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## Structure of Tetrakis(diisopropyldithiocarbamato)tellurium(IV)

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**Abstract.** [Te(C<sub>7</sub>H<sub>14</sub>NS<sub>2</sub>)<sub>4</sub>],  $M_r = 832.86$ , orthorhombic,  $P2_12_12_1$ ,  $a = 13.946$  (1),  $b = 14.833$  (1),  $c = 20.213$  (3) Å,  $V = 4181.54$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.35$ ,  $D_x = 1.32$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.119$  mm<sup>-1</sup>,  $F(000) = 1728$ ,  $T = 293$  K, final  $R(F) = 0.037$ ,  $S = 0.83$  for 2920 unique reflections. The central Te atom is eight coordinated so that the S atoms form a slightly distorted dodecahedral arrangement around the metal. The lone pair of electrons on Te<sup>IV</sup> is found to be stereochemically inert. Interligand S...S short contacts of 3.097 (3) and 3.246 (2) Å are observed.

**Introduction.** Dithiocarbamates are known to undergo redox complexation reactions with metal ions such as Se<sup>IV</sup> and Te<sup>IV</sup>, forming divalent selenium and tellurium complexes and the corresponding thiuram disulfides as the oxidation products (Fabiani, Spagna, Vaciego & Zambonelli, 1971; Schnabel, Deuten & Klar, 1980; Kumar, Aravamudan & Seshasayee, 1990). The general reaction between tellurium(IV) and dithiocarbamates ( $L$ ) can be given as:  $\text{Te}^{\text{IV}} + 4 L^- \rightleftharpoons \text{Te}^{\text{IV}}L_4 \rightleftharpoons \text{Te}^{\text{II}}L_2 + L-L$ , where  $L-L$  is the thiuram disulfide. In various solutions such as dichloromethane, carbon tetrachlo-

ride, benzene and acetonitrile, Te<sup>IV</sup>L<sub>4</sub> is found to undergo an autoredox reaction leading to the formation of the corresponding Te<sup>II</sup>L<sub>2</sub> species and the thiuram disulfide,  $L-L$ .

The structure determination of the title compound was carried out to study whether any structural feature in the solid state can account for its facile autoredox reaction in solutions, to examine whether the lone pair of electrons on tellurium has any stereochemical significance, and also to study the effect of the bulkiness of the ligand on the stereochemistry. Other structures of TeL<sub>4</sub> complexes which have been reported are those of tetrakis(diethyl-dithiocarbamato)tellurium(IV) (Husebye & Svaeren, 1973); tetrakis(4-morpholinecarbodithioato)tellurium(IV) (Esperas & Husebye, 1975); tetrakis[*N*-(2-hydroxyethyl)-*N*-methyl-dithiocarbamato]tellurium(IV) (Husebye, 1979) and tetrakis[bis(2-hydroxyethyl)dithiocarbamato]tellurium(IV) (Rout, Seshasayee, Aravamudan & Radha, 1984).

**Experimental.** The title compound was prepared as a yellow solid on addition of 50 ml of 2M acetic acid to 30 ml of 2M sodium hydroxide containing 4 mmol of sodium tellurite and 100 mmol of the sodium salt of diisopropyldithiocarbamic acid. The precipitate was washed with water and air dried. 1 mmol

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Table 1. Positional parameters and  $U_{eq}$  for non-H atoms with *e.s.d.*'s in parentheses
$$U_{eq} = 1/3 \sum_{i=1}^3 U_{ii}$$

	x	y	z	$U_{eq}$ (Å <sup>2</sup> )
Te	0.25349 (3)	0.11582 (2)	0.35267 (2)	0.0307 (2)
S(1)	0.0733 (1)	0.1139 (10)	0.3034 (1)	0.0445 (10)
S(2)	0.4335 (1)	0.0997 (1)	0.2920 (1)	0.0467 (10)
S(3)	0.3552 (1)	0.2292 (1)	0.4299 (1)	0.0534 (10)
S(4)	0.3630 (1)	-0.0140 (1)	0.4203 (1)	0.0480 (10)
S(5)	0.1525 (1)	0.2579 (1)	0.4000 (1)	0.0449 (10)
S(6)	0.1683 (1)	0.0393 (2)	0.4553 (1)	0.0581 (12)
S(7)	0.2890 (1)	0.2302 (1)	0.2499 (1)	0.0497 (10)
S(8)	0.2072 (1)	-0.0339 (1)	0.2805 (1)	0.0570 (12)
N(1)	0.2523 (4)	0.3673 (3)	0.4780 (3)	0.0426 (30)
N(2)	0.4777 (4)	0.2579 (4)	0.2357 (3)	0.0549 (38)
N(3)	0.2678 (4)	-0.0866 (4)	0.5219 (3)	0.0583 (38)
N(4)	0.0166 (4)	-0.0509 (4)	0.2671 (4)	0.0566 (38)
C(1)	0.2521 (5)	0.2939 (4)	0.4409 (3)	0.0407 (40)
C(2)	0.2673 (5)	-0.0270 (4)	0.4714 (4)	0.0418 (38)
C(3)	0.3363 (6)	0.3994 (6)	0.5184 (5)	0.0660 (56)
C(4)	0.4081 (5)	0.2014 (5)	0.2561 (4)	0.0399 (38)
C(5)	0.1603 (6)	0.4178 (6)	0.4897 (5)	0.0665 (54)
C(6)	0.4130 (7)	0.3640 (8)	0.1507 (6)	0.0902 (72)
C(7)	0.0903 (5)	0.0029 (4)	0.2813 (3)	0.0401 (36)
C(8)	0.1159 (8)	0.3928 (8)	0.5544 (6)	0.0947 (79)
C(9)	-0.0817 (6)	-0.0137 (7)	0.2723 (5)	0.0740 (59)
C(10)	-0.1403 (8)	-0.0635 (10)	0.3269 (6)	0.1078 (90)
C(11)	0.4139 (7)	0.4368 (8)	0.4744 (7)	0.1014 (83)
C(12)	0.4626 (7)	0.3539 (5)	0.2164 (5)	0.0623 (51)
C(13)	-0.1327 (8)	-0.0085 (9)	0.2038 (6)	0.1027 (84)
C(14)	0.1586 (11)	-0.0151 (11)	0.6054 (5)	0.134 (12)
C(15)	0.1860 (7)	-0.0997 (9)	0.5689 (6)	0.0978 (80)
C(16)	0.3286 (10)	-0.2410 (9)	0.5329 (8)	0.134 (12)
C(17)	0.0238 (6)	-0.1475 (6)	0.2484 (6)	0.0737 (60)
C(18)	0.5805 (6)	0.2278 (7)	0.2380 (6)	0.0888 (73)
C(19)	0.6328 (9)	0.2866 (15)	0.2932 (7)	0.199 (16)
C(20)	0.3680 (9)	0.3367 (8)	0.5690 (5)	0.0997 (81)
C(21)	0.0721 (8)	-0.1581 (8)	0.1838 (6)	0.0950 (77)
C(22)	0.6303 (7)	0.2375 (9)	0.1723 (6)	0.1062 (87)
C(23)	0.4207 (9)	0.4085 (6)	0.2697 (7)	0.1007 (81)
C(24)	0.1751 (9)	0.5210 (6)	0.4758 (6)	0.1027 (81)
C(25)	0.3534 (7)	-0.1390 (8)	0.5372 (5)	0.0890 (73)
C(26)	0.0635 (10)	-0.2063 (8)	0.3017 (8)	0.1218 (98)
C(27)	0.4013 (9)	-0.1113 (12)	0.6011 (7)	0.136 (11)
C(28)	0.0986 (8)	-0.1451 (10)	0.5321 (9)	0.142 (12)

Table 2. Bond lengths (Å) and angles (°) of non-H atoms with *e.s.d.*'s in parentheses

Te—S(1)	2.704 (2)	C(11)—C(3)	1.51 (2)
Te—S(2)	2.804 (2)	C(20)—C(3)	1.45 (2)
Te—S(3)	2.698 (2)	C(8)—C(5)	1.49 (2)
Te—S(4)	2.812 (2)	C(24)—C(5)	1.57 (1)
Te—S(5)	2.709 (2)	C(2)—N(3)	1.35 (1)
Te—S(6)	2.646 (2)	C(15)—N(3)	1.50 (1)
Te—S(7)	2.727 (2)	C(25)—N(3)	1.46 (1)
Te—S(8)	2.735 (2)	C(7)—N(4)	1.332 (9)
C(7)—S(1)	1.722 (7)	C(9)—N(4)	1.48 (1)
C(4)—S(2)	1.711 (7)	C(17)—N(4)	1.49 (1)
C(1)—S(3)	1.743 (7)	C(10)—C(9)	1.56 (2)
C(2)—S(4)	1.699 (7)	C(13)—C(19)	1.56 (2)
C(1)—S(5)	1.703 (7)	C(6)—C(12)	1.51 (2)
C(2)—S(6)	1.727 (7)	C(23)—C(12)	1.47 (2)
C(4)—S(7)	1.720 (7)	C(14)—C(15)	1.50 (2)
C(7)—S(8)	1.720 (7)	C(28)—C(15)	1.58 (2)
C(1)—N(1)	1.322 (8)	C(21)—C(17)	1.48 (2)
C(3)—N(1)	1.51 (1)	C(26)—C(17)	1.49 (2)
C(5)—N(1)	1.51 (1)	C(19)—C(18)	1.59 (2)
C(4)—N(2)	1.347 (9)	C(22)—C(18)	1.51 (2)
C(12)—N(2)	1.49 (1)	C(16)—C(25)	1.55 (2)
C(18)—N(2)	1.50 (1)	C(27)—C(25)	1.51 (2)
S(1)—Te—S(8)	64.9 (1)	S(7)—C(4)—S(2)	116.7 (4)
S(2)—Te—S(7)	63.7 (1)	N(2)—C(4)—S(2)	121.9 (5)
S(3)—Te—S(5)	65.4 (1)	N(2)—C(4)—S(7)	121.3 (5)
S(4)—Te—S(6)	64.5 (1)	C(8)—C(5)—N(1)	111.6 (8)
C(7)—S(1)—Te	88.7 (2)	C(24)—C(5)—N(1)	110.2 (7)
C(4)—S(2)—Te	85.7 (2)	C(24)—C(5)—C(8)	117.0 (9)
C(1)—S(3)—Te	89.0 (2)	C(15)—N(3)—C(2)	124.1 (7)
C(2)—S(4)—Te	86.9 (2)	C(25)—N(3)—C(2)	120.9 (7)
C(1)—S(5)—Te	89.5 (2)	C(25)—N(3)—C(15)	114.9 (8)
C(2)—S(6)—Te	91.9 (2)	C(9)—N(4)—C(7)	118.4 (7)
C(4)—S(7)—Te	88.0 (2)	C(17)—N(4)—C(7)	125.5 (6)
C(7)—S(8)—Te	87.7 (2)	C(17)—N(4)—C(9)	116.1 (6)
C(3)—N(1)—C(1)	124.8 (6)	S(8)—C(7)—S(1)	115.9 (4)
C(5)—N(1)—C(1)	119.8 (6)	N(4)—C(7)—S(1)	121.4 (5)
C(5)—N(1)—C(3)	114.9 (6)	N(4)—C(7)—S(8)	122.6 (5)
S(5)—C(1)—S(3)	116.0 (4)	C(10)—C(9)—N(4)	111.0 (8)
N(1)—C(1)—S(3)	121.6 (5)	C(13)—C(9)—N(4)	112.2 (8)
N(1)—C(1)—S(5)	122.4 (5)	C(13)—C(9)—C(10)	114.4 (8)
S(6)—C(2)—S(4)	116.6 (4)	C(6)—C(12)—N(2)	113.0 (7)
N(3)—C(2)—S(4)	122.0 (5)	C(23)—C(12)—N(2)	112.9 (8)
N(3)—C(2)—S(6)	121.3 (5)	C(23)—C(12)—C(6)	114.2 (9)
C(12)—N(2)—C(4)	124.9 (6)	C(14)—C(15)—N(3)	113.4 (10)
C(18)—N(2)—C(4)	119.6 (7)	C(28)—C(15)—N(3)	110.1 (10)
C(18)—N(2)—C(12)	115.2 (7)	C(28)—C(15)—C(14)	113.0 (10)
C(11)—C(3)—N(1)	110.8 (8)	C(21)—C(17)—N(4)	111.2 (8)
C(20)—C(3)—N(1)	114.6 (8)	C(26)—C(17)—N(4)	113.9 (9)
C(20)—C(3)—C(11)	115.7 (9)	C(26)—C(17)—C(21)	113.9 (9)
C(22)—C(18)—N(2)	112.7 (9)	C(27)—C(25)—C(16)	114.3 (11)
C(22)—C(18)—C(19)	110.7 (9)	C(19)—C(18)—N(2)	107.1 (9)
C(16)—C(25)—N(3)	109.0 (9)		
C(27)—C(25)—N(3)	113.5 (10)		

(0.831 g) of  $\text{TeL}_4$  was dissolved in 10 ml of dichloromethane and 5 ml of acetonitrile in the presence of 1 mmol (0.325 g) of the thiuram disulfide and allowed to evaporate slowly at room temperature giving orange red crystals. Any adhering disulfide was removed by washing with methanol. A suitable single crystal of dimensions  $0.72 \times 0.37 \times 0.25$  mm chosen.  $D_m$  by flotation in acetone-carbon tetrachloride mixture,  $P2_12_12_1$  from systematic absences; Enraf-Nonius CAD-4 diffractometer; cell parameters by least squares from setting angles of 40 reflections with  $22 \leq 2\theta \leq 28^\circ$ ; 3359 reflections with  $4 \leq 2\theta \leq 46^\circ$  and  $0 \leq h \leq 15$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 22$  ( $R_{int} = 0.03$ ) were collected using  $\omega$ - $2\theta$  scans; three standard reflections monitored every hour showed no significant change; correction for Lorentz and polarization effects; no absorption correction made; 2920 reflections ( $N$ ) with  $I > 3\sigma(I)$  used for structure

determination, 455 parameters ( $P$ ),  $N/P = 6.5$ ; structure solved by *SHELX76* (Sheldrick, 1976); Te position from Patterson map; successive difference Fourier maps based on Te position gave the locations of all non-H atoms; of the 56 H atoms, 21 appeared in the final difference Fourier map and were refined isotropically; positions of the remaining 35 H atoms geometrically fixed; non-H atoms refined anisotropically and H atoms with isotropic temperature factors; atomic scattering factors for non-H atoms from Cromer & Mann (1968); maximum and minimum electron density in the final difference Fourier map 0.25 and  $-0.67 \text{ e \AA}^{-3}$ ,  $(\Delta/\sigma)_{max} = 0.03$ ,  $R(F) = 0.037$ ,  $wR = 0.045$ ,  $w = 1/[\sigma^2(F_o) + 0.0039 |F_o|^2]$ ,  $S = 0.83$ .

**Discussion.** Table 1 contains the atomic coordinates and the thermal parameters of all non-H atoms.

Bond distances and angles are given in Table 2.\* Fig. 1 shows the *PLUTO* (Motherwell & Clegg, 1978) plot of the molecule. Fig. 2 shows the packing of the molecules in the unit cell.

In the title compound the four dithiocarbamate ligands are asymmetrically bound to the central Te

\* Lists of calculated and observed structure factors, anisotropic thermal parameters of non-H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53112 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

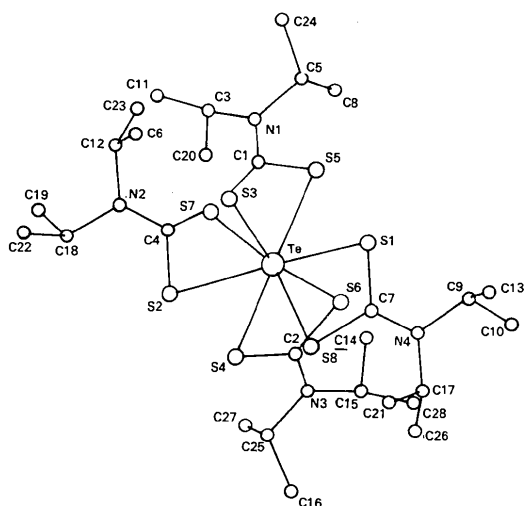


Fig. 1. *PLUTO* plot of the molecule.

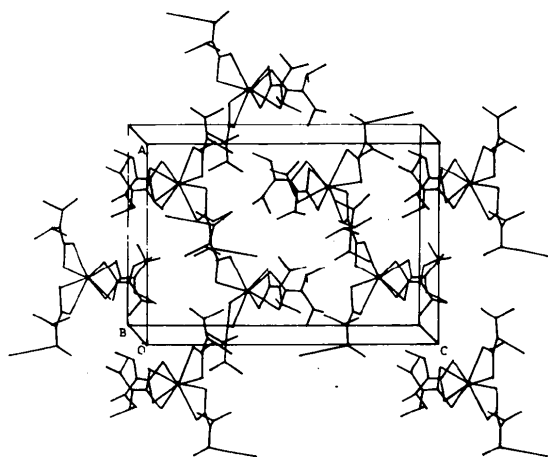


Fig. 2. Packing of the molecules in the unit cell.

atom. The  $\text{TeS}_8$  core is made up of two planar  $\text{TeS}_4$  trapezoids, namely Te, S(1), S(8), S(3), S(5) and Te, S(2), S(4), S(6), S(7) interlocking at the Te position at an angle of  $87.6^\circ$  to give a slightly distorted dodecahedral arrangement. The  $\text{TeS}_8$  core is similar to that found in the other reported  $\text{TeL}_4$  complexes. The ligands are nearly planar and the average C—S and C—N bond lengths of 1.72 (2) and 1.44 (4) Å respectively are normal.

According to Esperas & Husebye (1975), the S...S interligand distance is of importance in the stability of a  $\text{TeL}_4$  complex with respect to its transformation to  $\text{TeL}_2$  and  $L-L$ . Thus, the greater this S...S distance, the more stable the complex should be. Of all the  $\text{TeL}_4$  complexes, we find that the present compound, namely the isopropyl derivative, undergoes the most facile changeover to  $\text{TeL}_2$  and  $L-L$ . In the present compound in one of the  $\text{TeS}_4$  trapezoids, namely, Te, S(1), S(8), S(3), S(5), an interligand S...S short contact is observed with the S(1)...S(5) distance being 3.097 (3) Å {cf. 3.17 Å in  $[\text{Te}(\text{Et}_2\text{NCS}_2)_4]$ ; 3.39 Å in  $[\text{Te}(\text{OC}_4\text{H}_8\text{NCS}_2)_4]$ ; 3.25 Å in  $\text{Te}[(\text{OHC}_2\text{H}_4)_2\text{NCS}_2]_4$  and 3.16 Å in  $\text{Te}[\text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{NCS}_2]_4$ }. This short separation is consistent with the ease of the autoredox reaction. The proximity of the two S atoms for an intramolecular electron transfer may be the predominant reason for this behaviour, but other factors such as the reducing ability of the dithiocarbamate ligand have also to be taken into consideration.

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