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Structure of Bis[bis(2-hydroxyethyl)dithiocarbamato]diiodotellurium(IV), $[Te(C_5H_{10}NO_2S_2)_2I_2]$

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Abstract. $M_r = 741\cdot9$, triclinic, $P\bar{1}$, $a = 10\cdot740$ (7), $b = 11\cdot530$ (6), $c = 11\cdot000$ (8) Å, $\alpha = 108\cdot90$ (5), $\beta = 121\cdot94$ (5), $\gamma = 90\cdot86$ (5)°, $V = 1063\cdot78$ Å^3, $Z = 2$, $D_m = 2\cdot29$, $D_x = 2\cdot316$ Mg m^{-3}, Mo $K\alpha$, $\mu = 4\cdot394$ mm^{-1}, $\lambda = 0\cdot71069$ Å, room temperature, $F(000) = 696$, final $R = 0\cdot062$ for 1924 reflections. The Te atom is seven coordinated to four S atoms, to two axial I atoms and to an intermolecular bridging I in a distorted pentagonal-bipyramidal geometry. The two S atoms in each bidentate ligand form unequal bonds. The dithiocarbamate parts of the two ligands are planar.

Introduction. Mixed-ligand complexes of post transition metals like As^{III} (Manoussakis, Tsipis & Hadjikostas, 1975), and Hg^{II} (Chieh, 1977) with dithiocarbamates (dtc) and halogens are known but those of Te^{IV} are very rare. To date, only two reports of mixed-ligand complexes of Te^{IV} are known, namely Te(Ph)(dedtc)$_3$ (Foss, 1953; Esperas & Husebye, 1972) and Te(dedtc)$_3$Cl (Schnabel, Deuten & Klar, 1979).* Since dedtc is a strong ligand, mixed-ligand complexes of the above type could be obtained only with difficulty. However, by suitably substituting electron-withdrawing groups on the N atom of the dtc moiety, the ligand could be made weaker, and hence would allow the entry of other ligands into the coordination sphere. This is amply demonstrated by the ease with which complexes such as Te^{IV} (Memeadtc)$_3X$ (X = Cl, Br, I, SCN) are formed (Aravamudan, Janakiram & Sejekan, 1978). Te^{IV}(deadtc)$_3$I and Te^{IV}(deadtc)$_2$I$_2$ have also been reported (Sejekan, Janakiram & Aravamudan, 1978), and were prepared from aqueous solutions, the latter being the first Te^{IV}–dithiocarbamate–iodide mixed-ligand complex.

The title compound (TeL_2I$_2$) is the only mixed-ligand complex of Te^{IV} where more than one dtc ligand from the parent compound Te(deadtc)$_4$ has been replaced by another ligand. All other reported compounds contain a tris(dtc) moiety. Iodide is a much better ligand than Cl$^-$ or Br$^-$ or NCS$^-$ and hence two iodides are able to displace two dtc groups. The crystal structure of this complex is now reported.

Experimental. Crystals of TeL_2I$_2$ prepared by the method reported earlier (Sejekan, Janakiram & Aravamudan, 1978). Density measured by flotation. Preliminary X-ray photographs showed the crystal system to be triclinic. Since $Z = 2$, the space group was tentatively assigned as $P\bar{1}$, which proved to be correct. CAD-4 diffractometer; $2\theta_{\max} = 54°$, range of hkl: ±11, ±14, 8; two standard reflections, variation 6%; intensities of 3195 reflections collected from a crystal 0·05 × 0·2 × 0·33 mm; $R_{\rm int} = 0\cdot085$; cell parameters refined using the angular values of 25 high-angle reflections; data not corrected for absorption; 1924 observed reflections [$I > 3\sigma(I)$] used in structure analysis; $\sum w|\Delta F|^2$ minimized. Te and I positions from Patterson maps; successive Fourier maps based on the positions of Te and I gave the locations of all non-hydrogen atoms. Full-matrix refinement (*SHELX*76, Sheldrick, 1976) with anisotropic thermal parameters. Correlations found between the position parameters x and z and between anisotropic thermal parameters for all atoms; this was expected as β (121·94°) differs appreciably from 90°. Thermal parameters U_{13} for all atoms fixed in the refinement. H atoms could not be located from final difference Fourier maps; H atoms attached to methylene C atoms were fixed geometrically and assigned a fixed isotropic temperature factor $U = 0\cdot05$ Å^2. Final R and R_w values are 0·062 and 0·069 respectively; $w = 0\cdot014/[\sigma^2(F_o) + 0\cdot1595|F_o|^2]$ in the final refinement. Ratio of maximum least-squares shift to error 0·244; maximum and minimum heights in final difference Fourier map 1·35 and $-0\cdot75$ e Å^{-3}; no correction for secondary extinction; atomic scattering factors for non-hydrogen atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965); anomalous-dispersion correction factors for non-hydrogen atoms from Cromer & Liberman (1970).

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* Abbreviations: dedtc: diethyldithiocarbamato; Memeadtc: methyl (2-hydroxyethyl)dithiocarbamato; deadtc: bis(2-hydroxyethyl)dithiocarbamato.

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Discussion. Final fractional coordinates are given in Table 1, bond lengths and angles in Table 2. Fig. 1 gives an *ORTEP* (Johnson, 1965) plot of the molecule.*

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *with estimated standard deviations in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij}\, a_i^*\, a_j^*\, \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$ ($\text{Å}^2\times 10^4$)
Te	4017 (1)	8353 (1)	2528 (1)	309 (3)
I(1)	6672 (1)	10639 (1)	4637 (2)	409 (4)
I(2)	1468 (2)	6305 (1)	809 (2)	528 (4)
S(1)	5578 (6)	7169 (5)	4513 (7)	529 (15)
S(2)	5488 (6)	6982 (4)	1738 (6)	440 (14)
S(3)	2263 (5)	10098 (4)	1944 (6)	419 (15)
S(4)	3374 (6)	8684 (5)	127 (7)	534 (15)
O(1)	10349 (16)	6827 (13)	4824 (21)	685 (49)
O(2)	6618 (18)	3410 (13)	3527 (22)	779 (54)
O(3)	−106 (20)	8826 (16)	−3406 (20)	768 (56)
O(4)	3823 (20)	13160 (16)	914 (20)	822 (63)
N(1)	7240 (16)	5928 (13)	3679 (17)	320 (43)
N(2)	2113 (16)	10632 (13)	−283 (19)	323 (46)
C(1)	6243 (17)	6632 (14)	3398 (20)	259 (47)
C(2)	7817 (25)	5516 (18)	2704 (29)	683 (66)
C(3)	9140 (24)	6526 (20)	3228 (26)	575 (67)
C(4)	7905 (24)	5632 (18)	5091 (27)	601 (66)
C(5)	6862 (26)	4460 (19)	4761 (29)	667 (67)
C(6)	2501 (17)	9892 (14)	498 (20)	256 (47)
C(7)	2262 (22)	10378 (20)	−1638 (23)	486 (68)
C(8)	708 (23)	9934 (22)	−3127 (26)	540 (74)
C(9)	1573 (24)	11748 (18)	138 (25)	586 (61)
C(10)	2943 (29)	12897 (19)	1459 (25)	585 (70)

Table 2. *Bond distances* (Å) *and angles* (°)

Te–I(1)	3·044 (2)	C(5)–O(2)	1·38 (2)
Te–I(1′)	3·427 (2)	Te–S(3)	2·769 (5)
Te–I(2)	2·842 (2)	Te–S(4)	2·515 (6)
Te–S(1)	2·750 (5)	S(3)–C(6)	1·68 (1)
Te–S(2)	2·527 (5)	S(4)–C(6)	1·74 (1)
S(1)–C(1)	1·68 (1)	C(6)–N(2)	1·32 (2)
S(2)–C(1)	1·75 (1)	N(2)–C(7)	1·51 (2)
C(1)–N(1)	1·31 (1)	N(2)–C(9)	1·45 (2)
N(1)–C(2)	1·46 (2)	C(7)–C(8)	1·50 (2)
N(1)–C(4)	1·48 (2)	C(9)–C(10)	1·56 (3)
C(2)–C(3)	1·53 (2)	C(8)–O(3)	1·38 (2)
C(4)–C(5)	1·55 (2)	C(10)–O(4)	1·43 (2)
C(3)–O(1)	1·43 (2)		
I(1)–Te–I(2)	173·8 (1)	S(2)–Te–S(3)	145·7 (2)
I(1)–Te–S(1)	89·6 (1)	S(2)–Te–S(4)	78·9 (2)
I(1)–Te–S(2)	92·7 (1)	S(2)–Te–I(1′)	141·6 (2)
I(1)–Te–S(3)	85·0 (1)	S(3)–Te–S(4)	67·0 (1)
I(1)–Te–S(4)	92·1 (1)	S(3)–Te–I(1′)	72·5 (2)
I(1)–Te–I(1′)	85·4 (1)	S(4)–Te–I(1′)	139·5 (2)
I(2)–Te–S(1)	88·7 (1)	Te–S(1)–C(1)	84·5 (6)
I(2)–Te–S(2)	92·2 (1)	Te–S(2)–C(1)	90·3 (6)
I(2)–Te–S(3)	93·1 (1)	S(1)–C(1)–S(2)	117·3 (9)
I(2)–Te–S(4)	92·6 (1)	S(1)–C(1)–N(1)	123 (1)
I(2)–Te–I(1′)	88·3 (1)	S(2)–C(1)–N(1)	119 (1)
S(1)–Te–S(2)	67·5 (2)	C(1)–N(1)–C(2)	121 (2)
S(1)–Te–S(3)	146·5 (2)	C(1)–N(1)–C(4)	120 (2)
S(1)–Te–S(4)	146·4 (2)	C(2)–N(1)–C(4)	118 (2)
S(1)–Te–I(1′)	74·0 (2)	N(1)–C(2)–C(3)	111 (2)
		N(1)–C(4)–C(5)	110 (2)
C(2)–C(3)–O(1)	111 (2)	C(6)–N(2)–C(7)	121 (2)
C(4)–C(5)–O(2)	112 (2)	C(6)–N(2)–C(9)	122 (2)
Te–S(3)–C(6)	84·3 (6)	C(7)–N(2)–C(9)	117 (2)
Te–S(4)–C(6)	91·3 (6)	N(2)–C(7)–C(8)	109 (2)
S(3)–C(6)–S(4)	117 (1)	N(2)–C(9)–C(10)	110 (2)
S(3)–C(6)–N(2)	122 (1)	C(7)–C(8)–O(3)	113 (2)
S(4)–C(6)–N(2)	121 (1)	C(9)–C(10)–O(4)	110 (2)

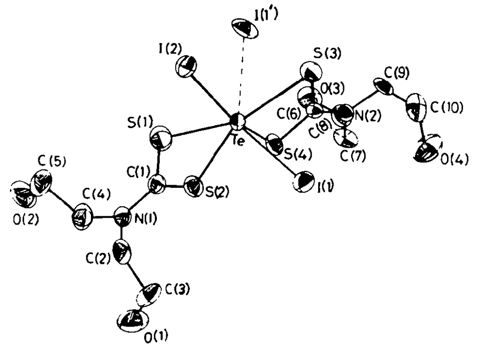

Fig. 1. An *ORTEP* plot of a molecule of $\mathrm{Te}L_2\mathrm{I}_2$.

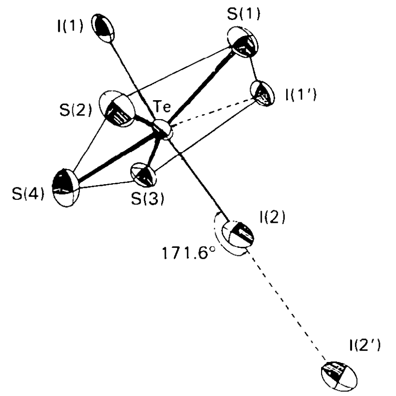

Fig. 2. Coordination around Te in $\mathrm{Te}L_2\mathrm{I}_2$. (See Table 2 and text for interatomic distances and angles.)

The Te atom has μ-iodo-bridged seven coordination which is shown in Fig. 2. Centrosymmetrically related iodine atoms I(1) and I(1′) (a prime indicates an atom related by a centre of inversion) bridge the two polyhedra around neighbouring Te atoms, also related by a centre of symmetry. The coordination polyhedron around Te is a distorted pentagonal bipyramid, with Te bonded to *trans* axial I atoms and with a planar pentagonal group containing all four S atoms and the intermolecular bridging I. The four nearly planar Te—S bond lengths range from 2·515 (6) to 2·769 (5) Å and the bridging Te—I(1′) has a length of 3·427 (2) Å. The interbond angles in the equatorial girdle range from 67·0 (1) to 78·9 (2)°. I(1) and I(2) lie above and below the equatorial plane, the I(1)—Te—I(2) angle being 173·8 (1)°. Of the two I atoms, one participates in bridging while the other forms a secondary intermolecular I···I short contact of 3·531 (3) Å.

The two molecules in the unit cell bridged *via* the I form a dimer with an associated centre of inversion. The Te···I(1)···Te′ bridging angle of 94·6 (3)° is close to 92·1 and 94·5°, the values found in (4-MeOPh)TeI_3 (Bird, Kumar & Pant, 1980). The plane containing Te,I(1), I(1′) and I(2) is nearly perpendicular to the equatorial plane.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38547 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

There are three types of Te—I interactions present, with considerable variations in interatomic distances: Te—I(2) 2·842 (2), Te—I(1) 3·044 (2) and Te—I(1′) 3·427 (2) Å. The first two are intramolecular and the third is intermolecular. Te—I(1) and Te—I(2) distances are longer than the sum of the covalent radii of Te and I (2·70 Å). This is expected, as the two I atoms I(1) and I(2) take part in other interactions as well, I(1) being the bridging I between the two Te atoms and I(2) forming a weak intermolecular contact with another I atom. The dimerization is asymmetric with unequal I bridging [3·044 (2), 3·427 (2)Å]. Te—I(1′) [3·427 (2)Å] is again significantly shorter than the sum of the van der Waals radii of Te and I (4·04 Å), indicating the strength of the intermolecular bridging interaction. These Te—I distances and the I—Te—I angle [173·8 (1)°] lie in the range found for similar compounds: $(CH_3)_2TeI_4$ 2·809, 3·404, 3·957 Å, 174·63° (Pritzkow, 1979); $(4\text{-MeOPh})TeI_3$ 2·788 (5), 3·097–3·192 Å, 174·6° (Bird, Kumar & Pant, 1980).

The I(2)···I(2′) interaction of 3·531 Å found in TeL_2I_2 is shorter than the van der Waals I—I distance of 4·30 Å, and forms chains I—Te—I···I—Te—I nearly parallel to the *b* axis. This is shorter than 3·66, 3·90 Å found in 1-thia-4-telluracyclohexane 4,4-diiodide (Knobler, McCullough & Hope, 1970) but larger than the 3·337 (1) Å found in 2-biphenylyltellurium triiodide (McCullough, 1977).

The average Te—S bond length of 2·64 (7) Å found in this compound is shorter than the values reported in tris(dedtc)(phenyl)tellurium [2·72 (4) Å] (Esperas & Husebye, 1972) and *trans*-tetrabromo-, and *trans*-tetrachlorobis(tmtu)tellurium [2·707 (10), 2·699 (8) Å] (tmtu = tetramethylthiourea) (Husebye & George, 1969), but closer to 2·59 Å, the sum of the octahedral radius of Te (Foss, 1967) and the covalent radius of S. The presence of a smaller number of dithiocarbamate groups around Te in TeL_2I_2 leads to stronger Te—S bonding, resulting in shorter Te—S lengths. Unequal Te—S lengths in both dithiocarbamate ligands occur along with unequal S—C lengths, the longer Te—S length corresponding to the shorter S—C distance, indicating the presence of canonical forms in the dithiocarbamate groups. Other bond distances and bond angles obtained in the structure agree with reported values for dithiocarbamate ligands (Husebye & Svaeren, 1973). The packing arrangement in the unit cell is shown in Fig. 3.

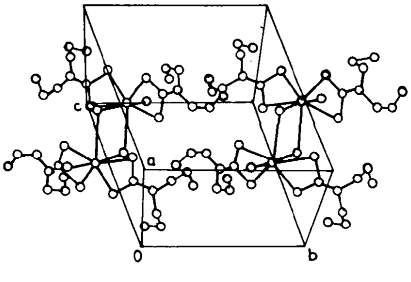

Fig. 3. Contents of the unit cell.

The pentagonal-bipyramidal coordination geometry around Te found in TeL_2I_2 agrees with the geometry predicted by Kepert (1975) from minimum-energy calculations for structures of the type [*M*(bidentate)$_2$-(unidentate)$_3$]. Here, the bridging I acts as the third unidentate ligand. Te in TeL_2I_2 may equally be considered as six-coordinated with an active lone pair. In this case, I(1′) can be regarded as not bonded to Te, with the active lone pair lying between S(1), I(1′) and S(3), which probably results in Te—S(1) and Te—S(3) bonds being significantly longer than the other Te—S bonds in the molecule.

References

Aravamudan, G., Janakiram, C. & Sejekan, B. G. (1978). *Phosphorus Sulfur*, **5**, 185–188.

Bird, P. H., Kumar, V. & Pant, B. C. (1980). *Inorg. Chem.* **19**, 2487–2493.

Chieh, C. (1977). *Can. J. Chem.* **55**, 65–69.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Esperas, S. & Husebye, S. (1972). *Acta Chem. Scand.* **26**, 3293–3304.

Foss, O. (1953). *Acta Chem. Scand.* **7**, 227–228.

Foss, O. (1967). *Selected Topics in Structural Chemistry*, p. 149. Oslo: Universitat Verlagt.

Husebye, S. & George, J. W. (1969). *Inorg. Chem.* **8**, 313–319.

Husebye, S. & Svaeren, S. E. (1973). *Acta Chem. Scand.* **27**, 763–778.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kepert, D. L. (1975) *J. Chem. Soc. Dalton Trans.* pp. 963–966.

Knobler, C., McCullough, J. D. & Hope, H. (1970). *Inorg. Chem.* **9**, 797–804.

McCullough, J. D. (1977). *Inorg. Chem.* **16**, 2318–2321.

Manoussakis, G. E., Tsipis, C. A. & Hadjikostas, C. C. (1975). *Can. J. Chem.* **53**, 1530–1535.

Pritzkow, H. (1979). *Inorg. Chem.* **18**, 311–313.

Schnabel, V. W., Deuten, K. V. & Klar, G. (1979). *Chem. Ztg*, p. 103.

Sejekan, B. G., Janakiram, C. & Aravamudan, G. (1978). *J. Inorg. Nucl. Chem.* **40**, 211–213.

Sheldrick, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.