The crystal structure of Co$_2$(OH)$_3$Cl. By P. M. de Wolff, *Technisch Physische Dienst, T.N.O. en T.H., Delft, Holland*

The formula Co$_2$(OH)$_3$Cl has been established by Feit-knecht (1935) for the lavender-coloured (*rosa-farbiges*) cobalt hydroxychloride. According to the X-ray powder pattern the structure was first described as being of the layer-lattice type (Feitknecht, 1936), while later (Feit-knecht & Magnet, 1949) a relationship with the atacamite structure was supposed. No unit-cell dimensions have been reported.

In the course of a study on basic salts, the present author has had occasion to examine the structure of this cobalt compound. A suitable sample has been obtained following one of the methods indicated by Feitknecht (1935), namely precipitation from a CoCl$_2$ solution by a Mg(OH)$_2$ suspension. The washed and dried product was analysed chemically at the Analytisch Instituut T.N.O. and was found to contain 55·7 % Co, corresponding theoretically to 16·8 % Cl and 24·2 % OH, whereas the experimental values were 17·0 % Cl, and difference 27·3 % including a Mg-content below 1·5 %. No trace of magnesium compounds has been found in the X-ray powder pattern.

This pattern was taken with the fourfold Guinier camera (de Wolff, 1948) using Fe $K\alpha$ radiation. The lines were appreciably broadened. The mean particle size was estimated at 200 Å, but the individual widths showed irregular variations. The pattern was indexed completely on the basis of a rhombohedral unit cell with hexagonal axes
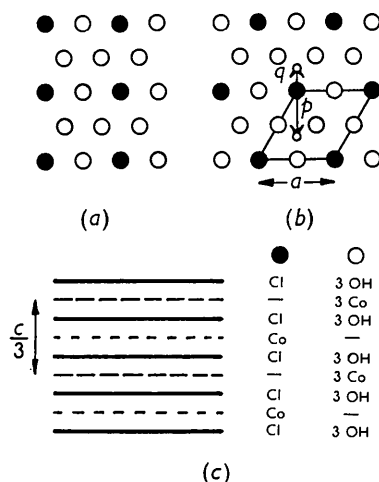
$$a = 6·84, \quad c = 14·50 \text{ Å} .$$

(a) *(b)*

(c)

Fig. 1. (*a*) Monatomic layer which, when stacked according to the scheme of Fig. 1(*c*), gives rise to the idealized atacamite Cu$_2$(OH)$_3$Cl structure.

(*b*) Monatomic layers from which the idealized Co$_2$(OH)$_3$Cl structure can be built in two different ways by stacking according to the scheme of Fig. 1(*c*). If the monatomic layers are those parallel to (001), a shift *p* should be applied; if they are supposed to belong to one of the three sets parallel to (101), the shift is given by *q*.

(*c*) Stacking scheme of monatomic layers.

Table 1. *Calculated and observed F values*

hkl	d (Å)	F_c	F_o
101	5·48	−30·2	25·4
003	4·83	21·6	20·6
10$\bar{2}$	4·59	− 7·9	7·4
110	3·42	8·9	9·3
104	3·09	2·7	< 4
20$\bar{1}$	2·900	21·8	17·3
113	2·791	−27·3	30·3
202	2·740	14·8	10·9
10$\bar{5}$	2·605	− 5·9	< 4
006	2·417	18·0	14·3
20$\bar{4}$	2·292	59·7	64·8
211	2·211	−10·3	7·3
21$\bar{2}$	2·141	− 5·9	4·5
205	2·070	21·8	20·6
116	1·971	− 3·2	< 4
300	1·970	4·5	< 6
10$\bar{7}$	1·957	−26·0	29·2
214	1·904	6·2	5·0
303	1·826	−14·6 ⎫ 24·3*	27·1
30$\bar{3}$	id.	−31·1 ⎭	
21$\bar{5}$	1·771	−14·4	12·0
10$\bar{8}$	1·734	1·1	< 7
220	1·710	49·7	53·0
20$\bar{7}$	1·699	13·0	15·8
31$\bar{1}$	1·631	−16·8	17·6
009	1·611	20·3 ⎫ 14·4*	14·5
223	1·611	13·3 ⎭	
312	1·602	− 9·7	14·7
208	1·546	42·5	40·4
217	1·520	−28·9	31·5
306	1·512	1·7 ⎫ 4·7*	< 6
30$\bar{6}$	id.	− 6·4 ⎭	

* Root mean square, averaged with weight *p*.

Extinctions proved to be non-systematic, so that five space-groups are possible.

Consideration of these data, combined with the indices of a few outstandingly strong reflexions, led to the assumption of a cubic close-packed array of anions. The simplest way to assign one-quarter of these positions to Cl is to place Cl in the origin of the pseudo-cubic sub-cell (which is obtained from the elementary rhombohedron by compressing it halfway in the *c* direction), and OH in the face centres. This picture was completed with Co-ions to form a layer lattice of the CdCl$_2$-type, modified in the following way:

All the metal sites from the CdCl$_2$ structure which coincide with body centres of the above-mentioned pseudo-cubic sub-cell are left vacant. They correspond to 25 % of the Co ions which, therefore, can still be disposed of. These cations are placed in the equal number of body-centres situated between the original layers. The resulting trial structure can also be described as a stacking of monatomic layers as illustrated in Fig. 1(*b*) and (*c*), with a constant shift $a/\sqrt{3}$ in the [120] direction.

Such a structure is compatible with *R*$\bar{3}$*m*, the most highly symmetrical space group of those possible. The following positions are then occupied (hexagonal co-ordinates):

1 Co_I in $0, 0, \frac{1}{2}$ (b) ,
2 Cl in $\pm 0, 0, w$ (c) ,
3 Co_{II} in $\frac{1}{2}, 0, 0$; $0, \frac{1}{2}, 0$; $\frac{1}{2}, \frac{1}{2}, 0$ (e) ,
6 OH in $\pm x, \bar{x}, z$; $x, 2x, z$; $2\bar{x}, \bar{x}, z$ (h);
$Z = 6$.

For the idealized structure sketched above the parameters would take the values $w = \frac{1}{4}$, $x = \frac{1}{6}$, $z = \frac{1}{12}$. Refinement by the Fourier method led to the final values

$$w = 0.225, \quad x = 0.197, \quad z = 0.072 .$$

For this Fourier synthesis, 'observed' structure factors F_o were calculated from integrated intensities I (measured from a photometer record) by the equation $F_o = (\sin \theta)\sqrt{(I/p)}$. The factor $\sin \theta$ is an empirical approximation of a complex combination of correction factors.

The agreement between observed and calculated F values (Table 1) is seen to be fair (reliability index 17%, calculated from all reflexions with $\theta < 40°$). However, the possibility of slight displacements leading to a space group of lower symmetry cannot be excluded, though such a deformation would be difficult to explain. The existing deviation from the idealized structure, on the contrary, can easily be accounted for by the difference in size of OH and Cl, and by the mutual repulsion of the anions surrounding a vacant metal site in the layers. The calculated interatomic distances (Table 2) approach normal values well within the experimental error, estimated at ± 0.05 Å r.m.s.

Table 2. *Coordination and distances*

(Distances in Ångström units)

Coordination

Co_I:	6 OH
Co_{II}:	4 OH + 2 Cl
Cl and OH:	2 Co_I + Co_{II}

Distances

Co_I–OH: 2.12	Co_{II}–Cl: 2.53	Co_{II}–OH: 2.16
Same z-level	Cl–OH: 3.46	OH–OH: 2.74 and 4.10
Opposite side of layer	Cl–OH: 3.07	OH–OH: 3.14
Opposite layer	Cl–OH: 3.22	OH–OH: 3.18

In Table 2 the 'layers' are of course those parallel to (001) forming the $CdCl_2$ structure, from which the present structure is derived in the way already described. It should be mentioned, however, that apart from this set of layers there exist three other sets parallel to the three (101) planes (cf. Fig. 2, showing clearly one of these sets). Ideally, these systems can be built from exactly the same monatomic layers as illustrated in Fig. 1(b) and (c) in the same sequence. The only essential difference is that the shift is now as indicated by the arrow q in Fig. 1(b).

The structure bears a close resemblance to that of atacamite, $Cu_2(OH)_3Cl$. The pseudo-rhombic unit cell corresponding to the elementary cell of atacamite has been indicated in Fig. 2. This projection is strikingly similar to the (001) projection of atacamite (cf. Wells, 1949).

Wells observed that the atacamite structure can be considered as a stack of monatomic layers of the type

sketched in Fig. 1(a) (the stacking sequence in this case, too, is given by Fig. 1(c), with Cu replacing Co) and pointed out that in compounds A_nBX_3 with $X = $ OH only these layers had hitherto been found, whereas other substituents often led to layers of the type illustrated in Fig. 1(b).
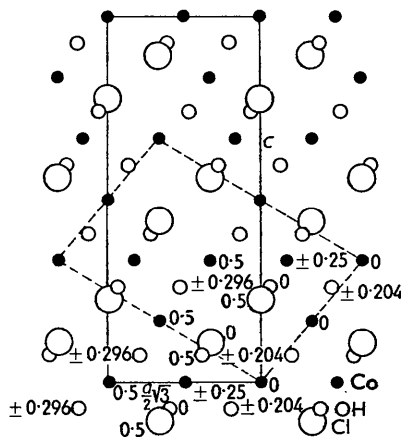

Fig. 2. Projection of the structure of $Co_2(OH)_3Cl$ in the [100] direction. The coordinates indicate the distance to the (210) plane containing the origin which is at right angles to [100], expressed as a fraction of a.

The present structure does not favour such a correlation, nor is it the only exception; according to Feitknecht & Magnet (1949), $Co_2(OH)_3Cl$ is isotypic with the analogous hydroxychlorides of Fe and Mn, and also with another modification of $Cu_2(OH)_3Cl$ which they termed $II\gamma$ as a synthetic product, and which seems to be identical with the mineral paratacamite. This is confirmed by the unit-cell determination of paratacamite in a paper by Frondel (1950), which Prof. Feitknecht kindly mentioned to me. Paratacamite has a rhombohedral lattice with (hexagonal) $a = 2 \times 6.83$ kX. and $c = 13.95$ kX. and 'a very strong pseudo-cell with a halved', probably a consequence of the peculiar (4+2)-coordination of Cu^{2+} ions. Apart from that, the only difference with $Co_2(OH)_3Cl$ is one of 3% in c. It seems, therefore, that at least four different metals, acting as substituent in $M_2(OH)_3Cl$ ($M = $ Co, Cu, Fe, Mn), are able to form structures of the type now described, consisting of monatomic layers with hexagonal symmetry as in Fig. 1(b).

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