

& Carroll (1960), and  $102.8^\circ$  for  $\text{Cl}_8\text{P}_4\text{N}_4$  by Hazekamp, Migchelsen & Vos (1962). The exocyclic N(8)–P(6)–N(9) angle of  $103.7^\circ$  in this structure is comparable to the corresponding value of  $103.8^\circ$  in  $(\text{NMe}_2)_8\text{P}_4\text{N}_4$ .

#### Intramolecular contacts

Although there are no intermolecular contacts shorter than expected, there are four short intramolecular contacts between some of the H atoms of the methyl groups and the N atoms of the ring. These are H(7)···N(5), 2.46; H(1)···N(3), 2.55; H(6)···N(5), 2.60; and H(17)···N(1), 2.62 ( $\sigma = 0.05\text{--}0.06$  Å, as identified in Fig. 1. The corresponding van der Waals contact based on the radii given by Pauling (1960) is 2.7 Å, and according to the statistics only the shortest of these contacts can be considered statistically different from the expected value. The C–H···N angles for these short contacts are 109, 106, 102, and  $106^\circ$  respectively.

#### Residual electron density

The residual electron density distribution in the mean plane of the phosphazene ring, and in the planes of the ligands is shown in Fig. 4. The positions of the P atoms have negative residual electron densities around them with troughs as low as  $-0.15$ ,  $-0.20$ , and  $-0.28$  e.Å<sup>-3</sup> at P(2), P(4), and P(6), respectively. The positions of the N atoms of the ring have positive residual electron densities of about 0.1–0.2 e.Å<sup>-3</sup> around them. The estimated standard deviations of the electron density is 0.08 e.Å<sup>-3</sup>.

The authors are indebted to Professor R. A. Shaw for various discussions on the phosphonitriles, to him

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## Barium Aluminate Hydrates. IV. The Crystal Structure of $\alpha\text{-Ba}_2[\text{Al}_4(\text{OH})_{16}]$

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The barium aluminate hydrate  $\alpha\text{-BaO}\cdot\text{Al}_2\text{O}_3\cdot 4\text{H}_2\text{O}$  has been shown by X-ray structural analysis to contain anions of formula  $[\text{Al}_4(\text{OH})_{16}]^{4-}$  consisting of a cluster of four  $\text{Al}(\text{OH})_6$  octahedra sharing edges. The anions are linked by the barium ions and by hydrogen bonding. The compound is thus a complex hydroxide whose formula should be written  $\text{Ba}_2[\text{Al}_4(\text{OH})_{16}]$ .

### Introduction

The existence of a compound of empirical formula  $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 4\text{H}_2\text{O}$  was first reported by Sainte-Claire

Deville (1862). Subsequent preparations have been reported and its stability relationships have been investigated (Carlson & Wells, 1948; Carlson, Chaconas & Wells, 1950). Thilo & Gessner (1965) also prepared it; they added the prefix  $\alpha$  to distinguish it from a different polymorph ( $\beta$ ) which they prepared by dehydration of a higher hydrate.

The single crystals used in the present study were

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tors of some of the oxygen atoms were persistently negative.

At this stage the data were critically re-examined, taking into consideration both the results of an error analysis and the original diffractometer output. In the light of this it was decided to rescale the different levels of data, to alter or delete a number of reflexions, and to restrict the portion of reciprocal space included to that with  $\sin^2 \theta < 0.16$ . A total of 825 reflexions then remained, of which 214 were 'unobserved'. Refinement was continued with these data; some temperature factors continued to run negative, and error analyses showed that agreement became distinctly worse as  $\sin^2 \theta$  increased. No reason for this could be found. Introduction and refinement of anisotropic temperature factors for the barium atom finally produced convergence with  $R=0.085$  calculated on 572 of the 611 observed reflexions. At this point none of the shifts was greater than one-third of the corresponding estimated standard deviation, and most were considerably less; all the temperature factors remained positive.

The final parameters are given in Table 2, and the observed and calculated structure factors in Table 3.

Table 2. Final atomic parameters

Positional parameters are multiplied by  $10^3$

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å <sup>2</sup> )
Ba	-1.3 (4)	301.8 (3)	125.0 (2)	*
Al(1)	320 (2)	847 (1)	225 (1)	0.8 (1)
Al(2)	313 (2)	825 (1)	557 (1)	0.8 (1)
O(1)	-28 (4)	746 (3)	558 (2)	0.5 (3)
O(2)	-26 (4)	736 (3)	197 (2)	0.7 (4)
O(3)	362 (4)	648 (3)	62 (2)	0.5 (3)
O(4)	277 (4)	43 (3)	107 (2)	0.6 (3)
O(5)	333 (4)	662 (3)	363 (2)	0.1 (3)
O(6)	332 (4)	25 (3)	424 (2)	0.1 (3)
O(7)	353 (4)	622 (3)	677 (2)	0.4 (3)
O(8)	337 (4)	23 (3)	741 (2)	0.5 (4)

\* Anisotropic temperature factors  $\times 10^4$  for Ba computed for the expression

$$f = f_0 \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$$

<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
70 (6)	89 (4)	17 (2)	20 (4)	17 (5)	21 (7)

Table 3. Observed and calculated structure factors ( $\times 10$ )

Reflexions marked with asterisks were treated as unobserved. Those marked with daggers represent additional poor agreements which were omitted from the final refinements.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>
0	0	0	2.082	2.082	0	0	0	2.082	2.082	0	0	0	2.082	2.082	0	0	0	2.082	2.082	0	0	0	2.082	2.082	0	0	0	2.082	2.082
1	0	0	0.699	0.730	1	0	0	0.636	0.773	1	0	0	0.562	0.593	1	0	0	0.498	0.530	1	0	0	0.434	0.466	1	0	0	0.370	0.402
2	0	0	1.524	1.551	2	0	0	1.462	1.493	2	0	0	1.400	1.431	2	0	0	1.338	1.369	2	0	0	1.276	1.307	2	0	0	1.214	1.245
3	0	0	2.358	2.385	3	0	0	2.296	2.327	3	0	0	2.234	2.265	3	0	0	2.172	2.203	3	0	0	2.110	2.141	3	0	0	2.048	2.079
4	0	0	3.192	3.219	4	0	0	3.130	3.161	4	0	0	3.068	3.099	4	0	0	3.006	3.037	4	0	0	2.944	2.975	4	0	0	2.882	2.913
5	0	0	4.026	4.053	5	0	0	3.964	3.995	5	0	0	3.902	3.933	5	0	0	3.840	3.871	5	0	0	3.778	3.809	5	0	0	3.716	3.747
6	0	0	4.860	4.887	6	0	0	4.798	4.829	6	0	0	4.736	4.767	6	0	0	4.674	4.705	6	0	0	4.612	4.643	6	0	0	4.550	4.581
7	0	0	5.694	5.721	7	0	0	5.632	5.663	7	0	0	5.570	5.601	7	0	0	5.508	5.539	7	0	0	5.446	5.477	7	0	0	5.384	5.415
8	0	0	6.528	6.555	8	0	0	6.466	6.497	8	0	0	6.404	6.435	8	0	0	6.342	6.373	8	0	0	6.280	6.311	8	0	0	6.218	6.249
9	0	0	7.362	7.389	9	0	0	7.300	7.331	9	0	0	7.238	7.269	9	0	0	7.176	7.207	9	0	0	7.114	7.145	9	0	0	7.052	7.083
10	0	0	8.196	8.223	10	0	0	8.134	8.165	10	0	0	8.072	8.103	10	0	0	8.010	8.041	10	0	0	7.948	7.979	10	0	0	7.886	7.917
11	0	0	9.030	9.057	11	0	0	8.968	9.000	11	0	0	8.906	8.937	11	0	0	8.844	8.875	11	0	0	8.782	8.813	11	0	0	8.720	8.751
12	0	0	9.864	9.891	12	0	0	9.802	9.833	12	0	0	9.740	9.771	12	0	0	9.678	9.709	12	0	0	9.616	9.647	12	0	0	9.554	9.585
13	0	0	10.698	10.725	13	0	0	10.636	10.667	13	0	0	10.574	10.605	13	0	0	10.512	10.543	13	0	0	10.450	10.481	13	0	0	10.388	10.419
14	0	0	11.532	11.559	14	0	0	11.470	11.501	14	0	0	11.408	11.439	14	0	0	11.346	11.377	14	0	0	11.284	11.315	14	0	0	11.222	11.253
15	0	0	12.366	12.393	15	0	0	12.304	12.335	15	0	0	12.242	12.273	15	0	0	12.180	12.211	15	0	0	12.118	12.149	15	0	0	12.056	12.087
16	0	0	13.200	13.227	16	0	0	13.138	13.169	16	0	0	13.076	13.107	16	0	0	13.014	13.045	16	0	0	12.952	12.983	16	0	0	12.890	12.921
17	0	0	14.034	14.061	17	0	0	13.972	14.003	17	0	0	13.910	13.941	17	0	0	13.848	13.879	17	0	0	13.786	13.817	17	0	0	13.724	13.755
18	0	0	14.868	14.895	18	0	0	14.806	14.837	18	0	0	14.744	14.775	18	0	0	14.682	14.713	18	0	0	14.620	14.651	18	0	0	14.558	14.589
19	0	0	15.702	15.729	19	0	0	15.640	15.671	19	0	0	15.578	15.609	19	0	0	15.516	15.547	19	0	0	15.454	15.485	19	0	0	15.392	15.423
20	0	0	16.536	16.563	20	0	0	16.474	16.505	20	0	0	16.412	16.443	20	0	0	16.350	16.381	20	0	0	16.288	16.319	20	0	0	16.226	16.257
21	0	0	17.370	17.397	21	0	0	17.308	17.339	21	0	0	17.246	17.277	21	0	0	17.184	17.215	21	0	0	17.122	17.153	21	0	0	17.060	17.091
22	0	0	18.204	18.231	22	0	0	18.142	18.173	22	0	0	18.080	18.111	22	0	0	18.018	18.049	22	0	0	17.956	17.987	22	0	0	17.894	17.925
23	0	0	19.038	19.065	23	0	0	18.976	19.007	23	0	0	18.914	18.945	23	0	0	18.852	18.883	23	0	0	18.790	18.821	23	0	0	18.728	18.759
24	0	0	19.872	19.899	24	0	0	19.810	19.841	24	0	0	19.748	19.779	24	0	0	19.686	19.717	24	0	0	19.624	19.655	24	0	0	19.562	19.593
25	0	0	20.706	20.733	25	0	0	20.644	20.675	25	0	0	20.582	20.613	25	0	0	20.520	20.551	25	0	0	20.458	20.489	25	0	0	20.396	20.427
26	0	0	21.540	21.567	26	0	0	21.478	21.509	26	0	0	21.416	21.447	26	0	0	21.354	21.385	26	0	0	21.292	21.323	26	0	0	21.230	21.261
27	0	0	22.374	22.401	27	0	0	22.312	22.343	27	0	0	22.250	22.281	27	0	0	22.188	22.219	27	0	0	22.126	22.157	27	0	0	22.064	22.095
28	0	0	23.208	23.235	28	0	0	23.146	23.177	28	0	0	23.084	23.115	28	0	0	23.022	23.053	28	0	0	22.960	22.991	28	0	0	22.898	22.929
29	0	0	24.042	24.069	29	0	0	23.980	24.011	29	0	0	23.918	23.949	29	0	0	23.856	23.887	29	0	0	23.794	23.825	29	0	0	23.732	23.763
30	0	0	24.876	24.903	30	0	0	24.814	24.845	30	0	0	24.752	24.783	30	0	0	24.690	24.721	30	0	0	24.628	24.659	30	0	0	24.566	24.597
31	0	0	25.710	25.737	31	0	0	25.648	25.679	31	0	0	25.586	25.617	31	0	0	25.524	25.555	31	0	0	25.462	25.493	31	0	0	25.400	25.431
32	0	0	26.544	26.571	32	0	0	26.482	26.513	32	0	0	26.420	26.451	32	0	0	26.358	26.389	32	0	0	26.296	26.327	32	0	0	26.234	26.265
33	0	0	27.378	27.405	33	0	0	27.316	27.347	33	0	0	27.254	27.285	33	0	0	27.192	27.223	33	0	0	27.130	27.161	33	0	0	27.068	27.099
34	0	0	28.212	28.239	34	0	0	28.150	28.181	34	0	0	28.088	28.119	34	0	0	28.026	28.057	34	0	0	27.964	27.995	34	0	0	27.902	27.933
35	0	0	29.046	29.073	35	0	0	28.984	29.015	35	0	0	28.922	28.953	35	0	0	28.860	28.891	35	0	0	28.798	28.829	35	0	0	28.736	28.767
36	0	0	29.880	29.907	36	0	0	29.818	29.849	36	0	0	29.756	29.787															

### Description of the structure

The anion, already described briefly in a short communication (Dent Glasser & Giovanoli, 1970), is shown in detail in Fig. 1, which also summarizes the interatomic distances found (see also Table 4). It is a cluster of four octahedra sharing edges. In agreement with the infrared evidence (Ahmed, 1969) all the water present appears as hydroxyl groups, and the formula of the complex hydroxy anion is  $[Al_4(OH)_{16}]^{4-}$ . There is considerable distortion of the octahedra, presumably caused by Al-Al repulsion across the shared edges; this can be seen particularly clearly by studying the O-O distances in Fig. 1(a). These range from 2.41 Å for the shortest shared edge up to 2.86 Å for some of the unshared edges. The angles at Al are also affected (Table 4). The e.s.d.'s of the individual Al-O distances are rather large, but it is instructive to divide the Al-O bonds into groups, according to the number of aluminum atoms attached to the hydroxyl group concerned, and the 'bond order' assigned using Pauling's rules (see below). The results are summarized in Table 5; the trends shown are not unexpected.

Table 4. *Coordination polyhedra in  $\alpha$ -Ba<sub>2</sub>[Al<sub>4</sub>(OH)<sub>16</sub>]*

(a) Al(OH)<sub>6</sub> octahedra

Bond distances (Å)

O(n)	Al(1)-O(n)	O(n)	Al(2)-O(n)
O(2)	1.88 (3)	O(1)	1.85 (2)
O(3)	1.90 (3)	O(5)	1.94 (2)
O(4)	1.88 (2)	O(6)	1.93 (2)
O(5)	1.91 (2)	O(6')	1.97 (2)
O(6)	1.98 (2)	O(7)	1.87 (2)
O(8')	1.89 (2)	O(8)	1.93 (2)

Bond angles (°) (all e.s.d.'s are 1°)

O(2)-Al(1)-O(3)	92	O(1)-Al(2)-O(5)	98
O(2)-Al(1)-O(4)	86	O(1)-Al(2)-O(6)	97
O(2)-Al(1)-O(5)	89	O(1)-Al(2)-O(7)	94
O(2)-Al(1)-O(6)	97	O(1)-Al(2)-O(8)	89
O(8)-Al(1)-O(3)	92	O(6')-Al(2)-O(5)	92
O(8)-Al(1)-O(4)	91	O(6')-Al(2)-O(6)	76*
O(8)-Al(1)-O(5)	92	O(6')-Al(2)-O(7)	95
O(8)-Al(1)-O(6)	80*	O(6')-Al(2)-O(8)	79*
O(3)-Al(1)-O(4)	97	O(5)-Al(2)-O(6)	79*
O(3)-Al(1)-O(5)	90	O(5)-Al(2)-O(7)	93
O(6)-Al(1)-O(4)	96	O(8)-Al(2)-O(6)	94
O(6)-Al(1)-O(5)	78*	O(8)-Al(2)-O(7)	92

\* indicates angles subtended by shared edges

(b) Ba-O polyhedron

Bond distances (Å)

O(n)	Ba-O(n)
O(1')	2.82 (2)
O(2)	2.97 (2)
O(2')	2.95 (2)
O(3)	2.86 (2)
O(3')	2.76 (2)
O(4)	2.66 (2)
O(4')	2.96 (2)
O(7')	2.82 (2)
O(8')	2.90 (2)
O(5)	3.05 (2)

Table 5. *Correlation of Al-O bond lengths with the number of aluminum atoms attached to the hydroxyl groups concerned (N<sub>Al</sub>) and bond order calculated as described in the text*

	N <sub>Al</sub>	Bond order	Bond lengths (Å)	
			Range	Mean
Al-O(6)	3	3	1.93-1.98	1.96
Al-O(5), O(8)	2	2	1.89-1.94	1.92
Al-O(2), O(3), O(4)	1	1	1.88-1.90	1.89
Al-O(1), O(7)	1	1	1.85-1.87	1.86

These anions are linked together through the barium atoms (Fig. 2) and through hydrogen bonding (Figs. 2 and 3). The coordination polyhedron of the barium is irregular; Table 4 gives ten Ba-O contacts varying from 2.66 to 3.05 Å; no other Ba contacts below 3.2 Å were found. Of these, those to O(5) and O(8'), which are among the longest contacts observed, probably do not represent bonds: these hydroxyl groups are already bonded to two Al atoms. It is notable that the only hydroxyl group which makes no contact with the barium atom is O(6) (closest approach 4.11 Å). This hydroxyl group is, of course, already bonded to *three* Al atoms. On the other hand, this group forms the shortest hydrogen bond found in the structure [2.62 to O(1')]; the attachment of the oxygen atom to three aluminum atoms presumably increases the polarity of the OH bond, enabling a strong hydrogen bond to form. Oxygen-oxygen distances between the anions are indicated on Figs. 2 and 3.

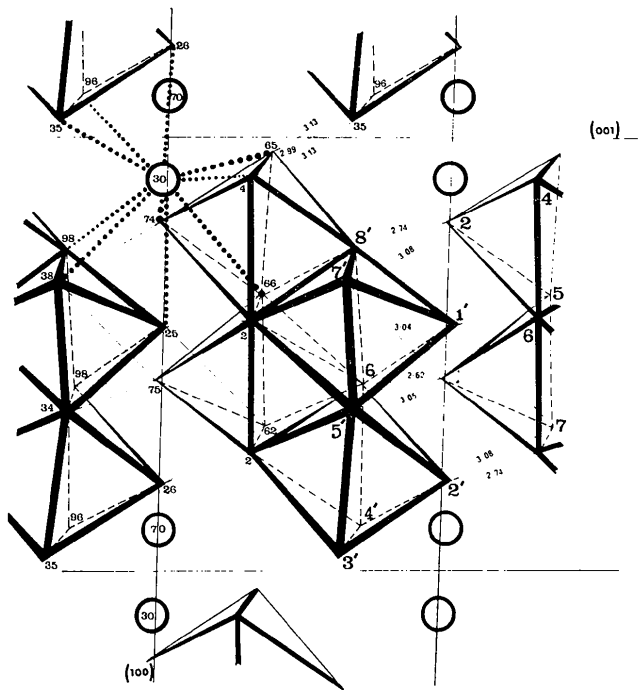


Fig. 2. The structure projected along *b*, showing barium atoms (open circles),  $[Al_4(OH)_{16}]^{4-}$  anions, and selected O-O distances between anions: *y* coordinates are given as 100 *y*/*b*.

After O(6), the next shortest contact is that between O(8) and O(2'); here O(8) is already bonded to two Al atoms, and this again would favour the formation of a strong hydrogen bond. All the other contacts, including rather surprisingly, those from O(5) (also bonded to two Al atoms), are long – 2.95 Å or longer – representing weak to extremely weak hydrogen bonds.

Pauling's electrostatic valency rule may be applied by counting each Al–O(6) bond as  $\frac{1}{3}$  and each Al–O(5) and Al–O(8) as  $\frac{1}{2}$ . Bonds from Al to O(2), O(3) and O(4) then become  $\frac{5}{6}$  and to O(1) and O(7),  $\frac{2}{3}$ . The trends in bond lengths shown in Table 5 suggest that this is a reasonable assignment. It then follows that bonds from Ba to O(2), O(3) and O(4) are  $\frac{2}{3}$  and to O(1) and O(7) are  $\frac{1}{3}$ ; the contacts with O(5) and O(8) do not represent bonds. This all adds up satisfactorily, but does not take account of the hydrogen bonding. (While it is possible in principle to modify the scheme to do this, in practice it is very difficult to decide on the proper set of ground rules to adopt). This may, in part, account for the marked lack of correlation between bond distances and bond order for the Ba–O contacts, but it is also likely that these distances, unlike the relatively short Al–O distances, are governed far more by the geometry of packing than by electrostatic considerations.

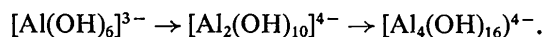
#### Relationship to other barium aluminates

The structures of two other barium aluminates containing octahedral aluminate ions have already been described; Ba<sub>3</sub>[Al(OH)<sub>6</sub>]<sub>2</sub> (Ahmed & Dent Glasser, 1969) is the barium analogue of hydrogarnet and contains isolated Al(OH)<sub>6</sub><sup>3-</sup> octahedra and Ba[Al<sub>2</sub>(OH)<sub>10</sub>]

(Louis & Moras, 1969; Ahmed & Dent Glasser, 1970a) contains pairs of octahedra sharing an edge. α-Ba<sub>2</sub>[Al<sub>2</sub>(OH)<sub>16</sub>] apparently represents a further step in the condensation of octahedra.

Perhaps the most interesting point is that this type of condensation should occur at all when the requirements of stoichiometry could be satisfied by other arrangements which would produce less Al–Al repulsion. The ratio observed in Ba<sub>2</sub>[Al<sub>2</sub>(OH)<sub>10</sub>] could equally well be produced from strings of octahedra sharing corners, and that in α-Ba<sub>2</sub>[Al<sub>4</sub>(OH)<sub>16</sub>] from layers of octahedra sharing corners; these would give anions analogous to those found in Ti<sub>2</sub>AlF<sub>5</sub> and TiAlF<sub>4</sub> (Brosset, 1937). It could be argued that these do not occur because of the peculiar bonding requirements of the OH<sup>-</sup> group, which is not of course strictly analogous to the F<sup>-</sup> ion. However, yet another arrangement is possible for α-Ba<sub>2</sub>[Al<sub>4</sub>(OH)<sub>16</sub>], namely infinite strings of octahedra sharing edges, similar to a half of one of the ribbons found in diaspore; it is very difficult to see any theoretical reason why this arrangement should not be favoured over that observed if the structure were dictated solely by the energy requirements of the solid state.

The three compounds being compared all crystallize from solution, Ba<sub>3</sub>[Al(OH)<sub>6</sub>]<sub>2</sub> from the most basic solutions and α-Ba<sub>2</sub>[Al<sub>4</sub>(OH)<sub>16</sub>] from the least basic ones. It is possible that the structures of the crystals reflect the anions present in the solutions, suggesting that with decreasing pH condensation occurs:



This would satisfactorily explain the non-occurrence of infinite strings or sheets of ions, because these would not be stable in solution.

It is known that polynuclear clusters of octahedra form in aluminum solutions as neutrality is approached from the acid side. Studies on alkaline solutions have been largely concentrated on sodium aluminate solutions, and the results tend to favour a tetrahedral Al(OH)<sub>4</sub><sup>-</sup> ion. Even if this is correct for sodium aluminate solutions, it is not necessarily inconsistent with the above suggestions for barium aluminate solutions. In the solid state, higher coordination of the central atom of a complex anion is favoured by increase in the electronegativity of the associated cation; there seems no good reason to suppose that a similar effect could not also operate in solution, particularly in such concentrated ones as those considered here. That is, in sodium aluminate solutions the aluminum might occur predominantly in tetrahedral coordination while in barium aluminate solutions octahedral coordination was favoured. Barium aluminate hydrates are known in which the aluminum is in tetrahedral coordination (Ahmed & Dent Glasser, 1970b; Giovanoli & Dent Glasser, 1971) but these are the results of hydrothermal preparations. A more comprehensive review of the factors governing the structures of aluminates has been given elsewhere (Dent Glasser, 1971).

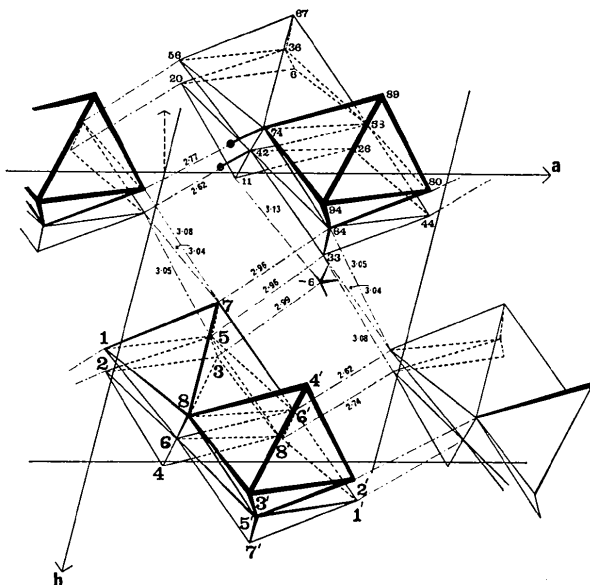


Fig. 3. The structure projected on (001), showing [Al<sub>4</sub>(OH)<sub>16</sub>]<sup>4-</sup> anions and O–O distances between anions; z coordinates are given as 100 z/c. The dashed line at the upper left corner of the cell indicates c.

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## Crystal Structure of the Four-layer Orthorhombic Polytype of Potassium Hexacyanocobaltate(III)

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A four-layer orthorhombic polytype of  $K_3Co(CN)_6$  has been identified and the crystal structure determined by three-dimensional X-ray methods using 854 intensities obtained by counter methods with Mo  $K\alpha$  radiation at room temperature. The crystal is orthorhombic with space group  $Pnc2$  and cell constants of  $a=26.69$ ,  $b=10.353$  and  $c=8.34$  Å. There are eight formula units per unit cell. The interdependence of parameters associated with the Co and K atoms occupying similar positions in the various layers gave rise to such large correlation coefficients that it was impossible to refine the parameters of all the atoms in the asymmetric unit simultaneously. Two groups of non-interfering parameters were therefore refined separately by full-matrix least squares to a conventional  $R$  of 0.09. Bond lengths and bond angles of the different octahedra are given and a possible distortion is discussed in terms thereof.

### Introduction

A crystal of Cr-doped  $K_3Co(CN)_6$  has been used in a number of nuclear magnetic resonance (n.m.r.) experiments in which, among other things, the second moment (Lourens & Reynhardt, 1971a) and the quadrupole interaction (Lourens & Reynhardt, 1971b) of the  $^{59}Co$  nuclei were measured. With a view to the interpretation of these results in terms of the atomic environments of the  $^{59}Co$  nuclei, the determination of this structure was undertaken, since a review of the available crystallographic literature on  $K_3Co(CN)_6$  shows complete confusion.

This confusion was partially resolved by Kohn & Townes (1961) who first demonstrated the existence of the  $1M$ ,  $20r$ ,  $3M$  and  $7M$  polytypes. The  $40r$  polytype should now be added to these. The early investigators obviously dealt with several of these and at-

tempted to assign a single space group to explain all their observations.

In this way Barkhatov & Zhdanov (1942) gave cell dimensions very similar to those for the  $40r$  polytype, but by analogy with the results of Gottfried & Nagelschmidt (1930) for  $K_3Fe(CN)_6$  they assigned the space group  $P2_1/c$  and called it pseudo-orthorhombic. Our impression is that these workers actually encountered the  $40r$  type and not only the  $1M$  type as suggested by Kohn & Townes (1961). Okaya & Pepinsky (1956), who first described the  $20r$  polytype correctly, also attempted to explain the earlier results (obtained for other polytypes) in terms of their observations.

Barkhatov (1942) proposed the first structure based on the unit cell of the  $1M$  polytype. In their neutron-diffraction study Curry & Runciman (1959) accepted the special positions of the cobalt and potassium atoms suggested by Barkhatov (1942) and determined the struc-