

SHORT STRUCTURAL PAPERS

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Structure of Tellurium(IV) Pyrosulphate

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Abstract. $\text{Te}(\text{S}_2\text{O}_7)_2$, $M_r = 278.84$, monoclinic, Cc , $a = 10.604$ (4), $b = 8.524$ (3), $c = 12.052$ (4) Å, $\beta = 102.20$ (3)°, $V = 1064.8$ Å³, $Z = 4$, $D_c = 2.99$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 3.01$ mm⁻¹. Final $R = 0.038$ for 909 diffractometer reflections. Two bidentate pyrosulphate ligands are bonded to each Te atom. The Te atom is in a ψ -trigonal-bipyramidal configuration with a lone pair at one of the equatorial positions. Distances and angles are Te–O(ax) = 2.06 (2), 2.07 (1), Te–O(eq) = 1.96 (1), 1.96 (1) Å, O(ax)–Te–O(ax) = 157.4 (3), O(eq)–Te–O(eq) = 94.8 (5)°.

Introduction. Elemental Te was dissolved in oleum under dry N₂. The solution was allowed to stand for several months during which time pale-yellow crystals of $\text{Te}(\text{S}_2\text{O}_7)_2$ were formed. One large crystal was removed from the solution in a dry box filled with N₂, cleaved and the fragments sealed in Lindemann tubes.

Weissenberg and precession photographs taken with Cu $K\alpha$ radiation on the best-formed fragment showed it to be suitable for data collection. Systematic absences $hkl: h + k = 2n + 1, h0l: l = 2n + 1$ indicated space group $C2/c$ or Cc .

Cell dimensions were obtained by least squares from the setting angles of ten reflexions with $2\theta > 44^\circ$ centred on a Picker FACS-1 four-circle diffractometer with Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å). The intensities of 947 unique reflexions with $2\theta \leq 50^\circ$ were measured and of these 909 with $I > 2.3\sigma_I$ (σ_I is the e.s.d. derived from counter statistics and a precision factor of 0.03) were regarded as observed and used in the analysis. A temperature of 295 K was maintained throughout the data collection. Operating conditions were a scan rate of 2° min⁻¹, a scan width of (1.2 + 0.692 tan θ)° and background counts of 10 s at each side of every peak. After every 75 reflections two standards were measured. These showed a small gradual decline in average intensity; the data were

scaled accordingly. A spherical-crystal absorption correction ($r = 0.18$ mm) was applied (*International Tables for X-ray Crystallography*, 1967).

The structure was solved by direct methods in $C2/c$. Full-matrix least-squares refinement of an ordered-atom model with anisotropic temperature factors for all atoms gave $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.087$. A difference map at this stage suggested that O(5), S(6), O(7) and O(8) were each disordered over two sites. This model [Te, S atoms, and O(9) anisotropic] refined to $R = 0.040$, but gave an unreasonably short O(7B)···O(7B') contact of 2.06 (5) Å.

Refinement was continued in Cc , removing the molecular twofold symmetry. Disorder was found in one ligand but not the other. In ligand (1) O(15), S(16) and O(17) indicated occupancies for the skew-boat and chair conformations of 0.55 and 0.45, respectively, but O(18) gave 0.33 and 0.67.

There are two explanations which could fit these observations. Firstly, the variation in occupancies might reflect unresolved inter-parameter correlation together with systematic errors in the data. Alternatively there could be an 'O₂SOSO₃' species, a new isomer of the dithionate ion, disordered with O₃SSO₃ in ligand (1) sites. We believe that the latter is less likely as the feature is confined to only one of the four S atoms and non-bonding contacts to O(18A) are not unusually short. We therefore decided to set the occupancies of O(18A) and O(18B) to 0.55 and 0.45, respectively, and to fix U for O(18A) at 0.036 Å².

Te, S(12), S(22) and S(26) were assigned anisotropic temperature factors in further refinement which converged to $R = 0.038$ and $R_w = [(\sum w|F_o| - |F_c|)^2 / \sum F_o^2]^{1/2} = 0.049$. The largest peaks in a final difference map [all < 0.43 (11) e Å⁻³] were grouped about the Te atom. A negative region of -0.38 (11) e Å⁻³ was found near O(18A) but is sufficiently small that we did not think it justified changing our treatment of O(18A). A

Table 1. *Positional and thermal* ($\times 10^3 \text{ \AA}^2$) *parameters for* $\text{Te}(\text{S}_2\text{O}_7)_2$

The least-squares e.s.d.'s of the least significant figures are given in parentheses. In the disordered region *A*-type atoms have occupancy 0.55, *B*-type 0.45.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Te	0.5000	0.44151 (6)	0.2500	15*
O(11)	0.4489 (15)	0.3973 (20)	0.0786 (13)	23 (3)
S(12)	0.4425 (6)	0.2528 (7)	0.0061 (6)	24*
O(13)	0.3557 (17)	0.1331 (22)	0.0316 (15)	49 (5)
O(14)	0.4384 (13)	0.2924 (17)	-0.1044 (12)	31 (3)
O(15 <i>A</i>)	0.5871 (17)	0.1758 (25)	0.0520 (16)	11 (4)
O(15 <i>B</i>)	0.6088 (22)	0.2253 (31)	0.0399 (18)	21 (5)
S(16 <i>A</i>)	0.6910 (7)	0.2344 (9)	0.1481 (7)	9 (2)
S(16 <i>B</i>)	0.6510 (6)	0.1483 (8)	0.1740 (5)	14 (1)
O(17 <i>A</i>)	0.7671 (19)	0.0893 (27)	0.1973 (17)	17 (4)
O(17 <i>B</i>)	0.5724 (21)	0.0363 (25)	0.2091 (18)	26 (4)
O(18 <i>A</i>)	0.7383 (24)	0.3741 (31)	0.1120 (21)	36†
O(18 <i>B</i>)	0.7911 (20)	0.1366 (28)	0.1804 (18)	9 (5)
O(19)	0.6275 (12)	0.2753 (15)	0.2509 (10)	24 (3)
O(21)	0.5601 (12)	0.3915 (18)	0.4210 (12)	15 (3)
S(22)	0.5565 (6)	0.2496 (6)	0.4962 (5)	55*
O(23)	0.6539 (17)	0.1402 (21)	0.4917 (15)	47 (5)
O(24)	0.5381 (14)	0.3013 (18)	0.6067 (13)	37 (4)
O(25)	0.4310 (11)	0.1450 (15)	0.4270 (11)	33 (3)
S(26)	0.3046 (8)	0.2321 (11)	0.3515 (7)	28*
O(27)	0.2236 (14)	0.1065 (20)	0.3257 (13)	27 (4)
O(28)	0.2789 (15)	0.3623 (22)	0.4145 (12)	54 (4)
O(29)	0.3578 (12)	0.2977 (16)	0.2571 (10)	26 (3)

* Equivalent isotropic thermal parameters given by $U = \frac{1}{3}$ trace \tilde{U} .

† Thermal parameters for O(18*A*) not refined – see text.

Hamilton (1965) *R*-factor test indicates that the non-centrosymmetric solution is favoured over the centrosymmetric at the 99% confidence level. The test is not entirely valid as it relies on there being only random errors which is not the case here with approximate twofold crystallographic symmetry, but we still believe that the non-centrosymmetric solution is the better since it successfully removes the disorder from part (2) of the molecule and also does not produce any unreasonable contacts. Results quoted in the tables and *Discussion* are for the non-centrosymmetric solution (the centrosymmetric values are similar but have lower standard errors). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = \sigma_F^{-2}$. Neutral-atom scattering factors and anomalous-dispersion corrections for Te and S were from *International Tables for X-ray Crystallography* (1974).^{*} Final positional parameters are given in Table 1.

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35573 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Bond distances and angles are given in Table 2. Two pyrosulphate ligands are chelated to each Te atom through terminal O atoms. The O–Te–O angles indicate the presence of a stereoactive lone pair on the Te atom. The lone pair and the four O atoms form a distorted ψ -trigonal-bipyramidal configuration with the lone pair, O(19) and O(29) constituting the equatorial plane and O(11) and O(21) the axes. The Te–O(ax) distances are equal [2.06 (2) and 2.07 (1) Å] and longer than the Te–O(eq) bonds [1.96 (1) and 1.96 (1) Å]. Angle O(19)–Te–O(29) is 94.8 (5) and O(11)–Te–O(21) 157.4 (3)°, showing the strong valence-shell-repulsion effect of the lone pair, though the latter is possibly also affected by the constraint of the bidentate pyrosulphate ligands.

Most Te^{IV} –O complexes have structures based on a trigonal bipyramid (Zemann, 1971), although in some cases one of the axial Te–O distances is much longer than the other [2.98 and 1.88 Å in $\text{CuTeO}_3 \cdot 2\text{H}_2\text{O}$ (Zemann & Zemann, 1962)]. $\text{Te}(\text{S}_2\text{O}_7)_2$ most closely resembles the compounds at the top of Zemann's Table 1 where both Te–O(ax) bonds are reasonably short, in particular tetragonal TeO_2 (Lindqvist, 1968), $\text{Ti}(\text{Te}_3\text{O}_8)$ (Meunier & Galy, 1971) and Te_2O_5 (Lindqvist & Moret, 1973) which have similar O–Te–O angles and Te–O(ax) bonds of equal length. In $\text{Te}(\text{S}_2\text{O}_7)_2$, however, the difference between Te–O(ax) and Te–O(eq) bond lengths is much less than in the other three.

Besides the major Te–O bonding there are also four longer Te···O contacts to O(17*A*) ($x - \frac{1}{2}, y + \frac{1}{2}, z$)

Table 2. *Bond distances* (Å) *and angles* (°) *for* $\text{Te}(\text{S}_2\text{O}_7)_2$

Where appropriate the value for orientation *A* precedes that for orientation *B*.

Te–O(11)	2.06 (2)	Te–O(21)	2.07 (1)
Te–O(19)	1.96 (1)	Te–O(29)	1.96 (1)
S(12)–O(11)	1.50 (2)	S(22)–O(21)	1.52 (2)
S(16)–O(19)	1.57 (1), 1.48 (1)	S(26)–O(29)	1.48 (1)
S(12)–O(15)	1.65 (2), 1.74 (2)	S(22)–O(25)	1.67 (1)
S(16)–O(15)	1.51 (2), 1.71 (2)	S(26)–O(25)	1.63 (1)
S(12)–O(13)	1.45 (2)	S(22)–O(23)	1.40 (2)
S(12)–O(14)	1.37 (2)	S(22)–O(24)	1.45 (2)
S(16)–O(17)	1.53 (2), 1.39 (2)	S(26)–O(27)	1.37 (2)
S(16)–O(18)	1.40 (3), 1.47 (2)	S(26)–O(28)	1.40 (2)
O(11)–Te–O(21)	157.4 (3)	O(19)–Te–O(29)	94.8 (5)
O(11)–Te–O(19)	84.7 (5)	O(21)–Te–O(29)	84.6 (5)
O(11)–Te–O(29)	83.5 (6)	O(21)–Te–O(19)	77.2 (5)
Te–O(11)–S(12)	134.7 (10)	Te–O(21)–S(22)	135.9 (9)
Te–O(19)–S(16)	124.6 (8), 137.2 (8)	Te–O(29)–S(26)	133.7 (8)
O(11)–S(12)–O(15)	102 (1), 93 (1)	O(21)–S(22)–O(25)	104 (1)
O(19)–S(16)–O(15)	108 (1), 105 (1)	O(29)–S(26)–O(25)	101 (1)
O(11)–S(12)–O(13)	114 (1)	O(21)–S(22)–O(23)	113 (1)
O(11)–S(12)–O(14)	111 (1)	O(21)–S(22)–O(24)	109 (1)
O(13)–S(12)–O(15)	104 (1), 121 (1)	O(23)–S(22)–O(25)	98 (1)
O(14)–S(12)–O(15)	105 (1), 95 (1)	O(24)–S(22)–O(25)	112 (1)
O(15)–S(16)–O(17)	106 (1), 120 (1)	O(25)–S(26)–O(27)	100 (1)
O(15)–S(16)–O(18)	107 (1), 98 (1)	O(25)–S(26)–O(28)	107 (1)
O(17)–S(16)–O(19)	99 (1), 97 (1)	O(27)–S(26)–O(29)	116 (1)
O(18)–S(16)–O(19)	107 (1), 109 (1)	O(28)–S(26)–O(29)	105 (1)
O(13)–S(12)–O(14)	119 (1)	O(23)–S(22)–O(24)	119 (1)
O(17)–S(16)–O(18)	128 (1), 127 (1)	O(27)–S(26)–O(28)	124 (1)
S(12)–O(15)–S(16)	127 (1), 109 (1)	S(22)–O(25)–S(26)	121 (1)

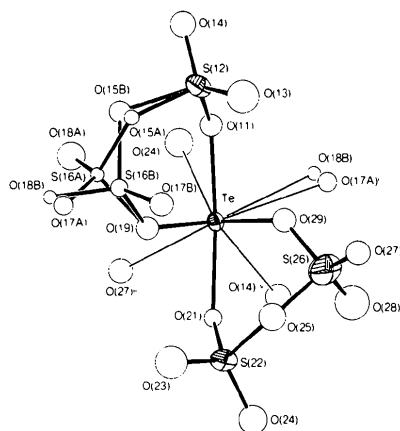


Fig. 1. ORTEP diagram (Johnson, 1965) of tellurium pyrosulphate projected down the approximate twofold axis showing the atom labelling and the disorder in ligand (1). Longer Te...O contacts are drawn with thin lines. Thermal ellipsoids indicate 50% probability levels.

2.73 (2) or O(18B) ($x - \frac{1}{2}, y + \frac{1}{2}, z$) 2.76 (2), O(27) ($x + \frac{1}{2}, y + \frac{1}{2}, z$) 2.74 (1), O(24) ($x, 1 - y, z - \frac{1}{2}$) 2.87 (2) and O(14) ($x, 1 - y, z + \frac{1}{2}$) 3.02 (1) Å. As can be seen in Fig. 1, these contacts are arranged in a staggered manner so as to minimize interaction with the O atoms of the coordination sphere and complete an irregular dodecahedron.

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The Structure of Calcium Orthotellurate

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Abstract. Ca_3TeO_6 , monoclinic, $P2_1/n$, $a = 5.5730$ (6), $b = 5.7964$ (2), $c = 8.0113$ (3) Å, $\beta = 90.24$ (1)°, $V = 258.8$ Å³, $Z = 2$, $D_c = 4.41$ Mg m⁻³. Final $R = 0.041$ for 583 reflections. A single-crystal study confirms that the compound is isostructural with cryolite, $\alpha\text{-Na}_3\text{AlF}_6$. The Te—O octahedron is regular, as is usual for Te^{VI} oxides.

Introduction. Ca_3TeO_6 has been known since 1956 (Merz, 1956) but so far only polycrystalline material has been available. Because of this and the fact that its monoclinic angle is close to 90°, the structure has been

The bond lengths and angles within the pyrosulphate ligands could not be determined very accurately on account of the disorder outlined above. The values are in agreement with those obtained (Lynton & Truter, 1960) for $\text{K}_2\text{S}_2\text{O}_7$ [S—O(bridging) 1.645 (5); S=O(terminal) 1.437 (7) Å; S—O—S 124.2 (5)°].

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described as isomorphous both with cryolite, Na_3AlF_6 , space group $P2_1/n$ (Naray-Szabo & Sasvári, 1938), and with Ca_3UO_6 , space group $P2_1$ (Rietveld, 1966; Loopstra & Rietveld, 1969). Baglio & Natansohn (1969) conclude from powder indexing that the space group is $P2_1$ with $a = 5.794$, $b = 5.575$, $c = 8.020$ Å, $\beta = 90.29^\circ$. Trömel (1972) points out that the same powder data can be described by $a = 5.575$, $b = 5.773$, $c = 8.006$ Å, $\beta = 90.23^\circ$.

This description is in accordance with the observation that for cryolite and related structures b is smaller than a . With these cell constants all indices