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The Crystal and Molecular Structure of Bis(*O*-isopropylxanthato)tellurium(II)

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It has been noted that for ϕ_2Bi(iprxa) [1], and $[\text{Bi(iprxa)}_3]_n$ [2] (where iprxa is *O*-isopropylxanthato) the presence of the isopropyl group promoted intermolecular interactions via sulphur bridges. Since Group VI xanthates, and in particular the methyl- and ethyl-xanthates of tellurium(II) [3, 4], exhibit a tendency to form weak central atom to sulphur bridges it was of interest to examine the effect of the isopropyl group on the structure of Te(iprxa)$_2$.

Te(iprxa)$_2$ was prepared by adding the stoichiometric amount of potassium isopropylxanthate to a stirred solution of TeO_2 (2g) in dilute HCl (50 ml). The product was extracted immediately with $CHCl_3$ (50 ml). The $CHCl_3$ was removed under reduced pressure and the resultant oil was taken up in CH_2Cl_2 (40 ml) and the solution allowed to stand until deep red crystals, suitable for X-ray analysis, were deposited. Characteristic infrared absorptions in the C–O, C–S and M–S regions were observed at 1245, 1235; 1030, 1020; and 460, 450, 395 cm^{-1} respectively.

Intensity data were collected at room temperature on an Enraf-Nonius CAD-4F diffractometer fitted with MoKα radiation using the ω:2θ scan technique. The remeasurement of three reference reflections during the data collection indicated that the crystal had decomposed about 10% and the data set was scaled accordingly. Of the 6771 reflections measured, 5108 were unique and 2882 satisfied the $I \geqslant 2\sigma(I)$ criterion of observability. The intensity data were corrected for Lorentz, polarization and absorption effects [5].

Crystal Data: Te(iprxa)$_2$: $C_8H_{14}O_2S_4Te$, M = 398.1, orthorhombic, $P2_12_12_1$ (D_2^4, No. 19), a = 16.707(2), b = 18.688(4), c = 9.576(2) Å, U = 2989.8 Å^3, D_m = 1.74, Z = 8, D_c = 1.768 Mg m^{-3}, F(000) = 1552, MoKα radiation (graphite monochromator) λ = 0.71069 Å, $1.0 \leqslant \theta \leqslant 25.0°$, μ = 2.48 mm^{-1}, absorption corrections applied, max. and min. transmission factors 0.7848 and 0.7296, no. parameters/no. variables = 10.

The structure was determined by Patterson and Fourier methods and refined using a least squares procedure [6]. After anisotropic thermal parameters for all non-hydrogen atoms and a weighting scheme, $w = 1/1[\sigma^2(F) + 0.001|F|^2]$ were applied the refinement converged with R 0.045 and R_w 0.045. It was not possible to determine the absolute configuration of the asymmetric unit since the Hamilton R factor significance test [7] showed, at a confidence level of 0.005, that there was no significant difference between the refinements for the two configurations. In addition there was no significant difference between any of the Friedel pairs included in the data set.

Fractional atomic coordinates are listed in Table I and the numbering scheme used is shown in Fig. 1. All relevant bond distances and bond angles are given in Tables II and III respectively. Tables of anisotropic thermal parameters and the observed and calculated structure factors with their phase angles have been deposited with the Editors.

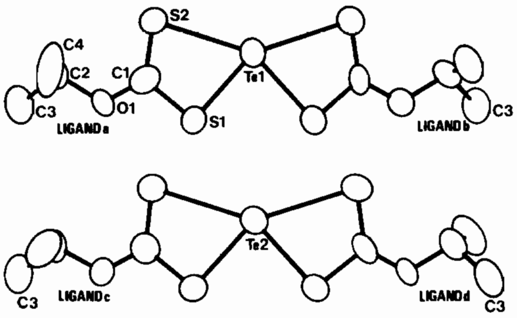

Fig. 1. The numbering scheme used for the asymmetric unit in Te(iprxa)$_2$. The planar projections highlight the different orientations of the terminal methyl groups of the two molecules comprising the asymmetric unit.

An unusual aspect [8] of the present structure is the presence of two molecules of Te(iprxa)$_2$ in the asymmetric unit of the acentric space group. The two molecules of Te(iprxa)$_2$ differ from each other in the relative orientation of the terminal methyl groups as is illustrated in Fig. 1. There are no significant intermolecular contacts between the two Te(iprxa)$_2$ molecules in the asymmetric unit; the Te...Te separation is 6.459(1) Å which is very much greater than 4.2 Å [9] the value of twice the van der Waals radii for Te and the closest Te...S contacts are between Te(1)–S(1)c (4.516(4) Å) and Te(2)–S(1)b (4.657(4) Å) which too are greater than the sum of the van der Waals radii for the Te and S atoms [9].

The iprxa ligands chelate the tellurium atoms with asymmetric Te–S bonds (approximately 2.5 and 2.9 Å) and this asymmetry is reflected in the associated C–S bonds. The two TeS_4 moieties are essentially planar and the arrangement of the six electron pairs about each Te atom is best described as conforming

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TABLE I. Fractional Atomic Coordinates for Te(iprxa)$_2$ (Estimated Standard Deviations in Parentheses).

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Te(1)	0.58441(6)	0.89722(4)	0.1144(1)	Te(2)	0.63405(5)	0.58324(4)	0.3826(1)
	Ligand a				Ligand c		
S(1)	0.5785(2)	0.7984(2)	−0.0586(4)	S(1)	0.5502(2)	0.6667(2)	0.2428(4)
S(2)	0.4812(3)	0.9262(2)	−0.1193(5)	S(2)	0.5627(2)	0.5198(2)	0.1351(5)
C(1)	0.5128(8)	0.8466(7)	−0.1639(15)	C(1)	0.5266(7)	0.6012(6)	0.1266(17)
O(1)	0.4977(6)	0.8118(5)	−0.2812(10)	O(1)	0.4752(6)	0.6252(5)	0.0289(10)
C(2)	0.4404(9)	0.8427(7)	−0.3831(17)	C(2)	0.4578(7)	0.5833(7)	−0.0965(16)
C(3)	0.4734(10)	0.8182(9)	−0.5257(16)	C(3)	0.3702(10)	0.6025(9)	−0.1375(19)
C(4)	0.3583(10)	0.8098(15)	−0.3453(20)	C(4)	0.5166(11)	0.6049(10)	−0.2064(18)
	Ligand b				Ligand d		
S(1)	0.6815(2)	0.8170(2)	0.2360(4)	S(1)	0.6541(2)	0.6892(2)	0.5357(4)
S(2)	0.6520(3)	0.9574(2)	0.3650(5)	S(2)	0.7361(3)	0.5577(2)	0.6251(6)
C(1)	0.6999(8)	0.8807(6)	0.3608(14)	C(1)	0.7147(8)	0.6435(7)	0.6496(15)
O(1)	0.7555(5)	0.8593(4)	0.4512(10)	O(1)	0.7416(6)	0.6854(5)	0.7511(11)
C(2)	0.7763(9)	−0.9042(7)	0.5754(16)	C(2)	0.7975(9)	0.6568(8)	0.8562(17)
C(3)	0.7167(12)	0.8879(10)	0.6904(17)	C(3)	0.8473(10)	0.7214(8)	0.9058(23)
C(4)	0.8620(9)	0.8855(10)	0.6053(22)	C(4)	0.7443(11)	0.6266(10)	0.9757(19)

TABLE II. Bond Distances (Å) for Te(iprxa)$_2$.

Atoms	ligand a	ligand b	ligand c	ligand d
Te–S(1)	2.483(4)	2.497(4)	2.487(4)	2.487(4)
Te–S(2)	2.877(5)	2.881(5)	2.906(5)	2.920(6)
S(1)–C(1)	1.74(1)	1.72(1)	1.70(1)	1.72(1)
S(2)–C(1)	1.64(1)	1.64(1)	1.64(1)	1.66(1)
C(1)–O(1)	1.32(2)	1.33(2)	1.35(2)	1.33(2)
O(1)–C(2)	1.48(2)	1.50(2)	1.46(2)	1.47(2)
C(2)–C(3)	1.54(2)	1.52(2)	1.56(2)	1.54(2)
C(2)–C(4)	1.55(2)	1.50(2)	1.50(2)	1.56(2)

to a trapezoidal planar geometry as was observed for the methyl [3] and ethyl [4] xanthates of tellurium(II). This tellurium atom geometry has been ascribed [10] to be the result of the combined effects of the restricted bite angle of the xanthate ligand and bond-pair/lone-pair repulsions.

The substitution of the methyl and ethyl groups by isopropyl in the xanthate ligand does not significantly alter the immediate environment about the tellurium atom. The major difference between the structure of Te(iprxa)$_2$ and those for Te(mexa)$_2$ [3] and Te(exa)$_2$ [4] is found in the nature of the intermolecular contacts. For both Te(mexa)$_2$ and Te(exa)$_2$ short Te–S(2)′ contacts of 3.513(1) and 3.605(15) Å respectively are observed between centrosymmetrically related molecules, whereas, for Te(iprxa)$_2$ the closest intermolecular Te–S distances are 4.133(4) Å for Te(1)–S(1)c' and 4.178(4) Å for Te(2)–S(1)a' (where primed atoms are related by the symmetry operation $\bar{x}$, 0.5 + y, 0.5 − z) both distances being greater than the sum of the van der Waals radii for tellurium and sulphur [9]. Clearly, in tellurium(II) xanthates, the introduction of the isopropyl group prevents close intermolecular contacts.

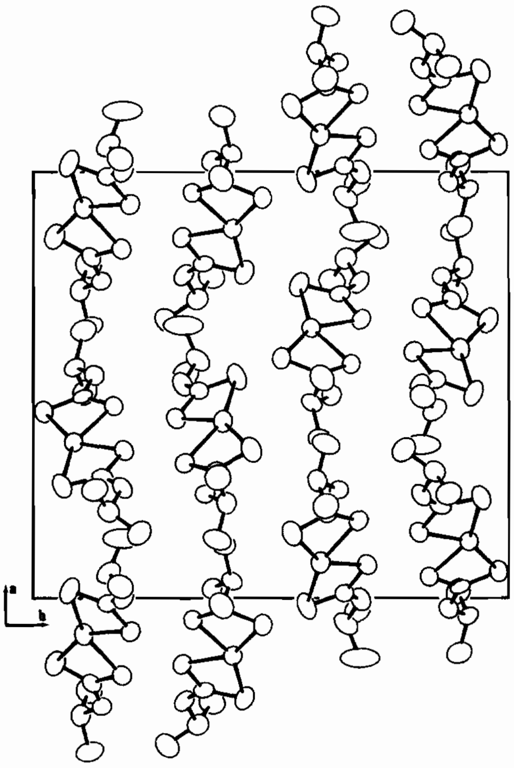

Fig. 2. Unit cell contents of Te(iprxa)$_2$ as viewed down the [001] direction.

TABLE III. Bond Angles (°) for $Te(iprxa)_2$.

Atoms	ligand a	ligand b	ligand c	ligand d
S(1)–Te–S(2)	66.2(1)	65.9(1)	65.5(1)	65.3(1)
Te–S(1)–C(1)	91.5(5)	91.4(5)	91.8(5)	93.3(5)
Te–S(2)–C(1)	80.7(5)	80.2(5)	79.2(6)	80.1(5)
S(1)–C(1)–S(2)	121.5(9)	122.4(8)	123.4(9)	121.2(9)
S(1)–C(1)–O(1)	111.0(9)	111.7(8)	111.3(8)	111.8(9)
S(2)–C(1)–O(1)	127(1)	126(1)	125(1)	127(1)
C(1)–O(1)–C(2)	119(1)	121(1)	121(1)	120(1)
O(1)–C(2)–C(3)	104(1)	104(1)	106(1)	106(1)
O(1)–C(2)–C(4)	105(1)	108(1)	108(1)	106(1)
C(3)–C(2)–C(4)	114(1)	116.2(1)	112(1)	111(1)
S(1)a–Te(1)–S(1)b	83.7(1)			
S(1)a–Te(1)–S(2)b	147.5(1)			
S(2)a–Te(1)–S(1)b	149.9(1)			
S(2)a–Te(1)–S(2)b	144.1(1)			
S(1)c–Te(2)–S(1)d			83.9(1)	
S(1)c–Te(2)–S(2)d			149.2(1)	
S(2)c–Te(2)–S(1)d			149.4(1)	
S(2)c–Te(2)–S(2)d			145.2(1)	

A further interesting feature of the present structure is the occurrence of two conformational isomers in the unit cell. Conformational isomers for metal xanthates have previously been observed in $Ni(exa)_2$ [11], $Hg(exa)_2$ [12, 13] and $Cl_2Sn(exa)_2$ [14, 15], however, in these cases each isomer exists as a different crystalline form.

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