

Dipotassium Ditellurium(IV) Pentaoxide Trihydrate, $K_2Te_2O_5 \cdot 3H_2O$

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Abstract. $M_r = 467.4$, monoclinic, $P2_1/c$, $a = 8.007$ (6), $b = 6.283$ (3), $c = 19.007$ (13) Å, $\beta = 102.32$ (6)°, $Z = 4$, $V = 934.2$ (9) Å³, $D_x = 3.323$ (3) Mg m⁻³, $\mu(\text{Mo } K\alpha) = 7.35$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $T = 293$ K; least-squares refinement based on 1651 diffractometer reflections gave $R = 0.031$. The Te_2O_5 groups are connected by O bridges to form chains. The Te—O distances within the group range from 1.849 (5) to 2.010 (5) Å. The bridging Te—O distances are 2.294 (5) and 2.264 (5) Å.


Introduction. The structure of $K_2Te_2O_5 \cdot 3H_2O$ has been determined in order to investigate whether the structure contains isolated $Te_2O_3^{2-}$ ions or condensed chains and to examine the Te^{IV} coordination.

Experimental. A saturated solution of $K_2TeO_3 \cdot 3H_2O$ in 99% ethanol was allowed to stand for 24 h at 277 K, whereupon needle-shaped crystals of $K_2Te_2O_5 \cdot 3H_2O$ were formed. Colourless needles $0.24 \times 0.08 \times 0.08$ mm, Syntex $P2_1$, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from settings of 15 reflections with $4.4^\circ < 2\theta < 17.5^\circ$, 2322 reflections (hkl and $h\bar{k}l$) with $2\theta < 60.0^\circ$, 1651 independent with $I < 3\sigma(I)$, intensities from profile analysis of $\omega/2\theta$ scans (*cf.* Lindqvist & Ljungström, 1979) according to Lehmann & Larsen (1974), 2θ -scan intervals $2.0 - 3.0^\circ$, standard reflection 040 stable; systematic absences: $h0l$ for l odd and $0k0$ for k odd; L_p correction (Syntex, 1973), semi-empirical absorption correction (Kopfmann & Huber, 1968; North, Phillips & Mathews, 1968), relative transmission factor from 0.75 to 1.0, Patterson methods (Syntex, 1973), H not located, anisotropic block-diagonal least-squares refinement (Lindgren, 1977) of positional and thermal parameters minimizing $w(|F_o| - |F_c|)^2$, final $R_w = 0.04$,* average


* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38204 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

ratio of shift to error = 0.5%, weights $w = 1/[\sigma(F_o)^2 + 0.0002(F_o)^2]$ from counting statistics gave acceptable weight analysis; $F(000) = 848$; scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic parameters are given in Table 1. The Te_2O_5 units in $K_2Te_2O_5 \cdot 3H_2O$ are connected *via*

fairly strong  Te double bridges to form puckered

chains running through the structure (*cf.* Fig. 1). Bond distances within the $[Te_2O_5]_n^{2n-}$ chain are shown in Fig. 2 (angles in Table 2), which also includes a comparison with corresponding chain fragments in the similar structures $(NH_4)_2Te_2O_5 \cdot 2H_2O$ (Johansson, 1978), $Na_2Te_2O_5 \cdot 2H_2O$ (Daniel, Moret, Maurin & Philippot, 1981) and $MgTe_2O_5$ (Trömel, 1975). The chain formation results in an O coordination intermediate between three- and fourfold, *i.e.* between trigonal pyramidal and trigonal bipyramidal with the Te lone pair in an equatorial position. For structures containing TeO_3^{2-} ions it has been found (Philippot, Maurin & Moret, 1979) that the higher the percentage of water of crystallization present the less distorted is the TeO_3^{2-} ion. Therefore, one may conclude that the arrangement in $K_2Te_2O_5 \cdot 3H_2O$ is typical for the $[Te_2O_5]_n^{2n-}$ chain structure with equatorial Te—O bonds of 1.85–1.89 Å, one axial bond of ~ 2.00 Å in the single Te—O—Te bridge and the other axial bond of 2.25–

2.30 Å in the double  Te bridge.

Other compounds containing the Te_2O_5 group as a structural building unit are denningite (Walitzi, 1965) and $CuTe_2O_5$ (Hanke, Kupčik & Lindqvist, 1973). These structures do not contain $[Te_2O_5]_n^{2n-}$ chains, and are better classified as three-dimensional double oxides $MOTe_2O_4$.

K—O distances and probable hydrogen-bond distances are listed in Table 3.

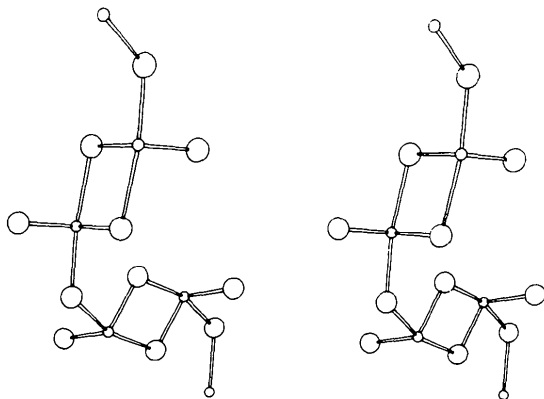


Fig. 1. A stereoscopic view of the Te_2O_5 chain (ORTEP, Johnson, 1965).

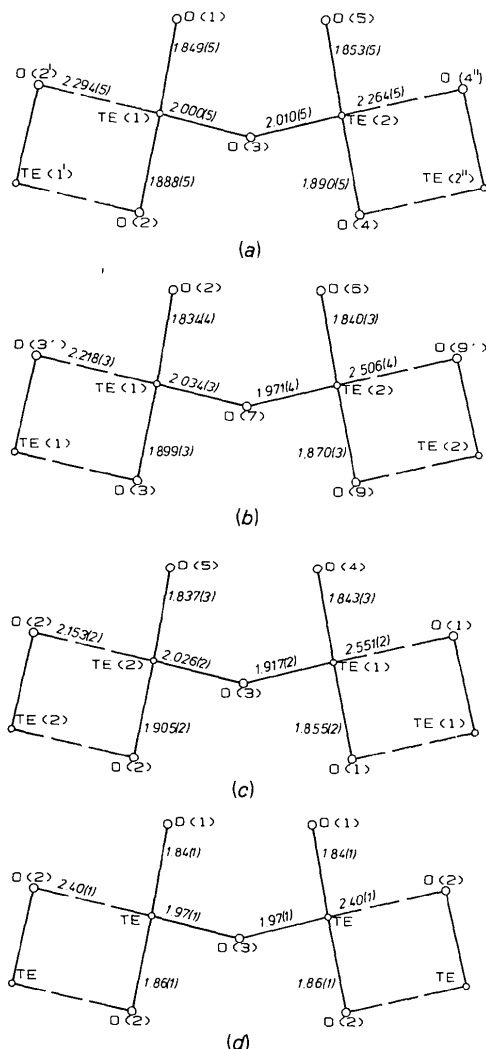


Fig. 2. Corresponding fractions of the $[\text{Te}_2\text{O}_5]_n^-$ chains in: (a) $\text{K}_2\text{Te}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ (this work); (b) $(\text{NH}_4)_2\text{Te}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ (Johansson, 1978); (c) $\text{Na}_2\text{Te}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ (Daniel, Moret, Maurin & Philippot, 1981); and (d) MgTe_2O_5 (Trömel, 1975). The numbering is in accordance with the original papers.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors (\AA^2) according to Hamilton (1959)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Te(1)	0.07122 (8)	1.00688 (7)	0.92446 (3)	0.91 (1)
Te(2)	0.31837 (8)	0.54526 (7)	0.94374 (3)	0.90 (1)
K(1)	0.4343 (3)	0.9584 (2)	0.1011 (1)	1.23 (4)
K(2)	0.8009 (3)	0.2420 (3)	0.2553 (1)	1.50 (4)
O(1)	-0.1240 (7)	0.8978 (8)	0.8656 (2)	1.1 (1)
O(2)	0.1017 (7)	0.8376 (8)	1.0083 (2)	0.9 (1)
O(3)	0.2310 (7)	0.8100 (8)	0.8887 (2)	1.2 (1)
O(4)	0.5143 (7)	0.7012 (7)	0.9883 (2)	0.9 (1)
O(5)	0.3788 (7)	0.4303 (8)	0.8629 (2)	1.0 (1)
W(1)	0.1462 (19)	0.5386 (8)	0.1168 (3)	2.3 (1)
W(2)	0.8514 (7)	0.7914 (8)	0.2360 (3)	1.5 (1)
W(3)	0.4879 (9)	0.4620 (8)	0.2469 (3)	2.0 (1)

W denotes the O atom of a water molecule.

Table 2. Angles ($^\circ$) in the Te_2O_5 unit

O(2)—Te(1)—O(3)	87.8 (2)	O(4)—Te(2)—O(3)	88.2 (3)
O(2)—Te(1)—O(1)	87.9 (2)	O(4 ⁱⁱ)—Te(2)—O(5)	88.8 (2)
O(2)—Te(1)—O(1)	104.0 (3)	O(4)—Te(2)—O(5)	103.6 (3)
O(2)—Te(1)—O(2)	75.8 (2)	O(4 ⁱⁱ)—Te(2)—O(4)	76.4 (1)
O(2)—Te(1)—O(3)	163.5 (3)	O(4 ⁱⁱ)—Te(2)—O(3)	164.0 (4)
O(1)—Te(1)—O(3)	94.8 (2)	O(3)—Te(2)—O(5)	90.8 (2)
Te(1)—O(3)—Te(2)	120.8 (2)	Te(2)—O(4)—Te(2 ⁱⁱ)	103.6 (2)
Te(1)—O(2)—Te(1 ⁱ)	104.2 (2)		

Symmetry code: (i) $-x, 2-y, 2-z$; (ii) $1-x, 1-y, 2-z$.

Table 3. Probable hydrogen-bond distances and distances (\AA) within the potassium coordination polyhedra

W(1)—O(2 ^{vi})	2.756 (7)	W(3)—O(5 ^{vii})	2.627 (8)
—O(1 ^{xii})	2.756 (7)	—W(2 ^v)	3.002 (9)
W(2)—O(1 ^x)	2.704 (7)		
—O(5 ^{vii})	2.719 (7)		
—W(3 ^{iv})	3.002 (9)		
K(1)—O(4 ⁱⁱⁱ)	2.816 (5)	K(2)—W(1 ^{iv})	2.698 (6)
—W(3 ^{iv})	2.823 (6)	—O(3 ^{vii})	2.714 (5)
—O(1 ^y)	2.840 (6)	—W(2 ^{viii})	2.771 (6)
—O(4 ⁱⁱⁱ)	2.865 (5)	—W(3)	2.837 (7)
—O(5 ^{vii})	2.870 (6)	—W(2 ^{ix})	2.894 (5)
—O(2 ^{vi})	2.963 (6)	—W(3 ^x)	2.898 (7)
—O(3 ⁱⁱⁱ)	3.019 (6)	—O(1 ^x)	3.055 (6)

Symmetry code: (iii) $1-x, 2-y, 1-z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $-x, 2-y, 1-z$; (vi) $x, y, z-1$; (vii) $1-x, 1-y, 1-z$; (viii) $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ix) $x, -1+y, z$; (x) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (xi) $1+x, \frac{3}{2}-y, -\frac{1}{2}+z$; (xii) $-x, 1-y, 1-z$.

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Structure of an Oxonium Antimony(III) Sulphate, $(\text{H}_3\text{O})_2\text{Sb}_2(\text{SO}_4)_4$

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Abstract. $M_r = 665.8$, orthorhombic, space group $Pbc2_1$, $a = 11.085$ (2), $b = 13.760$ (2), $c = 8.919$ (3) Å, $Z = 4$, $V = 1360.4$ Å³, $D_x = 3.25$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.7$ mm⁻¹, $T = 293$ K. Final $R = 0.038$ for 896 independent reflections. The structure is polymeric with sheets in which $-\text{Sb}-\text{O}-\text{S}-$ chains are linked together by SO_4 groups; an unusual SbO_3E polyhedron is described with one strong axial $\text{Sb}-\text{O}$ bond [2.012 (15) Å] and four equatorial $\text{Sb}-\text{O}$ bonds [between 2.214 (12) and 2.263 (13) Å]. Oxonium cations lie between the layers and interact with them by strong hydrogen bonds (mean $\text{O}\cdots\text{O}$ distance = 2.60 Å).

Introduction. This structure was examined as part of a systematic study of the influence of the lone pairs E in SbO_nE coordination. We hope to account for the differences between SbO_nE and AsO_nE polyhedra in similar 'sulphate' compounds in terms of ionic radii and the degree of covalency of the $M-\text{O}$ bonds ($M = \text{As}, \text{Sb}$). For arsenic(III) compounds such as $\text{As}_2(\text{SO}_4)_3$ (Douglade & Mercier, 1982), $\text{As}_2\text{O}(\text{SO}_4)_2$ (Mercier & Douglade, 1982*b*) and $\text{As}_2\text{O}_2(\text{SO}_4)$ (Mercier & Douglade, 1982*a*) only AsO_3E tetrahedra have been observed. On the other hand, in antimony 'sulphates', the coordination number of Sb is greater, and SbO_4E polyhedra are often observed; e.g. $\text{Sb}_2\text{O}(\text{SO}_4)_2$ (Mercier, Douglade & Theobald, 1975), $\text{Sb}_2(\text{SO}_4)_3$ (Mercier, Douglade & Bernard, 1976), $\text{Sb}_6\text{O}_7(\text{SO}_4)_2$ (Bovin, 1976), and $\text{Sb}_2(\text{OH})_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Douglade, Mercier

& Vivier, 1978). Recently an unusual SbO_3E coordination has been described by us in $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2) \cdot \text{H}_2\text{O}$ (Douglade & Mercier, 1980). In addition, such compounds may be good ionic proton conductors (Watelet, Picard, Baud, Besse & Chevalier, 1981), which could be of use in solid-state batteries. We also undertook this structural study to determine the composition and degree of hydration.

Experimental. Single crystals obtained at 293 K from a solution of Sb_2O_3 (20 g l⁻¹) dissolved in H_2SO_4 (~17 *M*). Chemical analysis (Sb^{3+} and SO_4^{2-}) of the mother liquor and the wet polycrystalline substrate only enabled us to show that the composition of the pure solid state lies between the 'limiting formulae' $\text{Sb}_2\text{O}_3 \cdot 2\text{SO}_3$ and $\text{Sb}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 4.5\text{H}_2\text{O}$, since the new phase appears only in a sharp concentration range in strong sulphuric acid ($1.40 < x < 1.52$ for $\text{SO}_3 \cdot x\text{H}_2\text{O}$). On removal from the sulphuric acid solution, the crystals revert rapidly to the anhydrous compound $\text{Sb}_2\text{O}(\text{SO}_4)_2$ and, because of this instability, the specific gravity was not determined.

Wet single crystals sealed in Lindemann tubes employed for X-ray measurement, systematic absences ($0kl \rightarrow k = 2n + 1$; $h0l \rightarrow l = 2n + 1$) in the orthorhombic system indicated space group $Pbcm$ or $Pbc2_1$, crystal approximately $0.2 \times 0.2 \times 0.25$ mm used for data collection, automated Nonius CAD-4 four-circle diffractometer of the Lyon-1 University, graphite monochromator, $\text{Mo } K\alpha$ radiation, cell dimensions