

Structure of Bis[bis(2-hydroxyethyl)dithiocarbamate]tellurium(II), $[\text{Te}(\text{C}_5\text{H}_{10}\text{NO}_2\text{S}_2)_2]$

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Abstract. $M_r = 488.12$, monoclinic, $P2_1/c$, $a = 11.303$ (5), $b = 5.543$ (1), $c = 28.724$ (5) Å, $\beta = 100.30$ (1)°, $V = 1770.54$ Å³, $D_m = 1.76$, $D_x = 1.83$ Mg m⁻³, $Z = 4$, $\lambda(\text{Mo } K\alpha_1) = 0.71069$ Å, $\mu = 2.002$ mm⁻¹, $F(000) = 968$, $T = 293$ K. Final $R = 0.066$ for 1314 unique observed reflections. Each Te^{II} atom is bonded to all four S atoms of the two ligands, forming an asymmetric, planar complex with the Te–S bond distances in the range 2.527 (7)–2.793 (8) Å. The molecules are linked in pairs by a short intermolecular contact Te...S(2') of 3.296 (7) Å indicating a tendency towards five-coordination around tellurium. Two of the four ethanol groups in the molecule show a disorder with a statistical distribution of orientations.

Introduction. The preparation of the title compound (hereafter called TeL_2) has been reported by Sejkan, Janakiram & Aravamudan (1978). We have observed that TeL_2 is much more reactive than bis(diethyldithiocarbamate)tellurium [$\text{Te}(\text{dedtc})_2$] (Fabiani, Spagna, Vaciego & Zarrantonelli, 1971) and bis(morpholydithiocarbamate)tellurium [$\text{Te}(\text{morphdte})_2$] (Husebye, 1970). These latter two complexes are very stable and unaffected by thiourea, whereas TeL_2 could be converted easily (and reversibly) to the dichlorotetrakis(thiourea)Te^{II} [$\text{Te}(\text{NH}_2\text{CSNH}_2)_4\text{Cl}_2$] by treatment with excess thiourea in 1M HCl. Also it has been observed that thioglycolic acid decomposes a solution of TeL_2 , while the other two are unaffected. Acidification of TeL_2 with methanolic HCl and treatment with mercaptobenzimidazole (mbi) has been found to give $\text{Te}(\text{mbi})_4\text{Cl}_2$, while the other two dithiocarbamate complexes are again unaffected. Finally, the Te^{II} in a methanolic solution of TeL_2 undergoes ready oxidation to Te^{IV} forming TeO_2 . This redox reaction does not take place in either $\text{Te}(\text{dedtc})_2$ or $\text{Te}(\text{morphdte})_2$. The higher reactivity of TeL_2 could possibly arise due to (i) weakening of the Te–S bond, (ii) less delocalization from the C–N group in the dithiocarbamate which would reduce the overall bonding tendencies and (iii) more subtle specific effects such as solvation and inductive factors.

Hence, we have undertaken the crystal-structure determination of TeL_2 .

Experimental. Excellent needle-shaped red crystals obtained by crystallization from acetone, single crystal with approximate dimensions 0.08 × 0.10 × 0.30 mm chosen. D_m measured by flotation. Enraf–Nonius CAD-4 computer-controlled four-circle diffractometer, graphite monochromator, Mo $K\alpha$ radiation. Lattice parameters determined by least-squares refinement of θ values for 25 reflections. ω – 2θ scan technique, scan interval $\Delta\omega = (0.8 + 0.45 \tan \theta)^\circ$. Background measured for one quarter of scan time at each end of peak scan interval. In range $2 < \theta < 28^\circ$, 1314 reflections (h –12–13, k 0–7, l 0–32) with $I > 3\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics, measured as a unique set. Two check reflections measured every 3000s of X-ray exposure time. No corrections made for absorption. $R_{\text{int}} = 0.0146$. Te atom located from Patterson map; a subsequent Fourier map yielded complete non-H skeleton. Structure refined isotropically to $R = 0.176$. At this stage, an examination of bond lengths, bond angles and temperature factors revealed two disturbing features. First, the bond lengths and angles in two of the four ethanol groups deviated substantially from normal values, indicating probable disorder. Secondly, O atoms attached to C(8) and C(10) had temperature factors higher than what one would expect normally. Difference Fourier maps phased on two sets of O-atom positions [O(31) and O(32) attached to C(8) and O(41) and O(42) attached to C(10)] indicated the existence of two conformers, with equal occupancy factors of the two ethanol groups.

Further anisotropic refinement of Te only reduced R to 0.131 indicating possible higher thermal motions in the molecule. Structure refined by full-matrix least-square methods on F with all non-H anisotropic and O(41) isotropic since it showed considerable movements. 17 H atoms out of 20 appeared in difference maps, and were included at these positions ($U = 0.05$ Å²) which remained fixed during refinement. 204 parameters refined. Final $R = 0.066$, $R_w = 0.075$; $w = 0.021[\sigma^2(F_o) + 0.1277F_o^2]^{-1}$. Ratio of max. LS shift to error 3.375, average 0.512. Max. and min. heights in final ΔF map 1.2 and $-0.67 e \text{ \AA}^{-3}$. Five reflections removed because they apparently suffered from secondary extinction; no correction for secondary

extinction. Scattering factors given by Cromer & Mann (1968) and for H by Stewart, Davidson & Simpson (1965). Anomalous-dispersion correction included (Cromer & Liberman, 1970). All calculations carried out with *SHELX* (Sheldrick, 1976), thermal-ellipsoid plots obtained with *ORTEP* (Johnson, 1965).

Discussion. Fig. 1 depicts the molecule and Tables 1 and 2 contain the positional, thermal and bonding parameters.* The Te atom and the four S atoms form a plane, the maximum deviation from which being 0.057 (8) Å. The planarity of the molecule in TeL_2 is not limited to TeS_4 , but includes the C—N bonds as well on both ligands (as reported for other dithiocarbamates), the maximum deviation from planarity being 0.127 (7) Å. Table 3 compares the different bond

* Lists of structure factors, anisotropic thermal parameters, least-squares-planes' data and fixed H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38546 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

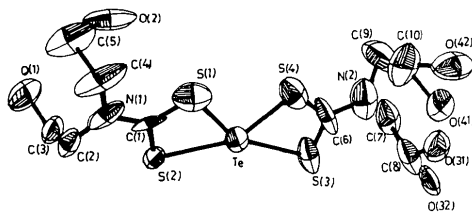


Fig. 1. *ORTEP* (Johnson, 1965) plot of the molecule TeL_2 .

Table 1. Final fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for non-H atoms with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Te	387 (1)	2607 (3)	8356 (1)	33 (1)
S(1)	-1128 (7)	-168 (14)	8656 (3)	95 (5)
S(2)	-923 (5)	-345 (10)	7663 (2)	56 (3)
S(3)	2180 (8)	6104 (12)	8570 (2)	87 (5)
S(4)	671 (7)	3980 (16)	9207 (2)	96 (5)
C(1)	-1521 (18)	-1402 (40)	8131 (9)	64 (9)
N(1)	-2339 (15)	-3295 (35)	8060 (10)	74 (9)
C(2)	-2597 (22)	-4570 (41)	7600 (13)	82 (11)
C(3)	-3482 (20)	-3428 (48)	7213 (12)	86 (10)
O(1)	-4703 (15)	-3794 (42)	7283 (9)	114 (9)
C(4)	-2824 (22)	-4111 (47)	8474 (13)	116 (10)
C(5)	-4224 (27)	-3661 (49)	8381 (13)	130 (11)
O(2)	-4239 (19)	-926 (45)	8498 (8)	149 (11)
C(6)	1723 (29)	6053 (47)	9114 (9)	104 (10)
N(2)	2167 (24)	7561 (41)	9478 (10)	109 (11)
C(7)	3017 (32)	9204 (54)	9411 (11)	125 (12)
C(8)	4335 (32)	8233 (50)	9442 (9)	98 (11)
O(31)	4566 (32)	7095 (61)	9919 (15)	113 (11)
O(32)	5386 (34)	9836 (58)	9298 (11)	96 (11)
C(9)	1637 (36)	7707 (60)	9953 (12)	150 (11)
C(10)	2283 (27)	6002 (57)	10273 (12)	116 (12)
O(41)	3675 (29)	5945 (54)	10326 (11)	76 (7)
O(42)	3222 (36)	7176 (70)	10602 (14)	116 (11)

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

Te—S(1)	2.562 (8)	C(3)—O(1)	1.45 (3)
Te—S(2)	2.788 (6)	C(4)—C(5)	1.58 (4)
Te—S(3)	2.793 (8)	C(5)—O(2)	1.55 (4)
Te—S(4)	2.527 (7)	C(6)—N(2)	1.36 (4)
Te—S(2')	3.296 (7)	N(2)—C(7)	1.36 (4)
S(1)—C(1)	1.64 (3)	N(2)—C(9)	1.59 (5)
S(2)—C(1)	1.71 (3)	C(7)—C(8)	1.57 (5)
S(3)—C(6)	1.73 (3)	C(8)—O(31)	1.49 (5)
S(4)—C(6)	1.71 (3)	C(8)—O(32)	1.60 (5)
C(1)—N(1)	1.39 (3)	C(9)—C(10)	1.43 (5)
N(1)—C(2)	1.48 (4)	C(10)—O(41)	1.55 (5)
N(1)—C(4)	1.47 (5)	C(10)—O(42)	1.44 (5)
C(2)—C(3)	1.50 (4)		
S(1)—Te—S(2)	65.6 (2)	C(1)—N(1)—C(2)	121 (2)
S(1)—Te—S(3)	147.6 (2)	C(1)—N(1)—C(4)	117 (2)
S(2)—Te—S(3)	146.8 (2)	C(2)—N(1)—C(4)	122 (2)
S(4)—Te—S(1)	80.3 (3)	N(1)—C(2)—C(3)	117 (2)
S(4)—Te—S(2)	145.8 (2)	C(2)—C(3)—O(1)	111 (3)
S(4)—Te—S(3)	67.4 (3)	N(1)—C(4)—C(5)	109 (3)
S(2)—Te—S(2')	74.1 (3)	C(4)—C(5)—O(2)	100 (2)
S(3)—Te—S(2')	73.4 (4)	C(6)—N(2)—C(7)	118 (3)
Te—S(1)—C(1)	91.6 (9)	C(6)—N(2)—C(9)	123 (3)
Te—S(2)—C(1)	82.8 (8)	C(7)—N(2)—C(9)	118 (3)
Te—S(3)—C(6)	82.3 (10)	N(2)—C(7)—C(8)	117 (3)
Te—S(4)—C(6)	91.3 (10)	C(7)—C(8)—O(31)	102 (3)
S(1)—C(1)—S(2)	120 (1)	C(7)—C(8)—O(32)	123 (2)
S(1)—C(1)—N(1)	121 (2)	O(31)—C(8)—O(32)	117 (3)
S(2)—C(1)—N(1)	119 (2)	N(2)—C(9)—C(10)	107 (3)
S(3)—C(6)—S(4)	119 (2)	C(9)—C(10)—O(41)	108 (3)
S(3)—C(6)—N(2)	124 (2)	C(9)—C(10)—O(42)	111 (3)
S(4)—C(6)—N(2)	118 (2)	O(41)—C(10)—O(42)	48 (2)

Symmetry code: (i) $-x, 0.5 + y, 0.5 - z$.

lengths and bond angles found in compounds similar in overall coordination but different in reactivities. In all these compounds there are two sets of Te—S bond lengths. Each dithiocarbamate group contributes to a short and long interaction. In addition there is an intermolecular Te—S contact of 3.296 (7) Å, which is shorter than the sum of van der Waals radii of Te and S (3.86 Å), but much longer than the sum of covalent radii (2.36 Å) (Alcock, 1972).

The following differences in bond lengths are found between TeL_2 and the other compounds in Table 3.

- The shorter Te—S bonds in TeL_2 are longer than those reported in compounds (I), (II) and (III) (refer to Table 3) and the longer Te—S bonds in TeL_2 are shorter in comparison. However, the average Te—S length [2.667 (5) Å] shows no significant variation.
- In all dithiocarbamate ligands studied so far, the asymmetry in the Te—S lengths in a ligand occurs along with a similar asymmetry in S—C lengths, the longer Te—S occurring along with shorter S—C lengths. In TeL_2 , such an effect is not observed. Assuming all four S—C bonds in TeL_2 to be equal, statistical significance tests (Cruickshank & Robertson, 1953) show that there is a 4% probability for the observed differences. The inference is that the S—C bond lengths are not significantly different.

Table 3. Comparison of bond lengths (Å) and bond angles (°) of the related compounds

Compound	Te—S		Te...S ^I	S—C		C=N	Angles around Te	
(I)	2.519 (4)	2.830 (3)	3.579 (5)	1.74 (2)	1.69 (2)	1.36 (2)	66.5 (1)	80.1 (1)
	2.518 (4)	2.893 (4)		1.73 (2)	1.71 (2)	1.33 (2)	65.8 (1)	147.8 (1)
	2.690 (10)*							
(II)	2.498 (7)	2.856 (8)	3.68	1.76 (3)	1.69 (2)	1.33 (4)	66.6 (2)	80.9 (2)
	2.530 (6)	2.834 (9)		1.74 (2)	1.67 (2)	1.33 (4)	66.8 (2)	145.7 (2)
	2.679 (9)*							
(III)	2.480 (13)	2.857 (14)	3.61	1.79 (4)	1.63 (4)	—	65.5 (4)	83.6 (4)
	2.486 (11)	2.897 (17)		1.67 (5)	1.69 (3)		66.4 (3)	144.5 (3)
	2.680 (13)*							
(IV)	2.562 (8)	2.788 (6)	3.296 (7)	1.64 (3)	1.71 (3)	1.39 (3)	65.6 (2)	80.3 (3)
	2.527 (7)	2.793 (8)		1.71 (3)	1.73 (3)	1.36 (4)	67.4 (3)	146.8 (2)
	2.667 (5)*							

(I) Te(dedtc)₂ (Fabiani *et al.*, 1971). (II) Te(morphdte)₂ (Husebye, 1970). (III) Te(S₂COEt)₂ (Husebye, 1967). (IV) This work.

* Corresponds to average Te—S distance.

Contrary to our expectations, the greater reactivity of TeL₂ (when compared to the compounds I and II) is not reflected in either the C—N distances or the Te—S bond lengths. Hence it is difficult to explain the higher reactivity of TeL₂ by molecular bond parameters since the observed differences are minimal. Apparently, more subtle influences such as solvation and inductive factors confer greater reactivity on TeL₂.

The two lone pairs of electrons of Te^{II} affect the stereochemistry of Te^{II} complexes significantly (Hoskins & Pannan, 1976). In dithiocarbamate complexes, the more subtle aspects of the effect can be discerned. In TeL₂, due to the shorter intermolecular Te—S contact, the two lone pairs lying above and below the TeS₄ plane would be slightly shifted away axially towards the shorter Te—S bonds. As a result, the shorter Te—S bond lengths become longer and the longer Te—S bond lengths shorter compared to the cases in the other two dithiocarbamates.

Bond lengths and angles around the C atoms in the dithiocarbamate ligands are normal, the disordered O atoms giving rise to slightly different values in the C—O

distances. Intermolecular O atoms approach each other within 2.63 Å indicating the presence of hydrogen bonding between them.

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