

References

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Refinement of the Structure of Tellurium Phosphate $\text{Te}_2\text{O}_3 \cdot \text{HPO}_4$ *

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Abstract. Te_2HPO_7 , orthorhombic, $Pca2_1$, $a = 10.239$ (1), $b = 7.018$ (1), $c = 7.933$ (1) Å, $V = 570.1$ (1) Å³, $Z = 4$, $M_r = 399.2$, $D_c = 4.65$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 105.2$ cm⁻¹; data for 696 diffractometer-observed reflections $|I/\sigma(I)| \geq 3.0$, $R = 0.022$. The two Te atoms adopt trigonal-bipyramidal geometry [Te–O 1.903 (9)–2.183 (8) Å] with several secondary interactions [Te...O 2.730 (10)–3.262 (8) Å], the shortest of which completes distorted square-based pyramidal geometry at Te(2).

Introduction. Several Te^{IV} oxy salts are reported to exist (Klein & Morel, 1885), including the nitrate $\text{Te}_2\text{O}_4 \cdot \text{HNO}_3$ (Swink & Carpenter, 1966), the sulphate $\text{Te}_2\text{O}_3\text{SO}_4$ (Johansson & Lindqvist, 1976; Hubková, Loub & Syneček, 1966) and the two phosphates $\text{Te}_2\text{O}_3 \cdot \text{HPO}_4$ (Mayer, 1975) and $\text{Te}_4\text{O}_5(\text{PO}_4)_2$ (Mayer & Pupp, 1977), whose structures are known. Reports of the perchlorate $2\text{TeO}_2 \cdot \text{HClO}_4$ (Fichter & Schmid, 1916), the periodate $2\text{TeO}_2 \cdot \text{HIO}_4$ (Montignie, 1945) and another phosphate $2\text{TeO}_2 \cdot \text{HPO}_4$ (Mayer, 1975) do not include structural information. The structures of several aryl-substituted Te salts (Alcock & Harrison, 1982) all contain secondary bonds and it was decided to investigate the remaining unsubstituted salts. We have found that the reported preparations of the perchlorate and periodate give only crystals of tetragonal α - TeO_2 and orthotelluric acid respectively.

We repeated the reported preparation of $2\text{TeO}_2 \cdot \text{H}_3\text{PO}_4$, isolating colourless platy crystals by

dissolving TeO_2 in orthophosphoric acid at 383 K and allowing the solution to cool. The air-stable crystals were collected, washed with water and acetone and dried in air. On examination by single-crystal X-ray analysis, the crystals were found to be identical to those of the previously reported $\text{Te}_2\text{O}_3 \cdot \text{HPO}_4$. As this structure was based on Weissenberg data, refined isotropically to $R = 0.10$, we describe here a refinement to higher accuracy enabling us to discuss the primary and secondary bonding in more detail.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. The maximum 2θ was 50° , with a scan range of $\pm 1.0^\circ$ (2θ) around the $K\alpha_1$ – $K\alpha_2$ angles, and the scan speed was 2 – 29° min⁻¹, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 100 reflections, and showed no significant changes during data collection. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. 696 observed reflections $|I/\sigma(I)| \geq 3.0$ were used in the refinement, and corrected for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1970). Systematic absences, $0kl$, $l \neq 2n$; $h0l$, $h \neq 2n$; $h00$ ($h \neq 2n$), indicate space group $Pca2_1$, as in the previous report.

The positions of two Te atoms were located by direct methods using *MULTAN* 80 (Main, 1980) and a trial solution, after two cycles of isotropic refinement, gave $R = 0.182$. The remaining non-H atoms were located by successive difference Fourier syntheses and anisotropic least-squares refinements. An empirical weighting scheme was employed giving decreased weight to reflections with high F_{obs} and low $\sin \theta$. The final R

*Secondary Bonding, 10. Part 9: Alcock & Harrison (1982).

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$), with *e.s.d.'s* in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Te(1)	1373.9 (6)	1656.4 (9)	0	7
O(1)	2483 (8)	709 (10)	1732 (12)	12
O(2)	1433 (8)	-1181 (11)	-815 (10)	11
O(4)	-143 (8)	840 (11)	1264 (12)	11
P(1)	716 (3)	4729 (4)	3074 (4)	9
O(5)	1089 (9)	6684 (12)	3647 (14)	57
O(3)	-763 (8)	4546 (12)	2784 (12)	57
O(7)	1112 (9)	3240 (14)	4482 (12)	57
O(6)	1463 (8)	4163 (11)	1488 (11)	57
Te(2)	3215.7 (6)	-1987.9 (9)	1936.1 (14)	57

Table 2. Bond lengths (\AA) and angles ($^\circ$) with *e.s.d.'s* in parentheses

Te(1)—O(1)	1.903 (9)	Te(2)—O(2 <i>b</i>)	1.906 (8)
Te(1)—O(4)	1.935 (8)	Te(2)—O(4 <i>c</i>)	1.939 (8)
Te(1)—O(2)	2.094 (8)	Te(2)—O(1)	2.042 (7)
Te(1)—O(6)	2.120 (8)	Te(2)—O(3 <i>c</i>)	2.183 (8)
Te(1)—O(7 <i>f</i>)	2.834 (10)	Te(2)—O(5 <i>a</i>)	2.730 (10)
Te(1)—O(1 <i>f</i>)	2.921 (9)	Te(2)—O(5 <i>d</i>)	2.860 (11)
Te(1)—O(5 <i>e</i>)	2.977 (9)	Te(2)—O(2)	2.901 (8)
Te(1)—O(3 <i>e</i>)	3.254 (9)	Te(2)—O(6 <i>a</i>)	3.262 (8)
P(1)—O(3)	1.537 (8)	O(3)—P(1)—O(5)	111.9 (5)
P(1)—O(5)	1.496 (9)	O(3)—P(1)—O(6)	110.4 (5)
P(1)—O(6)	1.526 (9)	O(3)—P(1)—O(7)	107.7 (5)
P(1)—O(7)	1.582 (10)	O(5)—P(1)—O(6)	111.2 (5)
		O(5)—P(1)—O(7)	109.0 (6)
		O(6)—P(1)—O(7)	106.4 (5)
O(1)—Te(1)—O(4)	90.1 (4)	O(1)—Te(2)—O(2 <i>b</i>)	82.4 (4)
O(1)—Te(1)—O(2)	82.7 (3)	O(1)—Te(2)—O(3 <i>c</i>)	164.2 (4)
O(1)—Te(1)—O(6)	82.1 (3)	O(1)—Te(2)—O(4 <i>c</i>)	84.9 (3)
O(4)—Te(1)—O(2)	84.4 (3)	O(2 <i>b</i>)—Te(2)—O(3 <i>c</i>)	82.3 (3)
O(4)—Te(1)—O(6)	89.5 (3)	O(2 <i>b</i>)—Te(2)—O(4 <i>c</i>)	88.3 (4)
O(2)—Te(1)—O(6)	163.6 (3)	O(3 <i>c</i>)—Te(2)—O(4 <i>c</i>)	90.6 (3)
Te(1)—O(4)—Te(2)	135.6 (4)	Te(1)—O(1)—Te(2)	126.9 (4)
Te(1)—O(2)—Te(2)	125.2 (4)		

Symmetry code

- | | | | |
|-----|---------------------------------------|-----|---|
| (a) | $x, y - 1, z$ | (d) | $\frac{1}{2} - x, y - 1, z - \frac{1}{2}$ |
| (b) | $\frac{1}{2} - x, y, \frac{1}{2} + z$ | (e) | $-x, 1 - y, z - \frac{1}{2}$ |
| (c) | $\frac{1}{2} + x, -y, z$ | (f) | $\frac{1}{2} - x, y, z - \frac{1}{2}$ |

value was 0.022.* A final difference Fourier synthesis showed no significant features. All refinement calculations were carried out using the XRAY 76 suite of programs (Stewart, 1976) on a Burroughs B6700 computer. Scattering factors (used in their analytical form) were from *International Tables for X-ray*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36744 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Crystallography (1974). Atom coordinates are given in Table 1 and bond lengths and angles in Table 2.

Discussion. The asymmetric unit consists of one molecule of $\text{Te}_2\text{O}_3 \cdot \text{HPO}_4$ (Fig. 1). Atoms O(1), O(2) and O(4) link the Te atoms into two-dimensional $(\text{TeO})_n$ layers. The atoms O(1) and O(2) form asymmetric μ -oxo bridges between the Te atoms [Te(1)—O(1) 1.903 (9), Te(2)—O(2) 1.906 (8), Te(1)—O(2) 2.094 (8), Te(2)—O(1) 2.042 (7) \AA ; Te(1)—O(1)—Te(2) 126.9 (4), Te(2)—O(2)—Te(1) 125.2 (4) $^\circ$]. Atom O(4) forms a more open, symmetrical μ -oxo bridge [Te(1)—O(4) 1.935 (8), Te(2)—O(4) 1.939 (8) \AA ; Te(1)—O(4)—Te(2) 135.6 (4) $^\circ$]; this large angle is unusual [cf. 98.2 (1.1) to 126.2 (8) $^\circ$ in $\text{Te}_2\text{O}_4 \cdot \text{HNO}_3$ and 119–127 $^\circ$ in $\text{Te}_2\text{O}_3\text{SO}_4$]. Each Te atom has one short contact to a phosphate O [Te(1)—O(6) 2.120 (8) and Te(2)—O(3) 2.183 (8) \AA]. The P—O distances vary; the shortest is P(1)—O(5) 1.496 (9) \AA , essentially a double bond, and the longest is P(1)—O(7) 1.582 (10) \AA , which is consistent with a single bond; O(7) is presumed to carry a proton (not located on the difference Fourier map) which could be hydrogen bonded to either O(1) [O(7)—O(1) 2.90 (1) \AA] or O(2) [O(7)—O(2) 2.99 (1) \AA]. The remaining P—O bonds are of intermediate length [P(1)—O(3) 1.537 (8) and P(1)—O(6) 1.526 (9) \AA] and it is these phosphate O atoms that form short bonds to the Te atoms.

About Te(1), the geometry is essentially distorted trigonal-bipyramidal with O(2) and O(6) occupying the axial positions [O(2)—Te(1)—O(6) 163.6 (3) $^\circ$] and O(1) and O(4) the equatorial positions [O(1)—Te(1)—O(4) 90.1 (4) $^\circ$]. Four weak secondary bonds (2.83–3.25 \AA) cluster around the lone pair in the vacant equatorial position; this is similar to the geometry in the aryltellurium nitrates (Alcock & Harrison, 1982). Te(2) has a shorter interaction with O(5) [2.730 (10) \AA], nearly *trans* to O(4) [O(5*a*)—Te(2)—O(4) 166.0 (4) $^\circ$], occupying the fifth

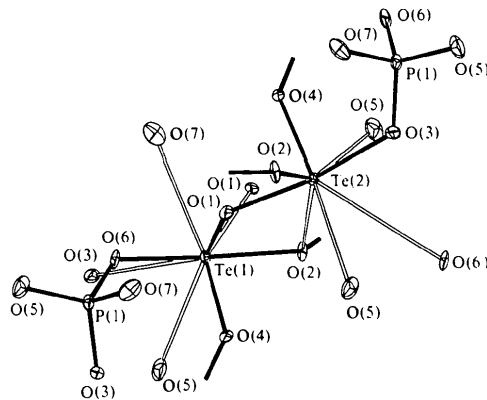


Fig. 1. $\text{Te}_2\text{O}_3 \cdot \text{HPO}_4$: the atomic numbering, the primary bonds (filled), and the secondary interactions (open).

position of a distorted octahedron with one vacant site (Alcock, 1972). However, the *trans* Te(2)–O(4) bond shows no apparent shortening, and Te(2) may better be regarded as showing the same geometry as Te(1), with four interactions (2.73–3.26 Å) clustered around the vacant face. Its primary geometry is also distorted trigonal-bipyramidal, with O(1) and O(3) axial [O(1)–Te(2)–O(3) 164.2 (4)°] and O(2) and O(4) equatorial [O(2)–Te(2)–O(4) 88.3 (4)°].

The structure contrasts with that of $\text{Te}_2\text{O}_4 \cdot \text{HNO}_3$ (Swink & Carpenter, 1966) which adopts a grossly distorted trigonal-bipyramidal geometry. The axial–axial ligand angle is as low as 147.8 (8)° and the equatorial angle is 100.0 (8)°. The four O atoms bound to the Te atom are all of the μ -oxo type and the nitrate groups are not directly bound to the Te atoms. As with the title compound there are three secondary bonds [2.800 (16)–2.888 (23) Å] which make no rational geometry at the Te atom. The structure also contrasts with that of $\text{Te}_2\text{O}_3\text{SO}_4$ (Johansson & Lindqvist, 1976) where the Te atom adopts a geometry with three bridging O atoms in a plane with the Te atom, and a fourth bridging O perpendicular to the plane. Two long interactions to sulphato O atoms complete a very distorted octahedral arrangement about the Te atom. The primary arrangement cannot be considered trigonal-bipyramidal, as the largest O–Te–O angle is only 130.5 (4)°.

All three compounds consist of two-dimensional layers of Te–O networks with anions between the layers. In the case of the title compound, the phosphate anions are strongly bound by two O atoms [O(3) and O(6)] to two Te atoms of one layer and weakly bound by O(5) to one Te in the next layer. In the sulphate the anions are bound to layers in a similar fashion. In the nitrate the nitric acid molecules are not directly

attached to the Te atoms but are attached to bridging O atoms by hydrogen bonding.

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