

The Crystal Structures of $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8] (\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8] (\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$

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The crystal structures of a basic aluminium sulfate, $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 11\text{H}_2\text{O}$, and the isomorphous selenate have been investigated by means of X-ray crystallographic methods. The crystals are monoclinic and the space group is $P2_1/n$. The unit cell dimensions are: $a = 8.15 \text{ \AA}$, $b = 12.48 \text{ \AA}$, $c = 8.40 \text{ \AA}$, $\beta = 101.9^\circ$ for the sulfate and $a = 8.26 \text{ \AA}$, $b = 12.76 \text{ \AA}$, $c = 8.48 \text{ \AA}$, $\beta = 102.1^\circ$ for the selenate.

The structure contains discrete aluminum-oxygen complexes of the composition Al_3O_{10} , which are built up from two AlO_6 octahedra sharing an edge. The hydrogen atoms have been located by indirect methods. Their positions indicate that the formula for the Al_3O_{10} group should be written $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$. These ions are joined by means of hydrogen bonds to the oxygen atoms of the sulfate or the selenate groups and the water molecules.

According to a previous structure determination^{1,2} some of the more basic of the aluminium salts contain discrete $\text{Al}_{13}\text{O}_{40}$ groups. Since these groups are joined in the crystals only by means of hydrogen bonds², it seems reasonable to assume that their structure reflects the structure of the polynuclear complexes that form when an aluminium salt solution is hydrolyzed by the addition of alkali^{3,4}. In order to elucidate the intermediate steps in the condensation process leading to these polynuclear ions, the structures of some less basic salts have been investigated. One of these is $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 11\text{H}_2\text{O}$, which has a composition corresponding to the loss of one proton for each $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion, compared with a ratio of about 2.5 to 1 for the compound containing the $\text{Al}_{13}\text{O}_{40}$ groups. The structure is of special interest as the number of oxygen atoms is sufficient to give the aluminium ion the expected coordination number of six without involving any of the oxygen atoms of the sulfate groups. This fact makes the existence of discrete aluminium-oxygen complexes possible.

The preparation of $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 11\text{H}_2\text{O}$ has been described by several authors. In Gmelin's »Handbuch der Chemie» the formula is given as $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 12\text{H}_2\text{O}$, but later work by Bassett and Goodwin⁵ has shown that only

11 moles of water are present and not 12. Bassett^{5,6} has suggested that the ion $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{++}$ is present in the structure, but this hypothesis is not supported by the results of the present structure determination.

EXPERIMENTAL

According to the phase diagram given by Bassett and Goodwin⁵ for the system $\text{Al}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O}$ at 25°C, the compound $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 11\text{H}_2\text{O}$ has only a small range of stability. Solutions, which according to the diagram should be supersaturated with respect to $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 11\text{H}_2\text{O}$, were prepared by dissolving pure aluminium metal (99.99 %) in sulfuric acid (p.a.). To make the reaction more rapid, a small amount of mercury was added as a catalyst. After filtration the solutions were left to crystallize at room temperature. Fairly large crystals were obtained from a solution prepared from 5.3 g Al, 24.5 g H_2SO_4 , and 70.2 g H_2O .

The crystals are readily soluble in water forming a clear solution. After some time or on dilution the solution becomes milky and a precipitate is formed.

Analysis. The amount of aluminium was determined by igniting a sample of the air-dried crystals and weighing the residue as Al_2O_3 . Water was determined by Brush and Penfield's method as described by Kolthoff and Sandell⁷. Sulfate was determined by precipitating and weighing BaSO_4 . The results, which are given in Table 1, confirm the results of Bassett and Goodwin that the composition corresponds to $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 11\text{H}_2\text{O}$.

Table 1.

	Found	Calculated for	
		$\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 11\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 12\text{H}_2\text{O}$
% Al_2O_3	22.4	22.15	21.32
% SO_3	34.7	34.79	33.48
% H_2O	43.4	43.06	45.20
Density	1.82	1.829	1.900

X-Ray data. Rotation and Weissenberg photographs showed that the crystals were monoclinic and approximate unit cell dimensions were calculated from them. The following more precise values were calculated from a powder photograph (Table 2) taken with $\text{CuK}\alpha$ radiation in a Guinier focusing camera using KCl ($a_0 = 6.293 \text{ \AA}$) as internal standard:

$$a = 8.15_1 \text{ \AA}, b = 12.47_6 \text{ \AA}, c = 8.39_9 \text{ \AA}, \beta = 101.9_0^\circ.$$

The density obtained from the apparent loss of weight in benzene was $1.82 \text{ g} \cdot \text{cm}^{-3}$. The calculated density for two formula weights per unit cell is 1.829 (Table 1).

The prism-shaped crystals are extended along the crystallographic a axis. The b and c axes lie in the directions of the diagonals of the base of the prism. Weissenberg photographs were taken about all three axes using CuK radiation. The multiple film technique was used, and the intensities were estimated visually by comparison with an intensity scale (prepared by timed exposures of one of the reflections from the crystal). The maximum dimension of the crystals used was about 0.15 mm. No correction for absorption was applied ($\mu = 50 \text{ cm}^{-1}$). The intensities were corrected for Lorentz and polarization factors in the usual manner and were placed on a common scale by means of reflections occurring on more than one photograph.

The systematic absences are $h0l$ with h $h+l$ odd and $0k0$ with k odd. This is characteristic for the space group $P2_1/n$.

The isomorphous selenate, $\text{Al}_2\text{O}_3 \cdot 2\text{SeO}_3 \cdot 11\text{H}_2\text{O}$, was prepared by dissolving aluminium hydroxide in selenic acid in the manner described by Bassett⁷. The crystals seemed to be similar in all respects to those of the sulfate. Rotation and Weissenberg photographs were used to calculate approximate unit cell dimensions and the following more accurate values were determined from Guinier powder photographs:

$$a = 8.25_6 \text{ \AA}, b = 12.76 \text{ \AA}, c = 8.48 \text{ \AA}, \beta = 102.1^\circ$$

Intensity data were collected in the same way as for the sulfate.

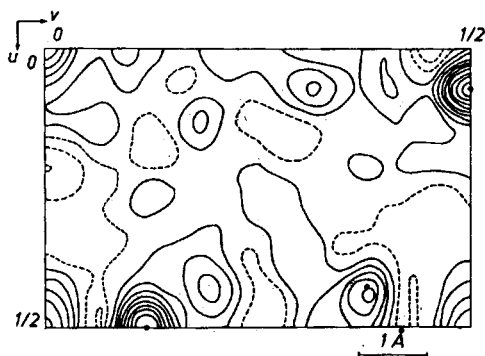


Fig. 1a. Difference Patterson projection along [001]. At the origin only every 5th contour has been drawn. Broken lines indicate negative regions. Small black circles indicate the positions of S-S (Se-Se) vectors.

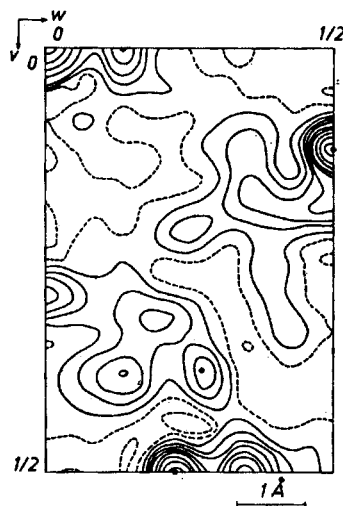


Fig. 1b. Difference Patterson projection along [100].

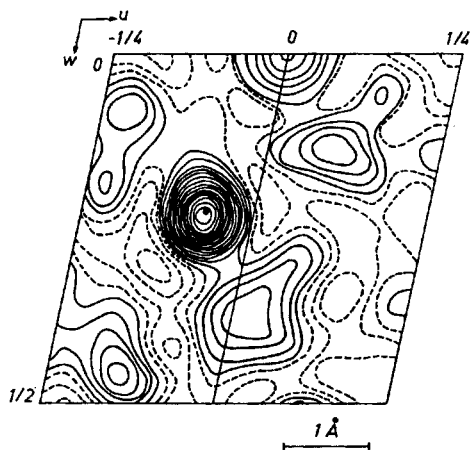


Fig. 1c. Difference Patterson projection along [010].

STRUCTURE DETERMINATION

Preliminary scale and temperature factors for both the sulfate and the selenate were obtained from the $hk0$ and $0kl$ intensities by means of Wilson's method. Difference Patterson projections along the a , b , and c axes were then calculated*. These are shown in Fig. 1. The ratio between the scale factors

* All calculations were carried out on the "Besk" computer using programs designed for the calculation of electron densities¹⁸ and structure factors¹⁹.

for the sulfate and the selenate obtained from the Wilson plot and used for the Patterson maps in Fig. 1 is approximately a factor of 1.3 higher than the ratio calculated from the $|F_c|^2$ values for the final structures, but this difference does not affect the following discussion.

In space group $P2_1/n$ the special positions are all centers of symmetry, and the four S (Se) atoms must therefore occupy one of the general four-fold positions: $\pm(x, y, z) \pm(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$.

The vectors connecting these points are:

$\frac{1}{2}\frac{1}{2} - 2y\frac{1}{2}$	weight	2
$\frac{1}{2} - 2x\frac{1}{2}\frac{1}{2} - 2z$	»	2
$2x\ 2y\ 2z$	»	1
$2x\ 2y\ 2z$	»	1

The first two vectors can be identified easily on the $hk0$ and $0kl$ projections (Figs. 1a and 1b). In the $hk0$ projection only the peaks at

$$u = \frac{1}{2}, v = 0.118 \text{ and } u = 0.072, v = \frac{1}{2}$$

are of sufficient heights to correspond to the difference between a Se — Se and a S — S vector. For the $0kl$ projection possible vectors are:

$$v = 0.120, w = \frac{1}{2} \text{ and } v = \frac{1}{2}, w = 0.225.$$

These vectors lead to the following parameter values:

$$\begin{aligned} x &= \pm 0.214 \text{ or } \pm 0.714 \\ y &= \pm 0.191 \text{ » } \pm 0.691 \\ z &= \pm 0.137 \text{ » } \pm 0.637 \end{aligned}$$

The only combinations of these parameters that are crystallographically non-equivalent can be written as

$$\begin{aligned} x &= 0.214 & x &= 0.214 \\ y &= 0.191 \text{ and } y &= 0.191 \\ z &= 0.137 & z &= -0.137 \end{aligned}$$

Of these only the second set is consistent with the vectors $(\frac{1}{2} - 2x, \frac{1}{2} - 2z)$ occurring in the $h0l$ projection (Fig. 1c).

There is another possible vector $v = \frac{1}{2}, w = \frac{1}{2} - 2z$ in the $0kl$ projection, as the peak at $v = \frac{1}{2}, w = 0.350$ is not much lower than the peak selected above. This possibility is ruled out by a comparison with the vectors in the $h0l$ projection.

The Patterson projections thus give the following parameters for the sulfur or the selenium atoms:

$$x = 0.214, y = 0.191, z = 0.863.$$

All vectors within the corresponding four-fold position are present as peaks in the Patterson maps (Fig. 1) and have the heights expected from the weights of the corresponding vectors.

The contributions to the structure factors from these atoms were now calculated, and $F_c^{\text{Se}} - F_c^{\text{S}}$ for each reflection was compared with the differences between the observed structure factors calculated for the four possible

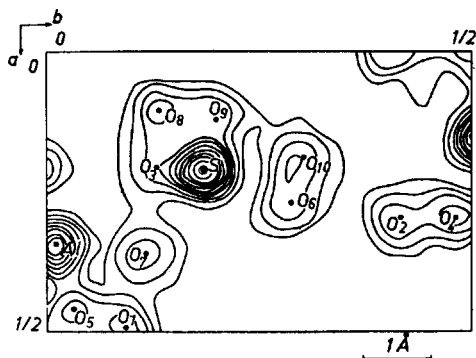


Fig. 2a. c -axis projection of the electron-density. Contours are drawn at intervals of $3 e \cdot \text{\AA}^{-2}$. The zero contour is omitted.

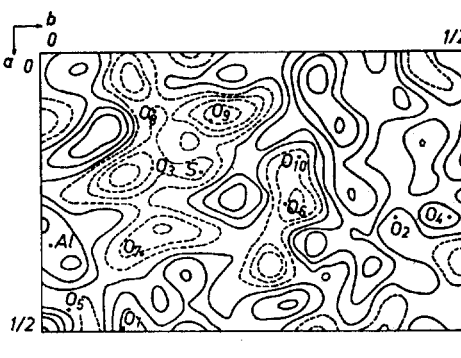


Fig. 2b. $F_0 - F_c$ synthesis along $[001]$. Contours are drawn at intervals of $0.3 e \cdot \text{\AA}^{-2}$. Dashed lines indicate negative regions.

sign combinations: $|F_o^{sel.}| + |F_o^{sulf.}|$, $|F_o^{sel.}| - |F_o^{sulf.}|$, $-|F_o^{sel.}| + |F_o^{sulf.}|$, and $-|F_o^{sel.}| - |F_o^{sulf.}|$. In this way signs were determined for 237 out of 275 observed independent $hk0$, $0kl$, and $h0l$ reflections for the sulfate. Only 12 of these signs were different from the signs calculated for the final structure, and as these were associated with relatively small structure factors, the Fourier maps, calculated at this stage of the structure determination, did not differ much from the final Fourier syntheses shown in Figs. 2a, 3a, and 4a.

The proportion of assigned and erroneous signs for the selenate was approximately the same, and the corresponding Fourier maps were very similar to those for the sulfate.

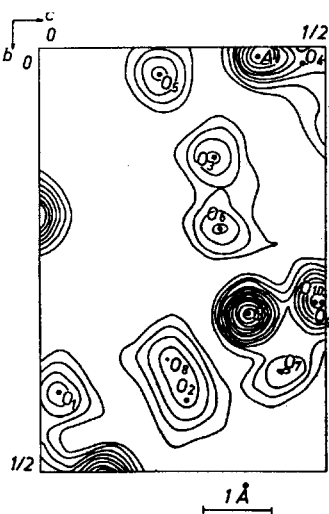


Fig. 3a. a -axis projection of the electron-density. Contours are drawn at intervals of $3 e \cdot \text{\AA}^{-2}$. The zero contour is omitted.



Fig. 3b. $F_0 - F_c$ synthesis along $[100]$. Contours are drawn at intervals of $0.3 e \cdot \text{\AA}^{-2}$. Dashed lines indicate negative regions.

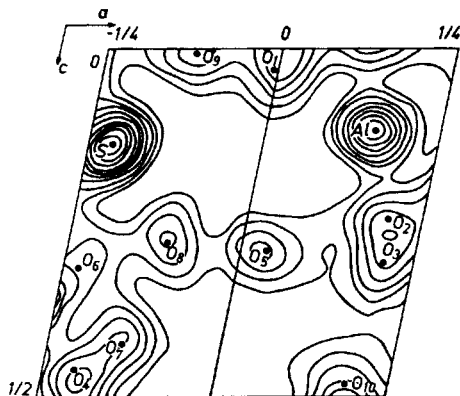


Fig. 4a. b -axis projection of the electron density. Contours are drawn at intervals of $3 e \cdot \text{\AA}^{-3}$. The zero contour is omitted.

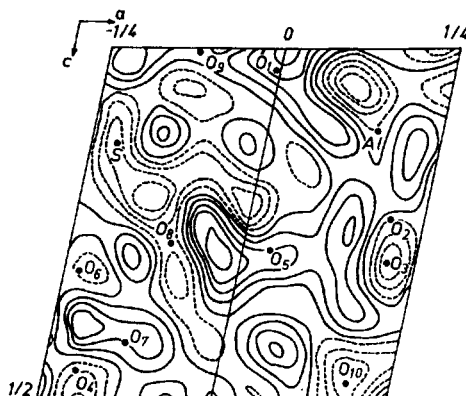


Fig. 4b. $F_o - F_c$ synthesis along $[010]$. Contours are drawn at intervals of $0.3 e \cdot \text{\AA}^{-3}$. Dashed lines indicate negative regions.

In addition to the maximum at the sulfur position, the $h0l$ and the $hk0$ projections both contain one peak that is higher than all the others. The x parameters for the two peaks are approximately the same, and in the $0kl$ projection a maximum of about the same height occurs at the point defined by the corresponding y and z parameters. These peaks were assumed to correspond to an aluminium atom in a four-fold position ($x = 0.15$, $y = 0.51$, $z = 0.11$). This assumption is supported by the octahedral arrangement of lower peaks around the assumed aluminium position and also by the smallest distance, 2.9 \AA , between the positions — the distance usually observed between two octahedrally coordinated aluminium atoms sharing an edge.

Despite some overlap of peaks the three dimensional arrangement of oxygen atoms in the AlO_6 octahedra could be deduced by a detailed comparison of the three projections, assuming that two AlO_6 octahedra have a shared edge. The Al — O and O — O distances calculated from the resulting parameters are approximately the same as those usually found for AlO_6 octahedra. The oxygen atoms of the sulfate groups were located in the same way by comparing the positions of peaks in the three Fourier projections. The obscuring of the oxygen peaks by diffraction effects from the heavier sulfur atoms and the more serious overlap of peaks in this case result in somewhat more uncertain parameters than above.

None of the oxygen atoms located in this way is shared between a sulfate group and an AlO_6 octahedron. The only oxygen atoms that are associated with more than one cation are those defining the shared edge of the AlO_6 octahedra. The electron density projections thus show the presence of discrete aluminium-oxygen complexes of the composition Al_2O_{10} each built up from two AlO_6 octahedra sharing an edge.

The two Al_2O_{10} groups and the four SO_4 groups in the unit cell account for 36 of the 40 oxygen atoms present. The positions of the remaining four oxygen atoms are uniquely determined by the still unexplained peaks in the Fourier maps.

Table 2. Powder photograph of $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 11\text{H}_2\text{O}$. Guinier camera. $\text{CuK}\alpha$ radiation..

hkl	$10^4 \sin^2\theta$ calc	$10^2 \sin^2\theta$ obs	I obs	hkl	$10^4 \sin^2\theta$ calc	$10^2 \sin^2\theta$ obs	I obs
0 1 1	0.0126	0.0125	m	1 0 3	0.0996	0.0995	vw
1 1 0	0.0131	0.0130	s	2 4 $\bar{1}$	0.0996		
1 0 $\bar{1}$	0.0144	0.0143	vw	3 1 $\bar{2}$	0.1005	0.1005	vvw
1 1 $\bar{1}$	0.0182	0.0181	s	2 2 2	0.1026	0.1026	vw
1 0 1	0.0218	0.0218	vvw	3 0 $\bar{3}$	0.1294	0.1293	vvw
0 2 1	0.0240	0.0240	m	3 3 $\bar{2}$	0.1310	0.1309	vvw
1 2 0	0.0246	0.0244	m	1 5 $\bar{2}$	0.1323	0.1324	vvw
1 1 1	0.0256	0.0255	vvw	2 5 0	0.1326		
1 2 $\bar{1}$	0.0296	0.0296	s	1 3 3	0.1339	0.1338	vvw
1 2 1	0.0371	0.0371	s	2 5 $\bar{1}$	0.1339		
2 0 0	0.0373	0.0373	s	3 2 $\bar{3}$	0.1446	0.1447	vvw
0 1 2	0.0389	0.0389	s	3 4 0	0.1449		
1 1 $\bar{2}$	0.0408	0.0408	m	4 1 $\bar{1}$	0.1469	0.1471	vvw
2 1 0	0.0411	0.0410	w	1 5 2	0.1472		
2 1 $\bar{1}$	0.0424	0.0423	vw	2 0 4	0.1480	0.1485	vw
0 3 1	0.0431	0.0431	s	2 4 2	0.1484		
1 3 0	0.0436	0.0436	m	2 5 1	0.1488	0.1548	vvw
2 2 0	0.0525	0.0525	w	4 0 $\bar{2}$	0.1545		
2 1 1	0.0574	0.0574	w	2 4 $\bar{3}$	0.1549		
2 0 $\bar{2}$	0.0575			4 1 $\bar{2}$	0.1583	0.1582	vvw
2 1 $\bar{2}$	0.0613	m	4 2 $\bar{1}$	0.1583			
2 2 1	0.0688	0.0688	vvw	1 4 3	0.1606	0.1607	vvw
1 4 0	0.0703	0.0703	vvw	4 2 0	0.1645	0.1647	m
1 3 $\bar{2}$	0.0713	0.0713	m	3 4 1	0.1649		
2 3 0	0.0716			1 6 $\bar{2}$	0.1742	0.1741	vvw
2 2 $\bar{2}$	0.0728	0 5 3	0.1743				
2 3 $\bar{1}$	0.0729	0.0728	m	2 6 0	0.1745	0.1835	w
1 1 $\bar{3}$	0.0810	0.0810	w	3 1 4	0.1835		
3 1 0	0.0877	0.0878	s	4 3 0	0.1835	0.1906	m
2 3 1	0.0879			3 4 $\bar{3}$	0.1904		
2 1 2	0.0912	0.0911	w	2 6 1	0.1908	0.1949	vvw
2 3 $\bar{2}$	0.0918	0.0917	vw	2 6 $\bar{2}$	0.1947		
2 1 $\bar{3}$	0.0978	0.0977	vvw	1 5 3	0.1949	0.1949	vvw
				3 2 $\bar{4}$	0.1949		

REFINEMENT OF THE STRUCTURE

With the parameters determined from the electron density projections and the temperature factor obtained from the Wilson plot as a starting point, the sulfate was refined by means of $F_o - F_c$ syntheses on (001), (010), and (100). The three projections were refined simultaneously rather than independently. When the indicated shifts differed from one projection to another, an intermediate value was chosen so as to take into account as far as possible the various amounts of overlap in the three projections. For the following refinement cycle identical shifts were then applied to all three projections.

The starting parameters gave R factors ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; only observed reflections were included) of 0.28 for the $h0l$, 0.25 for the $hk0$, and 0.25 for the $0kl$ structure factors. Two difference maps reduced the R factors to 0.16 for each of the three projections. At this stage of the refinement it was clear that there was a large difference between the temperature factors

Table 3 a. Final parameters for $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$

Atom	x	y	z
4 S	0.2130	0.1850	0.8640
4 Al	0.1545	0.5107	0.1160
4 O ₁	0.994	0.407	0.031
4 O ₂	0.298 _s	0.416	0.257
4 O ₃	0.292	0.628	0.193
4 O ₄	0.296	0.481 _s	0.960
4 O ₅	0.462	0.031	0.211
4 O ₆	0.729	0.713	0.183 _s
4 O ₇	0.640	0.883	0.079
4 O ₈	0.895	0.868 _s	0.278
4 O ₉	0.879	0.801	0.007
4 O ₁₀	0.312	0.802	0.020

of the sulfur and aluminium atoms on the one hand and of the oxygen atoms on the other. Individual isotropic temperature factors were therefore introduced. However, the individual variations for the oxygen atoms did not seem to be so large as to be significant, and throughout the refinement a single temperature factor was used for all oxygen atoms.

After four more difference syntheses significant shifts in positional parameters were no longer indicated, and the refinement was not continued further. The final parameters are given in Table 3a. The temperature factors used for the final calculation of structure factors, listed in Table 4, are 0.9 Å² for S and Al and 2.0 Å² for O. Atomic scattering factors were calculated from the analytical expressions given by Vand *et al.*⁹. The R factors, including observed reflections only, are 0.086 for the $h0l$, 0.087 for the $hk0$, and 0.091 for the $0kl$ structure factors. The final difference syntheses computed from the F_o and F_c values in Table 4 are shown in Figs. 2b, 3b, and 4b.

In order to check the parameters on some general reflections the hll structure factors were calculated. A comparison between observed and calculated values is given in Table 4. The resulting R factor is 0.091 for the 111 reflections observed.

The selenate was refined in the same way by means of five successive $F_o - F_c$ syntheses along the three axes. The final R factors are 0.110, 0.092, and 0.097 for the $hk0$, $0kl$, and $h0l$ structure factors, respectively. The tem-

Table 3 b. Final parameters for $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_6](\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$

Atom	x	y	z
4 Se	0.2148	0.1910	0.8610
4 Al	0.1525	0.5154	0.1160
4 O ₁	0.001	0.409 _s	0.037
4 O ₂	0.300	0.428	0.260
4 O ₃	0.282	0.635	0.184
4 O ₄	0.292	0.488	0.966
4 O ₅	0.461	0.033	0.213
4 O ₆	0.719	0.700	0.189
4 O ₇	0.624	0.887	0.075
4 O ₈	0.910	0.867	0.288
4 O ₉	0.887	0.795	0.996
4 O ₁₀	0.302	0.807	0.020

Table 4. Observed and calculated structure factors for $[\text{Al}_2(\text{OH})_6(\text{H}_2\text{O})_2](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$

hkl	F_o	F_c	hkl	F_o	F_c
0 0 0	—	436	6 5 0	30	29
2	118	—122	7	20	—17
4	17	16	8	13	—12
6	28	26	9	27	30
8	< 6	—2			
1 0	11	12	0 6 0	56	52
			1	30	37
1 1 0	54	—48	2	39	—40
2	54	—53	3	16	—18
3	48	—48	4	14	—14
4	26	26	5	< 5	—3
5	14	14	6	< 6	—5
6	14	—14	7	7	—6
7	52	—52	8	8	—7
8	22	25	9	7	—6
9	23	26			
10	6	—7	1 7 0	9	—7
			2	12	—13
0 2 0	17	15	3	28	28
1	58	—68	4	23	25
2	48	51	5	< 6	—1
3	37	—38	6	14	—11
4	13	—10	7	11	—9
5	6	6	8	19	18
6	33	32	9	5	5
7	9	9			
8	< 6	—2	0 8 0	< 5	—3
9	> 5	—4	1	29	—31
10	12	—16	2	15	18
			3	7	10
1 3 0	58	—64	4	29	—33
2	53	54	5	< 6	—5
3	37	36	6	14	14
4	25	—25	7	8	—8
5	9	—9	8	8	7
6	13	11			
7	9	10	1 9 0	16	—14
8	6	7	2	30	30
9	8	—11	3	19	17
10	5	4	4	20	—21
			5	10	—8
0 4 0	5	—3	6	11	11
1	36	37	7	15	—13
2	18	—16			
3	25	—21	0 1 0 0	64	66
4	5	1	1	< 6	—4
5	6	2	2	29	—31
6	14	12	3	30	—30
7	14	—11	4	< 6	—1
8	8	—6	5	19	20
9	16	—15	6	16	15
1 5 0	6	8	1 1 1 0	12	—9
2	51	51	2	10	7
3	15	12	3	7	—4
4	24	—24	4	< 6	—1
5	16	12			

Table 4. Continued.

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
5 11 0	10	13	0 3 1	101	-115
6	< 4	- 3	2	15	- 14
7	20	- 22	3	42	- 40
			4	15	16
0 12 0	< 6	- 7	5	52	51
1	26	- 27	6	12	- 11
2	< 6	0	7	49	- 47
3	<< 5	4	8	14	- 13
4	<< 5	3	9	12	- 13
5	< 4	2	10	11	- 10
6	12	12			
			0 4 1	19	- 22
1 13 0	6	- 5	2	36	32
2	20	20	3	41	- 39
3	16	14	4	29	- 25
4	< 4	- 3	5	25	25
5	6	- 6	6	9	11
			7	< 4	6
0 14 0	< 5	- 4	8	14	13
1	13	14	9	19	- 21
2	< 4	0	10	6	6
3	10	- 9			
4	12	- 12	0 5 1	32	31
			2	17	- 17
1 15 0	9	8	3	21	19
2	18	20	4	7	9
3	8	7	5	43	42
			6	< 4	3
0 0 2	< 1	- 1	7	22	24
4	28	29			
6	13	14	0 6 1	31	- 32
8	33	29	2	12	12
10	5	3	3	7	7
			4	46	- 42
0 1 1	44	- 41	5	26	- 25
2	96	94	6	15	11
3	8	- 3	7	< 4	4
4	13	- 12	8	23	22
5	5	1	9	13	15
6	13	- 14			
7	< 4	0	0 7 1	45	- 42
8	17	15	2	36	33
9	5	- 5	3	6	4
10	6	6	4	13	14
			5	< 4	1
0 2 1	53	51	6	22	- 23
2	16	- 14	7	13	- 12
3	32	31	8	23	22
4	3	2	9	16	- 19
5	25	26			
6	37	- 39	0 8 1	20	- 23
7	13	- 14	2	11	- 13
8	< 4	- 1	3	14	- 14
9	29	25	4	< 4	- 3
10	6	6	5	24	- 24

Table 4. Continued.

hkl	F_o	F_c	hkl	F_o	F_c
0 8 6	24	— 25	1 0 $\bar{9}$	< 6	— 4
7	< 4	3	$\bar{7}$	23	18
8	16	— 16	$\bar{5}$	10	— 5
9	8	— 8	$\bar{3}$	10	— 11
			$\bar{1}$	14	13
0 9 1	28	— 27	1	38	42
2	11	— 11	3	79	72
3	32	32	5	35	— 36
4	27	25	7	51	46
5	< 4	2	9	16	15
6	< 4	3	2 0 $\bar{10}$	8	9
7	10	— 11	$\bar{8}$	44	— 40
8	< 3	— 3	$\bar{6}$	20	— 20
			$\bar{4}$	58	57
0 10 1	44	— 44	$\bar{2}$	55	53
2	27	25	2	16	— 14
3	10	— 10	4	16	12
4	11	— 11	6	< 7	— 6
5	16	16	8	< 6	4
6	8	9			
7	< 3	1	3 0 $\bar{9}$	14	— 13
8	15	19	$\bar{7}$	26	— 26
			$\bar{5}$	7	— 5
0 11 1	< 4	5	$\bar{3}$	90	90
2	28	30	$\bar{1}$	40	36
3	21	— 21	1	13	13
4	11	11	3	21	21
5	9	11	5	61	65
6	< 4	— 6	7	24	— 23
7	9	9	9	28	— 29
0 12 1	7	6	4 0 $\bar{10}$	11	— 11
2	10	5	$\bar{8}$	< 7	6
3	9	8	$\bar{6}$	11	11
4	18	— 16	$\bar{4}$	13	— 15
5	10	— 12	$\bar{2}$	29	— 28
6	7	— 8	2	16	— 21
			4	17	17
			6	30	27
			8	20	— 19
0 13 1	32	— 32			
2	14	16	5 0 $\bar{9}$	13	— 9
3	8	9	$\bar{7}$	21	23
4	5	5	$\bar{5}$	< 6	— 6
5	7	9	$\bar{3}$	48	— 57
6	15	— 19	$\bar{1}$	15	— 17
			1	15	10
0 14 1	12	— 14	3	< 6	— 3
2	< 3	— 2	5	44	— 47
3	16	— 20	7	< 6	1
4	6	8			
5	6	7	6 0 $\bar{8}$	16	17
			$\bar{6}$	14	11
0 15 1	4	4	$\bar{4}$	7	9
2	5	— 6	$\bar{2}$	18	— 19
3	12	18			

Table 4. Continued.

hkl	F_o	F_c	hkl	F_o	F_c
602	63	65	21 $\bar{6}$	20	— 20
4	17	— 17	5	24	23
6	20	— 22	4	48	— 48
70 $\bar{9}$	< 4	5	3	50	— 43
7	11	— 13	2	72	69
5	23	26	1	30	— 34
3	8	6	211	37	35
4	44	46	2	92	— 88
1	13	— 13	3	< 6	— 5
3	20	19	4	< 7	4
5	7	10	5	< 7	— 2
80 $\bar{8}$	< 4	— 1	6	25	— 22
6	33	— 40	7	26	— 22
4	6	6	8	26	— 25
2	40	41	9	14	12
2	20	— 22	31 $\bar{10}$	12	14
4	< 5	— 2	9	18	18
907	6	6	8	< 8	6
5	9	— 13	7	< 8	— 4
3	14	16	6	13	— 12
1	13	14	5	21	— 21
1	< 5	— 1	4	88	— 92
3	< 4	— 4	3	53	— 53
100 $\bar{4}$	15	18	2	34	32
2	9	— 13	1	< 5	6
11 $\bar{10}$	11	— 12	311	10	— 9
9	< 7	— 2	2	20	18
8	< 8	5	3	43	— 44
7	9	— 12	4	20	— 17
6	47	47	5	< 8	2
5	28	29	6	15	— 13
4	20	16	7	20	20
3	63	61	8	11	11
2	83	— 74	9	14	— 16
1	71	— 62	41 $\bar{10}$	9	— 9
111	24	— 24	9	33	33
2	22	25	8	13	11
3	< 6	7	7	< 9	4
4	13	10	6	26	28
5	8	11	5	34	— 33
6	35	— 34	4	19	23
7	37	— 32	3	12	16
8	< 9	— 8	2	7	— 6
9	< 7	7	1	30	— 33
10	< 5	— 1	411	< 6	2
21 $\bar{10}$	12	12	2	28	33
9	11	— 9	3	74	— 80
8	< 8	— 3	4	44	— 44
7	< 8	— 6	5	< 9	2
			6	10	8
			7	10	8
			8	9	11

Table 4. Continued.

hkl	F_o	F_c	hkl	F_o	F_c
5 1 $\bar{9}$	10	— 13	7 1 $\bar{5}$	< 9	— 1
8	11	13	4	15	18
7	18	16	3	28	27
6	< 9	— 8	2	9	— 9
5	23	23	1	24	26
4	< 8	4			
3	10	10	7 1 1	< 9	1
2	24	21	2	< 9	4
1	< 7	1	3	< 8	— 6
			4	< 8	12
5 1 1	< 7	— 1	5	10	14
2	39	— 39	6	< 5	— 6
3	28	31			
4	17	— 15	8 1 $\bar{8}$	11	16
5	20	— 21	7	9	10
6	< 8	5	6	< 7	5
7	21	— 22	5	< 8	1
8	8	9	4	15	— 16
			3	< 8	6
6 1 $\bar{9}$	9	— 10	2	< 8	4
8	< 7	— 3	1	< 8	— 11
7	25	— 24			
6	< 9	— 8	8 1 1	< 8	7
5	16	16	2	< 8	— 6
4	29	29	3	< 7	2
3	11	— 15	4	9	— 12
2	< 8	— 2			
1	15	— 16	9 1 $\bar{7}$	9	17
			6	< 6	2
6 1 1	22	— 19	5	< 7	— 3
2	< 8	— 7	4	18	— 24
3	14	16	3	11	— 14
4	30	32	2	14	— 14
5	11	11	1	11	— 11
6	< 7	— 3			
7	< 5	— 1	9 1 1	< 5	5
			2	< 5	0
7 1 $\bar{9}$	10	16	3	< 5	— 1
8	6	— 7			
7	< 7	— 6	10 1 $\bar{5}$	7	— 13
6	18	19	4	9	13

perature factors used for the final calculation of structure factors are 0.85 \AA^2 for Al, 0.95 \AA^2 for Se, and 2.0 \AA^2 for O. The final parameters are listed in Table 3b.

For the sulfate the standard deviations in positional parameters calculated by means of Cruickshank's formula¹⁰ are 0.005 \AA for sulfur, 0.007 \AA for aluminium, and 0.01_6 \AA for oxygen atoms. These values lead to standard deviations of 0.01_7 \AA in S—O, 0.01_8 \AA in Al—O and 0.02_3 \AA in O—O distances. For Al—Al and O—O distances between atoms related by centers of symmetry, the standard deviations are 0.01_4 \AA and 0.03_3 \AA respectively. For the selenate the corresponding values are about twice as large.

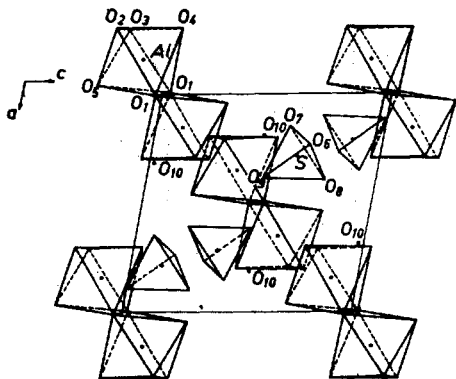


Fig. 5. Projection of the structure along the *b*-axis.

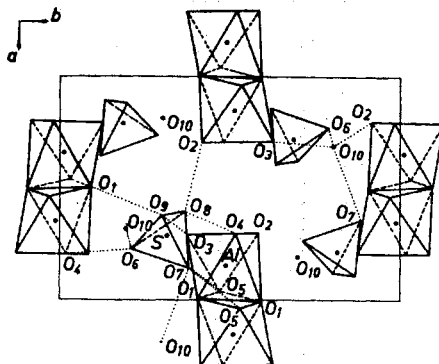


Fig. 6. Projection of the structure along the *c*-axis. Some of the postulated hydrogen bonds have been indicated by means of dotted lines.

The standard deviations calculated in this way may be somewhat too low for the oxygen atoms most affected by overlap. This is especially true for the oxygen atoms of the sulfate and selenate groups, which in all projections are rather close to the heavy atoms. Since for each refinement cycle an average value of the parameter shifts from the three projections was applied, small shifts are still indicated for some of the atoms in the final difference syntheses (Fig. 2b, 3b, and 4b). These remaining shifts are all less than the calculated standard deviations.

DISCUSSION OF THE STRUCTURE

Projections of the structure along the *b* and *c* axes are shown in Figs. 5 and 6.

The unit cell contains two discrete Al_2O_{10} groups, each built up from two AlO_6 octahedra sharing an edge. A projection of the group on a plane through the aluminium atoms and the two bridging oxygens is shown in Fig. 7a, and a projection on a plane perpendicular to this is shown in Fig. 7b. Interatomic distances are given in Table 5. For comparison, the corresponding distances are also given for the selenate.

The average value of the aluminium oxygen bond lengths is 1.89 Å, which is close to the sum of the crystal radii of the ions, 1.90 Å, and is similar to values found for other crystals with octahedral coordination of oxygen ions about aluminium¹¹. The bonds to the bridging oxygens are the shortest of the Al—O bond lengths listed in Table 5 although in view of the standard deviations the difference from the average value, 1.89 Å, is not significant.

The contraction of the shared edge, O_1-O_1 , to 2.39 Å is much more pronounced than is usually found for shared edge lengths in aluminium octahedra in other structures. The O_1 atoms are related by a center of symmetry which

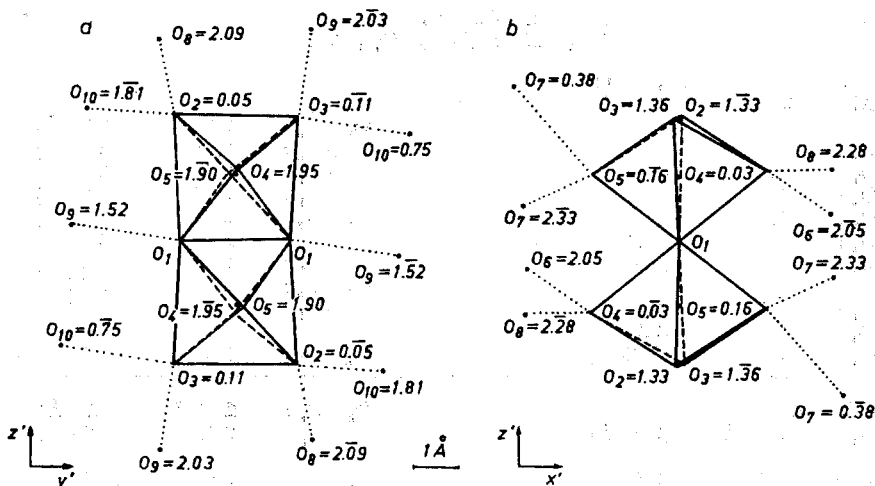


Fig. 7a. Projection of the Al_3O_{10} group on a plane through the aluminium atoms and the two bridging oxygens (O_1). The positions of the hydrogen bonded oxygen atoms are also shown. The height, in \AA , above or below the projection plane is given. Dotted lines indicate hydrogen bonds. The aluminium atoms are represented by small filled circles.

Fig. 7b. Projection of the Al_3O_{10} group on a plane through the aluminium atoms and perpendicular to the projection plane in Fig. 7a. Note that the figure is drawn with the y' axis pointing downwards from the viewer.

leads to a rather large standard deviation, 0.03_2 \AA , but the occurrence of the same short O_1-O_1 distance in both the sulfate and the selenate supports the conclusion that the shortening to 2.39 \AA is real. In diaspore¹² the length of an edge shared between two AlO_6 octahedra is 2.46 or 2.54 \AA as calculated from the parameters given, and in zunyite¹³ the shared edge length is reported to be 2.53 \AA . A comparison does not seem entirely justified, however, since in the structures referred to, one of the oxygen atoms of the shared edge also belongs to two other edges shared with a third octahedron. In the structure of $\text{Na}[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4(\text{H}_2\text{O})_{13}$ ² there are two kinds of shared edges; one is analogous to those in diaspore and zunyite and is 2.54 \AA , while the other, involving oxygen atoms each belonging to only two octahedra, has a length of 2.37 \AA . This is the same within the standard deviations as those found in the present structure determinations. According to a preliminary note on the refinement of dickite, $\text{Al}_2\text{Si}_2\text{H}_4\text{O}_5$, a similarly short shared edge length of 2.37 \AA occurs in the octahedral layers in this structure¹⁴.

The short O—O distances listed in Table 5 are indicative of hydrogen bonds. The number of such short distances is the same as the number of protons in the structure. Moreover, a comparison between the sulfate and the selenate shows that the short O—O contacts occur between the same atoms in both structures and also that the average difference between these O—O distances in the two structures is much less than between other O—O dis-

Table 5. Interatomic distances. (Values given in parentheses are distances in $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_6](\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$)

Distances within an Al_2O_{10} group					
Al—Al:	2.86 Å	(2.88 Å)			
Al—O ₁ :	1.87	(1.87)	O ₁ —O ₄ :	2.81 Å	(2.78 Å)
—O ₁ :	1.85	(1.87)	—O ₄ :	2.76	(2.75)
—O ₂ :	1.90	(1.90)	—O ₅ :	2.63	(2.61)
—O ₃ :	1.88	(1.88)	—O ₆ :	2.76	(2.79)
—O ₄ :	1.95	(1.92)	O ₂ —O ₃ :	2.70	(2.71)
—O ₅ :	1.91	(1.90)	—O ₄ :	2.62	(2.60)
			—O ₅ :	2.62	(2.59)
O ₁ —O ₁ :	2.39	(2.39)	O ₃ —O ₄ :	2.68	(2.65)
—O ₂ :	2.80	(2.79)	—O ₅ :	2.66	(2.69)
—O ₃ :	2.71	(2.73)			
			O ₄ —O ₆ :	3.08	(3.11)
Short O—O distances					
O ₁ —O ₆ :	2.84 Å	(2.80 Å)	O ₄ —O ₆ :	2.70 Å	(2.73 Å)
			—O ₅ :	2.65	(2.69)
O ₂ —O ₃ :	2.64	(2.63)	O ₅ —O ₇ :	2.63	(2.60)
—O ₁₀ :	2.65	(2.69)	—O ₇ :	2.72	(2.70)
O ₃ —O ₆ :	2.73	(2.75)	O ₁₀ —O ₇ :	2.77	(2.75)
—O ₁₀ :	2.64	(2.62)	—O ₇ :	2.80	(2.79)
Other O—O distances < 4 Å					
O ₁ —O ₆ :	3.50 Å	(3.58 Å)	O ₂ —O ₆ :	3.73 Å	(3.69 Å)
—O ₇ :	3.67	(3.66)	—O ₇ :	3.70	(3.82)
—O ₈ :	3.87	(4.01)	—O ₈ :	3.75	(3.73)
—O ₁₀ :	3.57	(3.69)			
O ₂ —O ₃ :	3.71	(3.85)	O ₄ —O ₄ :	3.29	(3.38)
—O ₆ :	3.28	(3.41)	—O ₇ :	3.61	(3.68)
—O ₈ :	3.61	(3.71)	—O ₈ :	3.30	(3.26)
			—O ₉ :	3.83	(3.94)
O ₃ —O ₆ :	3.80 Å	(3.89 Å)	O ₄ —O ₁₀ :	3.57 Å	(3.70 Å)
—O ₆ :	3.37	(3.36)	O ₇ —O ₇ :	3.77	(3.61)
—O ₈ :	3.66	(3.75)	O ₈ —O ₁₀ :	3.11	(3.21)
—O ₁₀ :	3.38	(3.44)	O ₉ —O ₁₀ :	3.51	(3.39)
—O ₁₀ :	3.60	(3.68)			
Distances within a SO_4 group in $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$:					
S—O ₆ :	1.44 Å		O ₆ —O ₇ :	2.35 Å	
—O ₇ :	1.47		—O ₈ :	2.40	
—O ₈ :	1.49		—O ₉ :	2.38	
—O ₉ :	1.45		O ₇ —O ₈ :	2.39	
			—O ₉ :	2.39	
			O ₈ —O ₉ :	2.41	
Distances within an SeO_4 group in $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_6](\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$:					
Se—O ₁ :	1.58 Å		O ₄ —O ₇ :	2.63 Å	
—O ₇ :	1.66		—O ₈ :	2.68	
—O ₈ :	1.63		—O ₉ :	2.65	
—O ₉ :	1.62		O ₇ —O ₈ :	2.67	
			—O ₉ :	2.67	
			O ₈ —O ₉ :	2.61	

Table 6. Angles about oxygen atoms involved in hydrogen bonds (calculated for $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$)

$\text{O}_1: \text{Al}-\text{O}_1-\text{Al}: 100.4^\circ$	$\text{O}_5: \text{O}_7-\text{O}_5-\text{O}_7: 89.6^\circ$
$\text{O}_9-\text{O}_1-\text{Al}: 115.6^\circ$	$\text{O}_7-\text{O}_5-\text{Al}: 127.6^\circ$
$\text{O}_8-\text{O}_1-\text{Al}: 129.5^\circ$	$\text{O}_7-\text{O}_5-\text{Al}: 130.2^\circ$
$\text{O}_2: \text{O}_{10}-\text{O}_2-\text{O}_8: 115.1^\circ$	$\text{O}_{10}: \text{O}_8-\text{O}_{10}-\text{O}_3: 89.1^\circ$
$\text{O}_{10}-\text{O}_2-\text{Al}: 121.2^\circ$	$\text{O}_8-\text{O}_{10}-\text{O}_7: 103.2^\circ$
$\text{O}_8-\text{O}_2-\text{Al}: 123.2^\circ$	$\text{O}_2-\text{O}_{10}-\text{O}_6: 135.1^\circ$
$\text{O}_3: \text{O}_9-\text{O}_3-\text{O}_{10}: 103.4^\circ$	$\text{O}_2-\text{O}_{10}-\text{O}_7: 97.6^\circ$
$\text{O}_{10}-\text{O}_3-\text{Al}: 123.6^\circ$	$\text{O}_3-\text{O}_{10}-\text{O}_6: 118.4^\circ$
$\text{O}_9-\text{O}_3-\text{Al}: 127.1^\circ$	$\text{O}_3-\text{O}_{10}-\text{O}_7: 111.4^\circ$
$\text{O}_4: \text{O}_8-\text{O}_4-\text{O}_3: 112.5^\circ$	
$\text{O}_8-\text{O}_4-\text{Al}: 117.9^\circ$	
$\text{O}_8-\text{O}_4-\text{Al}: 123.3^\circ$	

tances (Table 5). Thus, there seem to be strong indications that the oxygen atoms involved in these short O—O contacts are joined together by means of hydrogen bonds. This is supported by considerations of the sum of electrostatic bond strengths for each oxygen atom. Two hydrogen bonds are formed by each of O_2 , O_3 , O_4 , and O_5 , which are bonded to only one aluminium atom. The bridging oxygens, O_1 , are each involved in one short O—O distance, but the length of this bond, 2.84 Å, indicates that it is rather weak. The oxygen atom, O_{10} , which is not bonded to any aluminium or sulfur atoms and therefore probably is a H_2O molecule, forms four hydrogen bonds. Two of these are directed towards oxygen atoms of the sulfate groups and two towards oxygen atoms of the Al_2O_{10} group. A formula that is consistent with these results should therefore be written: $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8](\text{SO}_4)_2(\text{H}_2\text{O})_2$.

The arrangement of hydrogen bonds around the $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$ group is shown in Fig. 7. For each of O_2 , O_3 , and O_4 the angle between the short O—O contacts is approximately tetrahedral (Table 6). The sum of the angles about each of the oxygen atoms is rather close to 360° , which shows that the Al—O bond lies, very approximately, in the plane through the pair of hydrogen bonds associated with O_2 , O_3 , and O_4 . The same is true for O_5 , but the deviations are larger. In the case of O_1 , the single hydrogen bond and the two Al—O bonds are probably more accurately described as pointing towards three corners of a tetrahedron although the angles show rather large deviations from the tetrahedral value.

The average value of the S—O bond lengths in the sulfate group, 1.46 Å, does not differ significantly from those found in other structures, for example 1.44 Å in $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ ¹⁵ or 1.49 and 1.48 Å in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ¹⁶.

Of the oxygen atoms of the sulfate groups one (O_7) is involved in three hydrogen bonds and the remaining three (O_6 , O_8 , O_9) are each involved in two hydrogen bonds.

In the selenate the average value of the Se—O bond lengths is 1.62 Å and of the O—O distances 2.65 Å. For H_2SeO_4 corresponding distances have been reported to be 1.61 Å and 2.64 Å, respectively¹⁷.

Acknowledgements. I am much indebted to Professor Lars Gunnar Sillén for his continuous interest in this work. I also wish to thank Dr. Georg Lundgren and Dr. Howard T. Evans Jr. for discussions in connection with the work. The English text has been corrected by Dr. Denis McWhan. Free time at the "Besk" computer has been made available by the Swedish Board for Computing Machinery. The work has been supported by the *Office of Scientific Research, of the Office of Aerospace Research, United States Air Force*, through its European Office on contract number AF 61 (052)-162.

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Received July 21, 1961.