydroxide ions yields a phase of analytical composition  $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ . BACCAREDDA and BEATI<sup>3</sup> found that diffraction data point to a bayerite type lattice, an opinion maintained up to now<sup>4</sup>. This lattice, however, cannot accommodate the three hydrate waters. We have reproduced the early experiments and try in this present investigation to interpret analytical, X-ray, and IR data and to put forward a mechanism for the formation of this new lattice.

### 2. Experimental

A freshly prepared 0,1N  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution was precipitated with a stoichiometric amount of 0,1N ammonia at room temperature. The product was isolated by centrifuging, washed five times with water and dried in air. By a similar procedure a small portion of  $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$  was prepared using  $^{18}\text{O}$  enriched water,  $\text{H}_2^{18}\text{O}$ , as a solvent. Care was taken that only a negligible amount of  $\text{H}_2^{18}\text{O}$  entered the inner coordination sphere of the hexaquo chromium (III) ion prior to the precipitation of  $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ <sup>5</sup>. The X-ray powder pattern of this hydroxide was identical with that of the normal  $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ . The  $^{18}\text{O}$  abundances in the reactant solutions of chromium (III) nitrate and ammonia and in the washing water were determined by mass spectrometry using the  $\text{CO}_2$  exchange technique<sup>6</sup>. Similarly, the hydroxide was exchanged with  $\text{CO}_2$  in sealed quartz tubes by heating for 20 hours at 350°C. A cycloidal mass spectrometer CEC 21-620 A, kindly provided by the Federal Institute of Reactor Research (Würen-

lingen), was used for the isotope analysis. X-ray powder patterns were taken on a Guinier-de Wolff camera using copper radiation. An aluminium foil 0,08 mm thick directly in front of the film absorbed the fluorescence radiation of Cr. Infrared spectra were recorded on a Beckman IR-9 spectrometer in KBr pellets, Nujol mull, and Fluorolube mull.

### 3. Results

The following  $^{18}\text{O}$  abundances were found (atom %):

Mother liquid after precipitation	2,85
0,1 N $\text{Cr}(\text{NO}_3)_3$ solution before precipitation	2,85
0,1 N ammonia before precipitation	2,84
$\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$	0,519
Last (fifth) portion of washing water	0,250

The IR spectra showed two distinct OH stretching frequencies (fig. 1), a narrow one at about  $3500\text{ cm}^{-1}$  and a fairly broad one at about  $3000\text{ cm}^{-1}$ . The first can be attributed to a rather long OH...O bond, of the order of about 2,9 Å while the second points to a distinctly shorter hydrogen bond of the order 2,7 Å. For comparison we refer to NAKAMOTO *et al.*<sup>7</sup>. The shape of the second mentioned stretching frequency happens to be quite similar to that of diaspor  $\alpha\text{-AlOOH}$ <sup>7</sup>.

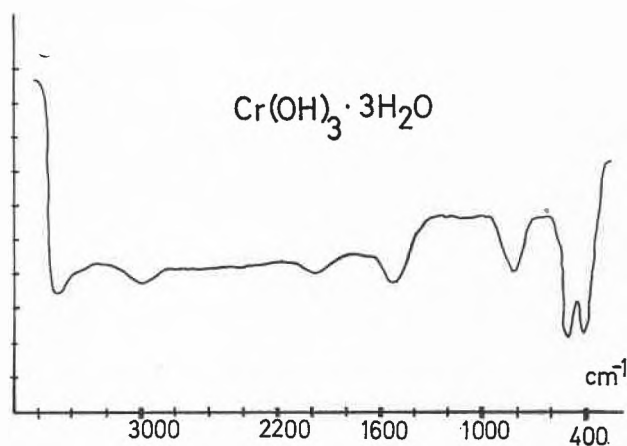


Figure 1. IR spectrum of chromium (III) hydroxide hydrate. Fluorolube mull technique

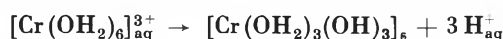
The X-ray powder pattern could be indexed with a pseudo-hexagonal unit cell using  $a_0 = 5,047$  and  $c_0 = 4,73$  Å as lattice constants. Four lines remained unexplained and suggest a super-cell. The appearance of the powder pattern is that of the bayerite type.

\* Received February 14, 1973.

#### 4. Discussion

The isotope analysis of the mother liquid and the solid hydroxide shows that  $H_2^*O$  essentially remains in the aqueous phase. The small enrichment left in the hydroxide can be explained by uncomplete removal of mother liquid from the finely divided solid. In such cases the washing process tends to be tedious; thus, after the fifth washing a slightly higher abundance of  $H_2^*O$  in the water was still detectable (0,250 instead of 0,197 atom<sup>0</sup>/<sub>100</sub>).

It can be assumed that the inner coordination sphere of  $Cr^{3+}$  remains unaltered during the crystallisation process of the hydroxide. This fact and the stoichiometry of the precipitate suggest strongly that the following deprotonation takes place:



The  $[Cr(OH_2)_3(OH)_3]$  units crystallise to a close packed arrangement as drawn out schematically in fig. 2\*.

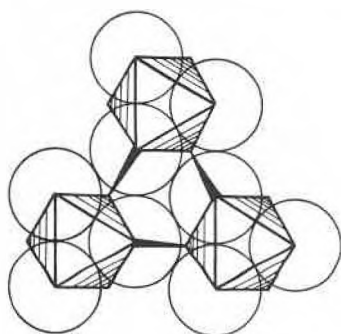


Figure 2. Part of a layer of the proposed anti-bayerite lattice for chromium (III) hydroxide hydrate. Circles represent oxygen ions. Protons and the next oxygen layer are omitted. Octahedra represent  $Cr^{3+}$  positions slightly above the plane of the drawing. Three black spikes indicate hydrogen bonds of the first of the two different sets

Fig. 2 shows part of a layer of close packed  $OH^-$  ions and water molecules. Octahedral sites occupied by  $Cr^{3+}$  ions are symbolised by octahedra. Some hydrogen bonds of one of the two sets mentioned are drawn. If this picture is carried on, an arrangement similar, but inverse, to the bayerite type lattice appears: sites occupied in this type are vacant in chromium (III) hydroxide hydrate, and *vice versa*. We propose to call this arrangement "anti-bayerite type".

\* We wish to point out that we are indebted to Professor G. SCHWARZENBACH, Zurich, for having given us the crucial idea to this interpretation.

Since the mentioned units are essentially isolated in this arrangement (as opposed to bayerite where edge, corner and face sharing  $OH^-$  octahedra hold the lattice together), it seems obvious to take the IR evidence into consideration and to assume a cross-linked hydrogen bond network. One  $OH \dots O$  bridge is shown in fig. 2, but another kind must also exist as per  $Cr^{3+}$  unit six more protons are available for bonding.

On ageing or by heating (even under water), chromium (III) hydroxide hydrate turns into a totally amorphous phase of undefined composition, and of distinctly deeper green colour. This is probably due to condensation of the isolated octahedral units to corner or edge sharing dimers or higher polynuclears. Under these circumstances no lattice order whatsoever beyond the first neighbour is detectable.

If polynuclears have had time to form in the  $Cr^{3+}$  solution, the simple deprotonation mechanism does not lead to the crystalline hydroxide. The latter dissolves readily in acids as opposed to the amorphous product where the inner coordination sphere of the  $Cr^{3+}$  ion must be attacked. This is further support to the anti-bayerite type described above.

A full account on this new hydroxide structure will be published elsewhere.

*Acknowledgments.* Authors are grateful to Professor W. FEITKNECHT for the suggestion to investigate this hydroxide, to Professor G. SCHWARZENBACH for valuable discussions, to Mr. P. BÜRKI for preparative work, to Mr. O. ANTONSEN (Federal Institute of Reactor Research, Würenlingen) for mass spectrometric measurements, and to the Swiss National Foundation for financial support.

RUDOLF GIOVANOLI, WILLY STADELMANN  
and HEINZ GAMSJÄGER

Institute of Inorganic Chemistry of the University of Berne,  
Freiestrasse 3, P.O.B. 140, CH-3000 Berne 9 (Switzerland)

- <sup>1</sup> R. FRICKE, *Z. anorg. allg. Chem.* 132 (1924) 273.
- <sup>2</sup> A. HANTZSCH und E. TORKE, *Z. anorg. allg. Chem.* 209 (1932) 60.
- <sup>3</sup> M. BACCAREDDA and E. BEATI, *Atti del X<sup>o</sup> Congresso Internazionale di Chimica, Roma 1938*, vol. 2, p. 99.
- <sup>4</sup> ASTM card No. 16-817 (new name: JCPDS, or Joint Committee for Powder Diffraction Standards).
- <sup>5</sup> J. P. HUNT and H. TAUBE, *J. Chem. Physics* 19 (1951) 602; R. A. PLANE and H. TAUBE, *J. Physic. Chem.* 56 (1952) 33; J. P. HUNT and R. A. PLANE, *J. Amer. Chem. Soc.* 76 (1954) 5960.
- <sup>6</sup> P. BAERTSCHI, *Helv. Chim. Acta* 36 (1953) 1352.
- <sup>7</sup> K. NAKAMOTO, M. MARGOSHES and R. E. RUNDLE, *J. Amer. Chem. Soc.* 77 (1955) 6480.