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The Crystal Structure of $Al_2(OH)_2TeO_3SO_4$

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$Al_2(OH)_2TeO_3SO_4$ crystallizes in space group $P2_1/m$ with $a=7{\cdot}013$ (2), $b=9{\cdot}539$ (4), $c=4{\cdot}880$ (2) Å, $\beta=92{\cdot}65$ (3)°, $Z=2$. The structure was solved from Patterson and electron density calculations with 1289 independent reflexions, and a final R of 0·032 was obtained. The structure consists of tetrahedral SO_4^{2-} ions and pyramidal TeO_3 units connected by Al to form infinite sheets. The Al coordination is approximately octahedral with Al–O distances of 1·864–1·934 Å. The Te–O and the S–O lengths are 1·902–1·939 and 1·467–1·487 Å respectively.

Introduction

A new Te^{IV} compound, $Al_2(OH)_2TeO_3SO_4$, has been prepared as part of an investigation of tellurate-(IV,VI) chemistry under hydrothermal conditions (Moret, 1972) and single crystals were kindly provided by Dr Moret. In most of the previously known M-tellurate(IV) structures, the metal atoms (Zn, Cu, Fe) are involved in three-dimensional covalent M–O–Te^{IV} nets (Lindqvist, 1973; Zeeman, 1971). Only in $BaTeO_3.H_2O$ (Rottersten-Nielsen, Grønbæk-Hazell & Rasmussen, 1971) can the building units be regarded as Ba^{2+} and TeO_3^{2-} ions.

The aim of the present investigation was to examine the effect of the Al atoms on the Te^{IV} coordination.

Data collection

Crystals of $Al_2(OH)_2TeO_3SO_4$ were first investigated with Weissenberg techniques, the reflexion pattern indicating the space groups $P2_1$ or $P2_1/m$. Accurate cell dimensions were determined from a Guinier powder photograph (Table 1) with KCl as an internal standard ($a_{KCl}=6{\cdot}2919_4$ Å at 20°C; Hambling, 1953), (*POWDER*; Lindqvist & Wengelin, 1967). Crystallographic data are given in Table 2. The density was determined by flotation in aqueous thallium(I) formate and malonate ('Clericis Lösung').

The crystal was mounted along **c** (for dimensions see Fig. 1) and intensities were collected on a two-

Table 1. *Powder data for* $Al_2(OH)_2TeO_3SO_4$; Cu $K\alpha_1$ *radiation* (1·54050 Å)

h	*k*	*l*	sin² θ (obs)	sin² θ (calc)	*d*(calc) (Å)	*I*
1	0	0	0·01213	0·01209	7·006	*vw*
1	1	0	0·01864	0·01861	5·647	*w*
0	2	0	0·02625	0·02608	4·769	*m*
0	1	$\bar{1}$	0·03155	0·03149	4·340	*w*
1	0	$\bar{1}$	0·03566	0·03545	4·091	*w*
1	0	1	0·03859	0·03866	3·917	*m*
1	1	$\bar{1}$	0·04226	0·04197	3·760	*w*
1	1	1	0·04513	0·04518	3·624	*w*
2	1	0	0·05489	0·05487	3·288	*w*
1	2	$\bar{1}$	0·06160	0·06154	3·105	*m*
1	2	1	0·06483	0·06475	3·027	*w*
2	0	$\bar{1}$	0·07020	0·07011	2·909	*m*
1	3	0	0·07087	0·07077	2·895	*w*
2	2	0	0·74061	0·07443	2·823	*w*
2	0	1	0·07646	0·07653	2·784	*s*
2	1	$\bar{1}$	0·07646	0·07663	2·782	*s*
0	3	$\bar{1}$	0·08370	0·08366	2·663	*m*
1	3	$\bar{1}$	0·09424	0·09414	2·510	*m*
0	0	$\bar{2}$	0·10006	0·09988	2·437	*m*
2	2	1	0·10271	0·10261	2·405	*s*
0	4	0	0·10435	0·10433	2·385	*m*
0	1	$\bar{2}$	0·10631	0·10640	2·361	*m*
1	0	$\bar{2}$	0·10887	0·10876	2·269	*w*
1	1	$\bar{2}$	0·11511	0·11528	2·269	*s*
0	4	$\bar{1}$	0·12933	0·12930	2·142	*w*
3	1	$\bar{1}$	0·13514	0·13546	2·093	*vs*
3	0	1	0·13862	0·13858	2·069	*w*
1	4	1	0·14302	0·14299	2·037	*w*
2	0	2	0·15478	0·15466	1·959	*w*
0	3	$\bar{2}$	0·15865	0·15857	1·934	*w*
1	3	2	0·17384	0·17387	1·847	*w*
3	3	1	0·19734	0·19726	1·734	*w*
4	1	0	0·20014	0·19992	1·723	*w*

Table 2. *Crystallographic data for* $Al_2(OH)_2TeO_3SO_4$

$a = 7{\cdot}013\ (2)$ Å
$b = 9{\cdot}539\ (4)$
$c = 4{\cdot}880\ (2)$
$\beta = 92{\cdot}65\ (3)^\circ$
$V = 326{\cdot}1\ (2)$ Å^3
$Z = 2$
$M = 359{\cdot}64$
$\varrho_o = 3{\cdot}7$ g cm^{-3}
$\varrho_c = 3{\cdot}66$
Space group: $P2_1/m$
Equivalent positions: $\pm(x,y,z)$; $\pm(x,\frac{1}{2}-y,z)$
μ(Mo $K\alpha$) = 53·4 cm^{-1}
Crystal habit: colourless plates (Fig. 1)

circle single-crystal diffractometer (Pailred) with graphite-monochromated Mo $K\alpha$ radiation. The ω-scanning procedure was used with a scan speed of 2·5° min^{-1}, the background being measured for 24 s at both ends of the scan interval. The layers $hk0$–$hk6$ were recorded up to $2\theta \sim 60^\circ$. 1531 independent reflexions were measured of which 1289 with $\sigma(I)/I < 0{\cdot}4$ were regarded as significant and used in the subsequent analysis. Intensity statistics and Lp corrections were performed with *DATAP*1 (Lindgren, 1975). Absorption effects were calculated with *DATAP*2 (Coppens, Leiserowitz & Rabinovich, 1965). The transmission factors varied from 0·53 to 0·90, but were not applied until a preliminary structure was known.

Structure determination and refinement

The exact chemical composition was not known at the start, but Te and Al were known to be present. From the Patterson function (*DRF*; Zalkin, Berkeley), it was apparent that there were two Te and four Al atoms in the cell occupying positions 2(*e*) and 4(*f*) in space group $P2_1/m$. A complete model was obtained from successive electron density calculations. It then also became obvious that the crystals contained sulphate ions from the $Al_2(SO_4)_3$ solutions used in the preparation.

A refinement based on all 1289 observed reflexions and including anisotropic temperature factors and an isotropic extinction factor (*LINUS*; Coppens & Hamilton, 1970) yielded an R of 0·032. Scattering factors for uncharged Te (Cromer & Waber, 1965), Al, S and O (Doyle & Turner, 1968) corrected for the real part of the anomalous scattering (Cromer, 1965) were used.

Weights $w = (ca/F)^{-1/2}$ for $F \le a$ and $w = [c-(F-a)^{1/2}]^{-1/2}$ for $F \ge a$ gave a reasonable analysis for $a = 30{\cdot}0$ and $c = 50{\cdot}0$ (Table 3).

Table 3. *Weight analysis after the last cycle of refinement*

The quantities $w\Delta^2$ are normalized sums and N is the number of reflexions within each F_o interval.

F_o interval	N	$w\Delta^2$
0·0– 14·2	126	0·90
14·2– 17·8	125	0·73
17·8– 22·0	133	0·71
22·0– 25·4	125	0·68
25·4– 29·0	126	0·55
29·0– 32·7	130	1·10
32·7– 37·8	128	0·84
37·8– 44·7	134	0·91
44·7– 57·1	129	0·93
57·1–136·2	133	2·59

$R = \sum \lvert F_o - \lvert F_c \rvert \rvert / \sum F_o = 0{\cdot}032$
$R_w = (\sum w \lvert F_o - \lvert F_c \rvert \rvert^2 / \sum w F_o^2)^{1/2} = 0{\cdot}032$

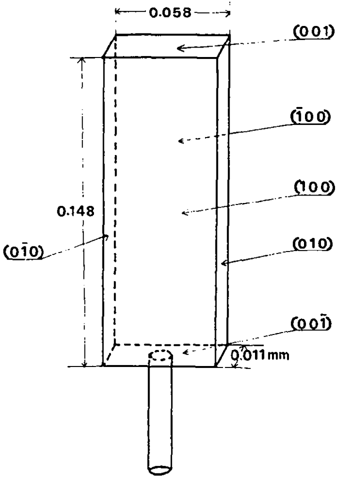

Fig. 1. The crystal used for data collection. The crystal volume is 7·56 × 10^{-4} mm^3.

Table 4. *Final atomic parameters in* $Al_2(OH)_2TeO_3SO_4$

The anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$. Estimated standard deviations in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	0·18867 (5)	$\frac{1}{4}$	0·31015 (7)	0·00485 (18)	0·00479 (11)	0·00510 (11)		0·00034 (7)	
Al	0·0544 (2)	0·5752 (1)	0·2552 (2)	0·0080 (2)	0·0044 (5)	0·0066 (5)	0·0004 (5)	0·0007 (3)	0·0000 (3)
S	0·6069 (2)	$\frac{1}{4}$	0·9623 (2)	0·0049 (5)	0·0092 (5)	0·0095 (5)		0·0009 (4)	
O(1)	−0·0067 (6)	$\frac{1}{4}$	0·5801 (8)	0·0139 (16)	0·0080 (16)	0·0037 (16)		0·0031 (11)	
O(2)	0·0686 (4)	0·3920 (3)	0·0887 (5)	0·0109 (11)	0·0030 (10)	0·0062 (11)	0·0008 (8)	−0·0014 (7)	0·0000 (7)
O(3)	0·1682 (4)	0·4846 (3)	0·5657 (5)	0·0045 (10)	0·0091 (11)	0·0085 (11)	−0·0007 (9)	0·0003 (7)	−0·0003 (10)
O(4)	0·4058 (6)	$\frac{1}{4}$	0·8663 (10)	0·0054 (17)	0·0168 (21)	0·0250 (24)		−0·0018 (14)	
O(5)	0·6250 (7)	$\frac{1}{4}$	0·2619 (10)	0·0134 (21)	0·0414 (31)	0·0107 (22)		−0·0008 (15)	
O(6)	0·7031 (4)	0·3760 (3)	0·8528 (7)	0·0106 (12)	0·0095 (12)	0·0221 (16)	−0·0015 (10)	0·0065 (10)	0·0001 (10)

Isotropic extinction parameter (Coppens & Hamilton, 1970): $g \times 10^{-4} = 0{\cdot}031\ (5)$.

The refinement indicated only small extinction effects, the isotropic extinction parameter *g* (Coppens & Hamilton, 1970) being 0·031 (5) × 10^4. The final parameter list is given in Table 4.*

The structure was checked with a difference synthesis (*FFT*; Ten Eyck, 1973). The maximum residual density of 2·4 e Å^{-3} occurred close to the Te atoms.

Interatomic distances and angles (*DISTAN*; Zalkin, Berkeley) are presented in Table 5.

Table 5. *Coordination distances and angles in* $Al_2(OH)_2TeO_3SO_4$

The notation is in accordance with Figs. 4 and 5.

Te–O(1)		1·939 (4) Å	O(1)–Te–O(2)		94·4 (1)°
Te–O(2)	(2×)	1·902 (3)	O(1)–Te–O(3)	(2×)	67·4 (1)
Te–O(3)	(2×)	2·567 (3)	O(1)–Te–O(4)		169·3 (2)
Te–O(4)		2·705 (5)	O(2)–Te–O′(2)		90·6 (2)
Al–O(1)		1·889 (2)	O(2)–Te–O(3)	(2×)	67·9 (1)
Al–O(2)		1·934 (3)	O(2)–Te–O′(3)	(2×)	149·6 (1)
Al–O′(2)		1·881 (3)	O(2)–Te–O(4)	(2×)	78·1 (1)
Al–O(3)		1·910 (3)	O(3)–Te–O′(3)		121·2 (1)
Al–O′(3)		1·888 (3)	O(3)–Te–O(4)	(2×)	115·8 (1)
Al–O(6)		1·864 (3)	O(1)–Al–O(2)		172·7 (2)
S—O(4)		1·467 (5)	O(1)–Al–O′(2)		98·7 (2)
S—O(5)		1·467 (5)	O(1)–Al–O′(3)		98·0 (2)
S—O(6)	(2×)	1·487 (3)	O(1)–Al–O(3)		84·4 (2)
			O(1)–Al–O(6)		94·7 (2)
			O(2)–Al–O′(2)		78·9 (1)
			O(2)–Al–O′(3)		83·9 (1)
			O(2)–Al–O(3)		89·0 (1)
			O(2)–Al–O(6)		92·3 (1)
			O′(2)–Al–O(3)		96·1 (1)
			O′(2)–Al–O′(3)		162·3 (1)
			O′(2)–Al–O(6)		95·4 (1)
			O(3)–Al–O′(3)		79·9 (1)
			O(3)–Al–O(6)		168·5 (1)
			O′(3)–Al–O(6)		89·1 (1)
			O(4)–S—O(5)		111·0 (3)
			O(4)–S—O(6)	(2×)	109·2 (2)
			O(5)–S—O(6)	(2×)	109·8 (2)
			O(6)–S—O′(6)		107·8 (3)

Discussion

$Al_2(OH)_2TeO_3SO_4$ is not readily classified as either a covalent or an ionic compound. The structure contains TeO_3 pyramids, SO_4 tetrahedra and dimeric Al–O octahedra, $Al_2(OH)_2O_8$. The building units share O atoms to form infinite sheets. (Figs. 2 and 3).

The layers are held together by van der Waals forces.

Table 6. O–O *distances less than* 4 Å

An asterisk indicates interlayer contacts, and the notation –*A*– means that both O atoms belong to the coordination polyhedron of *A*.

O(6)–O(6)	2·403 (6) Å	–S–
O(4)–O(6) (2×)	2·407 (5)	–S–
O(5)–O(6) (2×)	2·416 (5)	–S–
O(4)–O(5)	2·419 (7)	–S–
O(2)–O(2)	2·424 (5)	–Al–
O(3)–O(3)	2·434 (5)	–Al–
O(1)–O(3) (2×)	2·553 (3)	–Al–
O(2)–O(3)	2·555 (4)	–Al–
O(3)–O(6)	2·663 (4)	–Al–
O(2)–O(3)	2·695 (4)	–Al–
O(2)–O(2)	2·705 (5)	–Te–
O(2)–O(6)	2·740 (4)	–Al–
O(1)–O(6) (2×)	2·761 (5)	–Al–
O(2)–O(6)	2·769 (4)	–Al–
O(2)–O(3)	2·819 (4)	–Al–
O(1)–O(2) (2×)	2·819 (4)	–Te–
O(1)–O(3) (2×)	2·851 (3)	–Al–
O(1)–O(2) (2×)	2·860 (4)	–Al–
O(1)–O(5)	2·948(6)	
O(2)–O(4) (2×)	2·970 (5)	*
O(3)–O(5) (2×)	3·020 (4)	
O(3)–O(4) (2×)	3·114 (4)	*
O(5)–O(6) (2×)	3·146 (6)	
O(1)–O(4)	3·155 (6)	*
O(3)–O(6)	3·227 (4)	
O(4)–O(5)	3·379 (7)	
O(2)–O(5) (2×)	3·533 (5)	
O(2)–O(3)	3·725 (4)	–Al–
O(3)–O(6)	3·755 (4)	–Al–
O(2)–O(6)	3·764 (4)	
O(1)–O(2) (2×)	3·816 (3)	–Al–
O(4)–O(6) (2×)	3·911 (4)	*

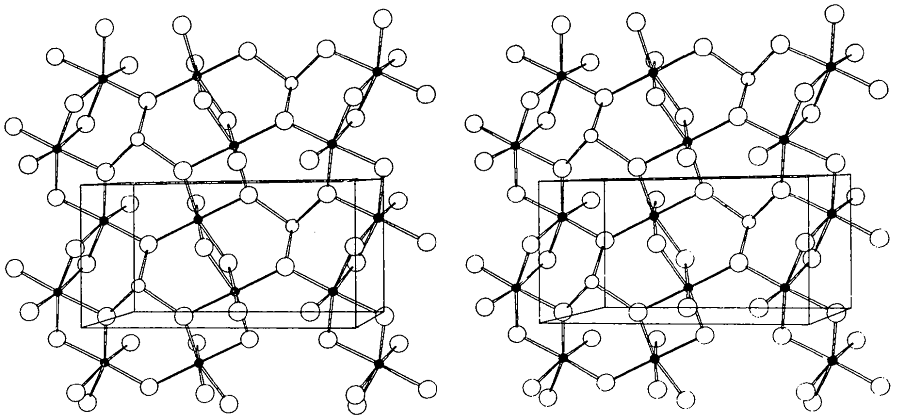

Fig. 2. A stereoscopic view along a showing how the dimeric Al–O octahedra are connected by the TeO_3 groups to form infinite sheets (*ORTEP*; Johnson, 1965).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementray Publication No. SUP 31205 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, White Friars, Chester CH1 1NZ, England.

The positions of the sulphate groups give the sheets a bulky shape (Fig. 3) which may stabilize the ordered packing. The sulphate O(4) is involved in short interlayer O–O van der Waals contacts (Table 6). It is also possible that weak Te^{IV}–O interactions contribute slightly to the bonding. The Te^{IV}–O(4) distance is only 2·705 (5) Å, which is comparable to the 2·64 (2) found for similar interactions in $Te(C_6H_4O_2)_2$ (Lindqvist, 1967) and 2·706 (4) Å in Te_2O_5 (Lindqvist & Moret, 1973). In these two compounds there was reason to consider such Te^{IV}–O distances as weak bonds.

The H atom positions could not be deduced from the X-ray investigation, but it is reasonable to assume that they are attached to O(3) atoms, which form bridges between two Al atoms (Fig. 4). Similar double $\mathrm{Al}{<}^{\mathrm{OH}}_{\mathrm{OH}}{>}\mathrm{Al}$ bridges have been found in diaspore (Busing & Levy, 1958) and in $[Al_2(OH)_2(H_2O)_8](SO_4)_2.2H_2O$ and the corresponding selenate (Johansson, 1962); the bridging hydroxide groups participated only in weak hydrogen bonds. In $Al_2(OH)_2TeO_3SO_4$ only one of the distances O(3)–O(5) (intralayer) of 3·020 or O(3)–O(4) (interlayer) of 3·114 may correspond to a hydrogen bond (Table 6). However, since both distances are long, it is doubtful if there are any hydrogen bonds in the structure.

The octahedral Al coordination includes, apart from the two O(3) bridge bonds, O atoms from three different TeO_3 groups and one sulphate O (Figs. 2 and 4, Table 5). The Al–O distances are similar to the 1·851 (2)–1·980 (3) in diaspore (Busing & Levy, 1958) and the 1·85–1·95 Å (Johansson, 1962) in $[Al_2(OH)_2(H_2O)_8](SO_4)_2.2H_2O$ (Fig. 4). The dimeric anion $[Al_2(OH)_2(H_2O)_8]^{4-}$ has a very short O–O distance across the double bridge of 2·39 Å. The corresponding value for $Al_2(OH)_2TeO_3SO_4$ is only slightly longer, 2·434 (5) Å.

The coordination of Te is threefold pyramidal (Fig. 5, Table 5), similar to that found in other tellurates(IV) (Zeeman, 1971; Lindqvist, 1973) with Te–O distances of 1·85–2·00 Å. In addition, there are three longer bonds: Te–O(3) (2×) of 2·567 (3) and Te–O(4) of 2·705 (5) Å.

Generally, the weaker Te^{IV}–O bonds have rather asymmetrical geometry, since the O positions are determined mainly by stronger bonds to other atoms

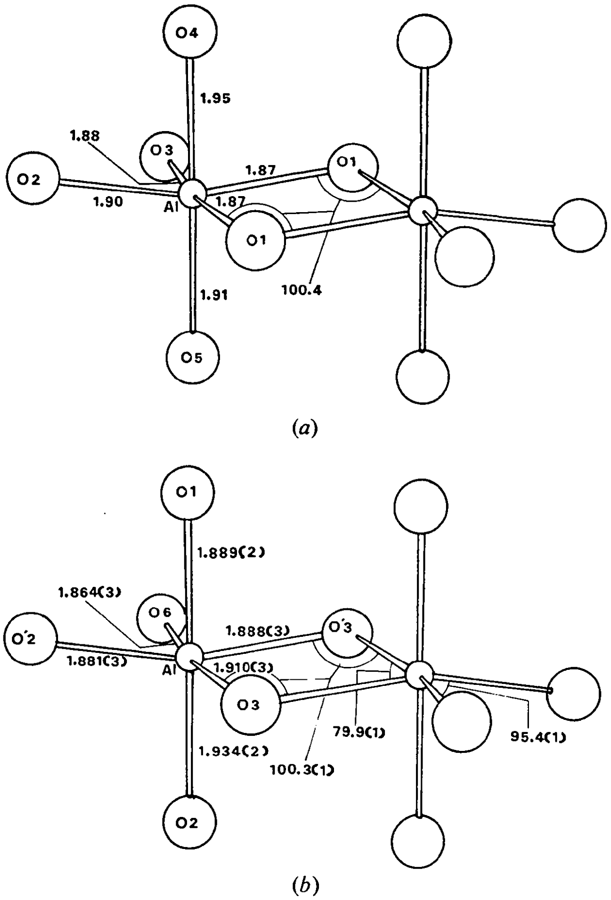

Fig. 4. The O coordination within the dimeric group in (*a*) $[Al_2(OH)_2(H_2O)_8]\ (SO_4)_2.2H_2O$ and (*b*) $Al_2(OH)_2TeO_3SO_4$. The H atoms are probably bonded to the bridging O atoms.

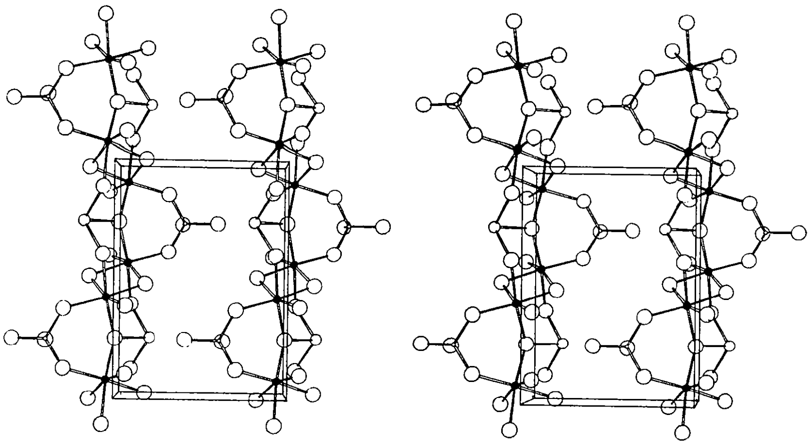

Fig. 3. A stereoscopic drawing of the structure along c showing the adjacent layers of $Al_2(OH)_2TeO_3SO_4$ (*ORTEP*; Johnson, 1965).

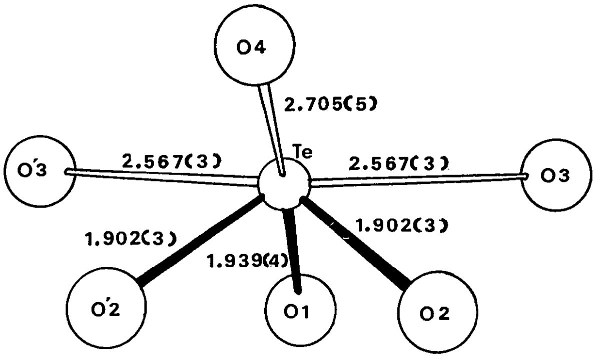

Fig. 5. The O coordination of Te^{IV}.

(Lindqvist, 1973). However, in $Al_2(OH)_2TeO_3SO_4$ the Te^{IV} coordination may be regarded as distorted octahedral. Such octahedral Te^{IV} coordination has been found in $TeCl_4$ (Buss & Krebs, 1971) and $TeCl_3^+AlCl_4^-$ (Krebs, Buss & Altena, 1971) where the short Te–Cl distances are 2·311 and 2·276 Å and the longer ones 2·929 and 3·062 Å, respectively. Buss & Krebs (1971) suggest that this arrangement is due to the ionic character of the structures. Correspondingly, the octahedral distribution of O atoms at short and long distances around Te^{IV} may indicate the presence of TeO_3^{2-} ions in $Al_2(OH)_2TeO_3SO_4$. On the other hand, the Te–O distances in $Al_2(OH)_2TeO_3SO_4$ are slightly longer than those of 1·847 (7)–1·859 (6) Å found in the ionic $BaTeO_3.H_2O$ (Rottersten-Nielsen *et al.*, 1971). This elongation is probably due to the presence of the three weak Te^{IV}–O interactions in $Al_2(OH)_2TeO_3SO_4$, but can also be due to the fact that the TeO_3 oxygen atoms participate in the Al coordination octahedra.

The sulphate groups have the usual bond distances and angles (Table 5). The slight distortion from a regular tetrahedron is presumably due to the fact that O(6) is coordinated to Al.

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