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Structural Studies of Metal Dithiocarbamates. V. The Crystal and Molecular Structure of Bis-(*N*,*N*-Diethyldithiocarbamato)tellurium(II)*

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Tellurium(II) bis-(*N*,*N*-diethyldithiocarbamate), [Te(S_2CNEt_2)$_2$], forms red monoclinic crystals, $a=$ 15·191, $b=$ 8·425, $c=$ 14·841 Å, $\beta=$ 117·66°, space group $P2_1/c$, with four formula units in the unit cell. The structure has been solved by standard methods and refined by block-diagonal matrix least-squares methods, using 2012 photographic observations, to a final R value of 0·081. The four sulphur atoms in the molecule are bound to tellurium with two short bonds [average 2·519 (3) Å] and two long ones [2·830 (3) and 2·893 (4) Å]. A fifth sulphur atom, belonging to the centrosymmetrically related molecule, approaches tellurium at a distance of 3·579 (5) Å. Tellurium and the five sulphur atoms lie approximately in a plane. Rationalization of the coordination around the tellurium atom is attempted on the basis of both the three-centre bond and the full hybridization theories.

For many of the heavier non-transition elements, the presence of low-lying *d* orbitals means that the number of electron pairs in the valence shell may exceed four. Thus the stereochemistry and bonding in compounds of these elements are varied and often complex, especially when the ligands can form chelates with the metal. Moreover the presence of one or more lone pairs in the valence shell of the metal makes rationalization of the shape of the molecule more difficult.

As part of the current studies of this Laboratory on metal dithiocarbamates, we investigated the structure of tellurium(II) (*N*,*N*-diethyldithiocarbamate), in which tellurium has low-lying *d* orbitals and two lone pairs in its valence shell, in order to contribute to the understanding of the stereochemistry of these compounds.

Experimental

(with technical assistance from Mr P. Mura)

Crystal data

Tellurium(II) bis-(*N*,*N*-diethyldithiocarbamate), [Te(S_2CNEt_2)$_2$], was synthesized as described in the literature (Foss & Pitha, 1953). Red crystals suitable for single-crystal X-ray analysis were grown from carbon disulphide–ether solutions; they are stable in air and to X-rays.

Preliminary X-ray and optical examinations of the crystals indicated that they belong to the monoclinic system. The space group, $P2_1/c$ (No. 14), was assigned on the basis of the systematic absences ($h0l$, $l=2n+1$; $0k0$, $k=2n+1$).

Unit-cell dimensions at about 23 °C are: $a=$ 15·191 ± 0·002, $b=$ 8·425 ± 0·002, $c=$ 14·841 ± 0·002 Å, $\beta=$ 117·66 ± 0·02°; these were determined by a least-squares refinement of seventy 2θ values measured on $hk0$ and $h0l$ Weissenberg photographs calibrated with superimposed ZnO powder lines, using Cu $K\alpha$ radiation ($\lambda=$ 1·5418 Å). The measured density (by flotation in a $ZnCl_2$ solution) of 1·68 ± 0·01 g.cm^{-3} agrees well with the value of 1·670 g.cm^{-3} calculated for four [Te(S_2CNEt_2)$_2$] units of formula weight 424·14 in the cell of volume 1687·31 Å^3.

The X-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken at room-temperature about the b (8 layers, $h0l$ to $h7l$) and c (5 layers $hk0$ to $hk4$) axes, with Ni-filtered Cu $K\alpha$ radiation, using two different crystals. They were both well formed, with the following forms developed: {100}, {001}, {10$\bar{1}$}, {011}, {110} and {11$\bar{1}$}. The approximate dimensions of the crystals were 0·20 × 0·20 × 0·25 and 0·20 × 0·25 × 0·50 mm respectivcly.

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* Part IV: *J. Chem. Soc.* (*A*) (1968) p. 1351. Preliminary results on the structure of other metal dithiocarbamates not yet described in this series have been published in *Chem. Commun.* (1966) p. 476; (1967) p. 583; (1968) p. 302; (1968) p. 572; (1970) p. 743.

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Table 1. *Final positional and thermal parameters for the non-hydrogen atoms*

Estimated standard deviations are given in parentheses. Coefficients b_{ij} are defined by the expression

$$T=\exp\left[-10^{-4}(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\right]$$

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Te	0·19639 (6)	0·06910 (11)	0·05784 (6)	61 (0)	15 (1)	64 (1)	157 (1)	3 (2)	63 (0)
S(1)	0·1952 (2)	0·0865 (4)	−0·1122 (3)	57 (1)	−3 (5)	58 (3)	204 (7)	2 (5)	65 (2)
S(2)	0·0100 (3)	−0·0023 (6)	−0·1074 (3)	62 (2)	−23 (6)	74 (3)	277 (8)	12 (7)	80 (2)
C(1)	0·0702 (11)	0·0353 (19)	−0·1768 (12)	69 (8)	8 (24)	73 (15)	205 (28)	64 (27)	87 (10)
N(1)	0·0248 (9)	0·0309 (16)	−0·2800 (9)	79 (7)	−49 (21)	66 (12)	210 (24)	−18 (21)	73 (7)
C(2)	−0·0755 (11)	−0·0195 (20)	−0·3362 (11)	71 (8)	−74 (25)	48 (14)	203 (28)	28 (26)	75 (9)
C(3)	−0·1486 (12)	0·1096 (27)	−0·3694 (15)	67 (9)	−66 (33)	66 (20)	334 (47)	60 (41)	122 (16)
C(4)	0·0804 (12)	0·0638 (22)	−0·3367 (12)	83 (9)	−23 (30)	82 (16)	258 (35)	19 (31)	78 (9)
C(5)	0·1111 (14)	−0·0767 (26)	−0·3747 (14)	91 (11)	−14 (38)	65 (18)	350 (48)	4 (37)	82 (11)
S(3)	0·3714 (2)	0·1609 (5)	0·1127 (2)	70 (2)	−24 (5)	64 (3)	201 (7)	−1 (5)	60 (2)
S(4)	0·3176 (3)	0·0827 (5)	0·2754 (3)	85 (2)	−15 (7)	97 (4)	242 (8)	−9 (7)	73 (2)
C(6)	0·4059 (10)	0·1362 (18)	0·2406 (10)	73 (7)	−6 (23)	77 (13)	163 (21)	7 (23)	70 (8)
N(2)	0·5008 (9)	0·1552 (16)	0·3068 (9)	91 (8)	−83 (22)	50 (13)	177 (23)	−8 (22)	70 (7)
C(7)	0·5747 (11)	0·2062 (22)	0·2736 (10)	71 (8)	−80 (27)	51 (13)	265 (33)	4 (26)	61 (8)
C(8)	0·6207 (13)	0·0720 (27)	0·2408 (15)	75 (10)	58 (38)	73 (18)	438 (58)	61 (44)	96 (13)
C(9)	0·5406 (13)	0·1154 (23)	0·4171 (11)	103 (11)	−43 (32)	45 (16)	228 (32)	39 (26)	61 (8)
C(10)	0·5508 (20)	0·2558 (27)	0·4828 (15)	211 (25)	−24 (57)	159 (30)	277 (45)	−24 (38)	84 (12)

The intensities were corrected for Lorentz and polarization effects, and for spot extension (Phillips, 1954), and then for absorption. The absorption coefficient for the compound is $\mu(\text{Cu } K\alpha)=189·7\ \text{cm}^{-1}$ and the calculated transmission factors ranged from 0·053 to 0·178 for the first set and from 0·013 to 0·131 for the second set of data.

The two sets of data were correlated by the method of Hamilton, Rollett & Sparks (1965). 2012 independent non-zero reflexions were collected and used in the analysis.

Structure determinations

The structure was solved by the usual combination of Patterson and Fourier syntheses. Refinement was carried out by the block-diagonal matrix, (4×4) and (9×9), least-squares method, the quantity minimized being $w(|F_o|-|F_c|)^2$. The weighting scheme used, $w=(a+F_o+bF_o^2)^{-1}$, was checked at intervals, and a and b adjusted, by least-squares procedure, to keep a relatively constant average $\langle w|\Delta F|^2\rangle$ in groups of F_o or $\sin\theta/\lambda$ (Cruickshank, 1965). For the last cycles of the refinement, values of $a=3·17$ and $b=0·0339$ were used.

The initial refinement, with individual isotropic temperature factors assigned to all atoms, converged to an R value of 0·097. A further refinement was performed in which all atoms were allowed to vibrate anisotropically; this converged to $R=0·085$.

At this stage in no region of the difference Fourier synthesis did the electronic density exceed $\pm 3\sigma(\varrho)$ $[\sigma(\varrho)=0·40\ \text{e.Å}^{-3}]$.

The introduction of the hydrogen atoms in positions calculated to make the C–H bond lengths equal to 1·00 Å and to complete tetrahedra around the carbon atoms brought the R index to the final value of 0·081.*

The hydrogen atoms were assumed to vibrate isotropically, the B values being tose of the nearest carbon at the end of the isotropic refinement.

Table 1 gives the final positional and anisotropic thermal parameters for the non-hydrogen atoms. In Table 2 the assumed coordinates and temperature factors for the hydrogen atoms are given. The magnitudes and orientation of the thermal vibrational ellipsoids for the non-hydrogen atoms are reported in Table 3. The final values of observed and calculated structure factors (in electrons ×10) for the reflections used are listed in Table 4.

Table 2. *Coordinates and isotropic temperature factors for the hydrogen atoms*

	x	y	z	B(Å^2)
H(2)*a*	−0·0910	−0·0934	−0·2927	5·2
H(2)*b*	−0·0821	−0·0773	−0·3979	5·2
H(3)*a*	−0·2167	0·0643	−0·4081	7·7
H(3)*b*	−0·1438	0·1682	−0·3087	7·7
H(3)*c*	−0·1350	0·1842	−0·4139	7·7
H(4)*a*	0·1415	0·1239	−0·2911	6·2
H(4)*b*	0·0379	0·1312	−0·3964	6·2
H(5)*a*	0·1483	−0·0418	−0·4120	6·9
H(5)*b*	0·1548	−0·1455	−0·3162	6·9
H(5)*c*	0·0511	−0·1382	−0·4215	6·9
H(7)*a*	0·6292	0·2634	0·3313	5·3

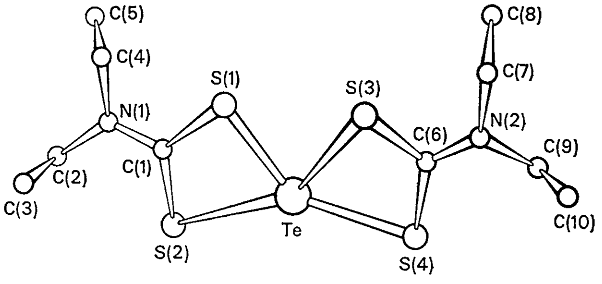

Fig. 1. The $[\text{Te}(\text{S}_2\text{CNEt}_2)_2]$ molecule viewed along the b axis.

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* When the choice of the hydrogen positions was not unique, as in the methyl groups, a staggered conformation was assumed.

Table 2 (*cont.*)

	x	y	z	B(Å^2)
H(7)*b*	0·5412	0·2804	0·2150	5·3
H(8)*a*	0·6694	0·1169	0·2198	7·4
H(8)*b*	0·6555	−0·0030	0·2987	7·4
H(8)*c*	0·5675	0·0139	0·1824	7·4
H(9)*a*	0·4947	0·0376	0·4246	6·5
H(9)*b*	0·6074	0·0658	0·4410	6·5
H(10)*a*	0·5777	0·2206	0·5550	9·2
H(10)*b*	0·4845	0·3062	0·4605	9·2
H(10)*c*	0·5972	0·3344	0·4769	9·2

Atomic form factors given by Cromer & Mann (1968) for tellurium, sulphur, nitrogen and carbon, and by Hanson, Herman, Lea & Skillman (1964) for hydrogen, were used. The effects of anomalous dispersion were included in the calculated structure factors (Ibers & Hamilton, 1964); the values of $\Delta f'$ for Te and S were those computed by Cromer (1965), and the imaginary part of the anomalous dispersion factors was ignored.

Calculations were carried out on the UNIVAC 1108 computer of Rome University and were performed with the system of programs developed in this Laboratory (Domenicano, Spagna & Vaciago, 1969). The transmission factors were calculated by means of a local modification of the original program developed by Coppens, Leiserowitz & Rabinovich (1965).

Results and discussion

The structure of tellurium(II) bis-(*N*,*N*-diethyldithiocarbamate), [Te(S_2CNEt_2)$_2$], is shown in Fig. 1. Intramolecular bond lengths and angles are given in Table 5.

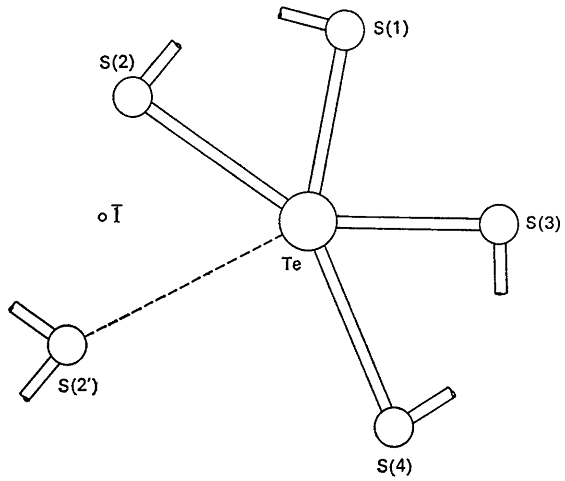


Fig. 2. The central part of the molecule as seen along the normal to the best plane through the TeS$_4$ group. The weak intermolecular Te···S(2′) bond is indicated by a dotted line.

Table 3. *Magnitudes and orientation of thermal ellipsoids of the non-hydrogen atoms*

	R.m.s. amplitudes	Angles with respect to *a*	*b*	*c*		R.m.s. amplitudes	Angles with respect to *a*	*b*	*c*
Te	0·220 Å	146°	66°	43°	S(3)	0·224 Å	117°	98°	8°
	0·235	86	128	48		0·247	42	60	86
	0·247	56	48	80		0·277	60	149	97
S(1)	0·228	5	87	114	S(4)	0·222	134	91	17
	0·240	93	93	25		0·280	51	62	75
	0·271	94	4	86		0·299	70	152	83
S(2)	0·224	167	101	57	C(6)	0·229	129	120	35
	0·264	83	94	35		0·246	108	30	60
	0·319	100	12	80		0·263	44	93	73
C(1)	0·236	116	135	46	N(2)	0·218	62	36	84
	0·252	29	101	90		0·251	95	111	30
	0·308	102	47	44		0·333	151	62	61
N(1)	0·244	57	51	76	C(7)	0·229	49	67	75
	0·257	120	107	17		0·235	122	112	23
	0·298	48	136	100		0·335	123	33	74
C(2)	0·215	46	45	105	C(8)	0·257	31	101	88
	0·250	80	105	40		0·294	121	98	9
	0·326	134	49	54		0·403	85	13	82
C(3)	0·232	26	70	100	C(9)	0·224	92	110	32
	0·310	91	126	43		0·273	61	35	87
	0·387	116	43	49		0·350	151	62	58
C(4)	0·247	129	109	23	C(10)	0·242	108	83	11
	0·276	47	78	72		0·316	96	172	83
	0·312	112	22	75		0·445	19	94	98
C(5)	0·267	78	90	39					
	0·303	165	99	51					
	0·356	99	9	85					

Table 4. *Observed and calculated structure factors* (*in electrons* × 10)

$F(000) = 841{\cdot}44$

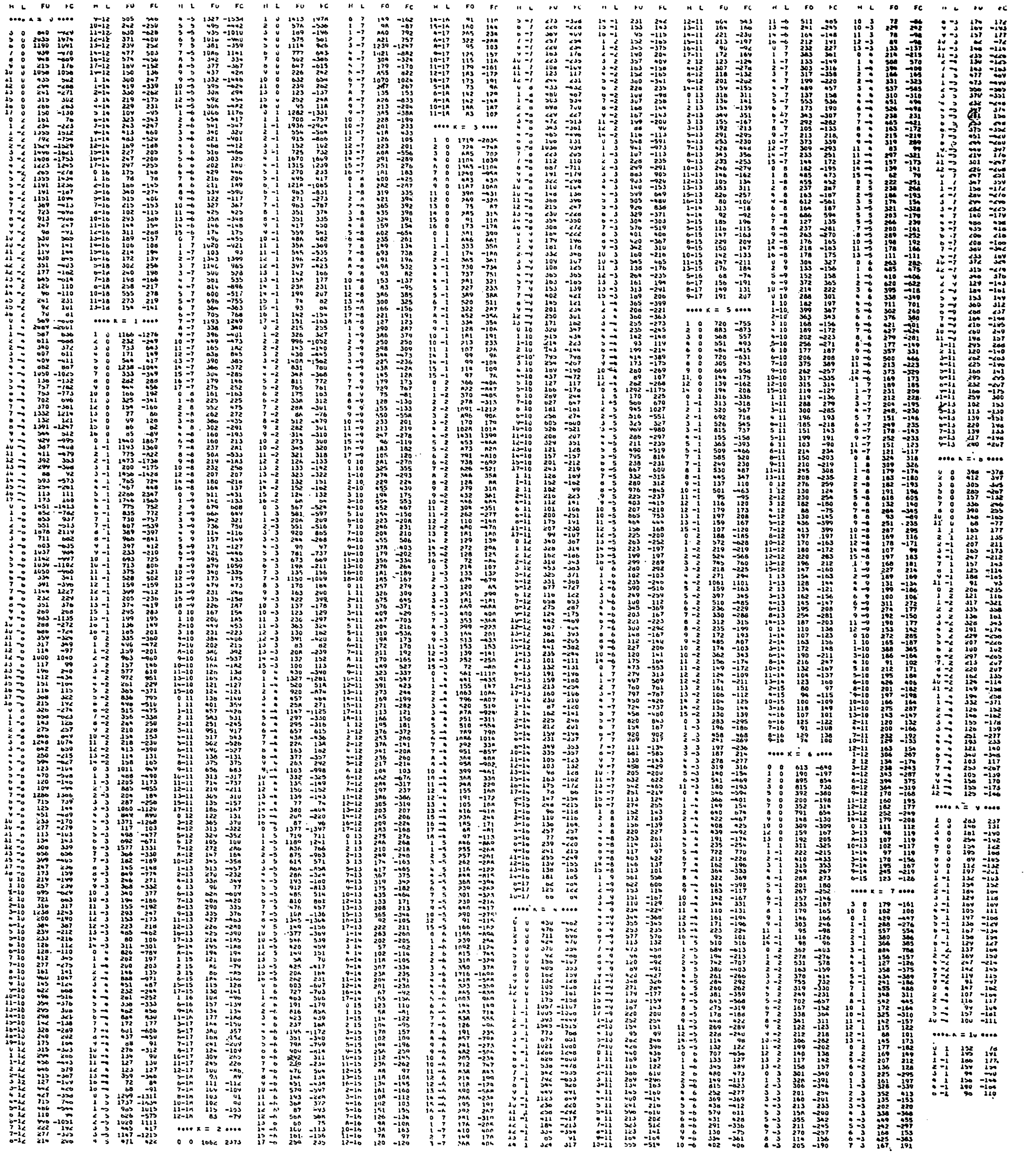


Table 5. *Bond lengths and angles in the compound* $[\mathrm{Te(S_2CNEt_2)_2}]$

Estimated standard deviations are given in parentheses.

Te—S(1)	2·519 (4) Å	S(1)–Te—S(2)	66·5 (1) °
Te—S(2)	2·830 (3)	S(1)–Te—S(3)	80·1 (1)

Table 5 (*cont.*)

C(1)–S(1)	1·74 (2)	S(1)–Te—S(4)	145·5 (1)
C(1)–S(2)	1·69 (2)	S(2)–Te—S(3)	146·4 (1)
C(1)–N(1)	1·36 (2)	S(2)–Te—S(4)	147·8 (1)
N(1)–C(2)	1·43 (2)	S(3)–Te—S(4)	65·8 (1)
N(1)–C(4)	1·47 (3)	Te—S(1)–C(1)	92·4 (7)

Table 5 (*cont.*)

C(2)–C(3)	1·47 (3)	Te---S(2) –C(1)	83·3 (5)
C(4)–C(5)	1·48 (3)	S(1) –C(1)–S(2)	117·9 (9)
Te---S(3)	2·518 (4)	S(1) –C(1)–N(1)	219·1 (15)
Te---S(4)	2·893 (4)	S(2) –C(1)–N(1)	123·0 (12)
C(6)–S(3)	1·73 (2)	C(1)–N(1)–C(2)	121·3 (16)
C(6)–S(4)	1·71 (2)	C(1)–N(1)–C(4)	120·9 (13)
C(6)–N(2)	1·33 (2)	C(2)–N(1)–C(4)	117·6 (12)
N(2)–C(7)	1·48 (3)	N(1)–C(2)–C(3)	114·6 (14)
N(2)–C(9)	1·50 (2)	N(1)–C(4)–C(5)	115·7 (16)
C(7)–C(8)	1·52 (3)	Te---S(3) –C(6)	93·5 (5)
C(9)–C(10)	1·50 (3)	Te---S(4) –C(6)	81·9 (4)
		S(3) –C(6)–S(4)	118·6 (7)
		S(3) –C(6)–N(2)	118·4 (13)
		S(4) –C(6)–N(2)	123·0 (12)
		C(6)–N(2)–C(7)	121·2 (13)
		C(6)–N(2)–C(9)	122·5 (16)
		C(7)–N(2)–C(9)	116·1 (12)
		N(2)–C(7)–C(8)	114·9 (16)
		N(2)–C(9)–C(10)	113·8 (15)

The coordination sphere of the metal

The two *N,N*-diethyldithiocarbamate moieties act as bidentate chelating ligands. However, the two tellurium–sulphur contacts of each chelate ring are quite different, and are both longer than the sum of the covalent radii, 2·39 Å (Pauling, 1960). Thus in the TeS_4 group there are two short Te–S bonds, Te–S(1) and Te–S(3), of average length 2·519 (3) Å, and two long ones, Te–S(2) [2·830 (3) Å] and Te–S(4) [2·893 (4) Å].

Tellurium lies almost exactly in the plane defined by the four sulphur atoms bound to it: the maximum deviation from the best plane through the five atoms Te, S(1), S(2), S(3) and S(4) ($-0{\cdot}294x+0{\cdot}955y+0{\cdot}105z+0{\cdot}266=0$ in terms of monoclinic coordinates) is 0·09 Å. The S(2′) sulphur atom of the centrosymmetrically related molecule approaches the tellurium atom at a distance of 3·579 (5) Å [the sum of the van der Waals radii is 4·05 Å (Pauling, 1960)] along the direction approximately bisecting the angle S(2)–Te–S(4), Fig. 2. The S(2′) atom is at 0·50 Å from the previously defined plane through Te, S(1), S(2), S(3), S(4); the angles S(2)–Te···S(2′) and S(4)–Te···S(2′) are 61·5 and 86·9° respectively, the angle S(2)–Te–S(4) being 147·8°.

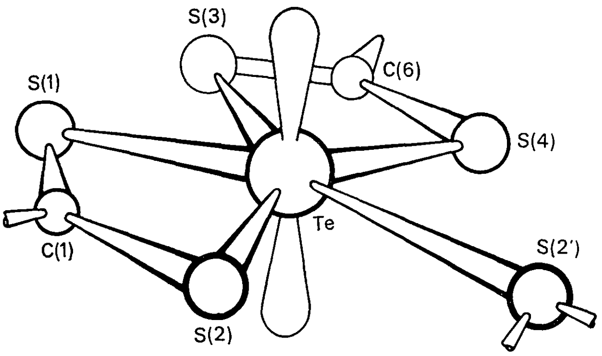


Fig. 3. Idealized arrangement of the sulphur atoms around tellurium in the crystal of $[Te(S_2CNEt_2)_2]$ according to the model given by the full hybridization theory. The hybrid orbitals depicted in the axial positions of the pentagonal bipyramid contain the two lone pairs.

The configuration around the tellurium atom in $[Te(S_2CNEt_2)_2]$ is very similar to that found in tellurium (II) bis-(*O*-ethylxanthate) (Husebye, 1967), and tellurium(II) bis(morpholyldithiocarbamate) (Husebye, 1970). In all these three compounds of tellurium with dithio-chelating ligands the metal shows a slight tendency towards planar five-coordination.

The interpretation of the stereochemistry around the tellurium atom in these compounds, if based on two ordinary two-centre bonds, and considering the other Te–S contacts as principally ionic, does not seem to be quite satisfactory. In the present case Te–S(1) and Te–S(3) would be the two-centre bonds, formed by the overlap of two *p* (or two hybrid sp^3) orbitals of tellurium with the σ orbitals of the sulphur atoms, and the two lone pairs would then occupy the other *p* and *s* (or the other two sp^3 hybrid) orbitals. The inter-bond angle between the two covalent Te–S bonds should be 90° (or more in the case of some degree of sp^3 hybridization). However, in these compounds this angle ranges between 80° and 84° [80·1(1)° in the present compound], and the distance between the two sulphur atoms bound to tellurium is 3·2 to 3·3 Å [3·239(4) Å in the present compound] which is even less than the sum of the van der Waals radii (3·75 Å) (Pauling, 1960). Moreover, as the remaining Te–S contacts should then have mainly ionic character, there would be no reason for the TeS_4 group to be planar.

A different interpretation of the stereochemical arrangement of the atoms around tellurium is given by the three-centre bond theory (Cotton & Wilkinson, 1966). According to this theory in the TeS_4 group there should be two linear three-centre–four-electron (*3c–4e*) bonds, S–Te–S, each formed by the overlap of a *p* orbital of the central atom and the σ orbitals of the two outer atoms.

S(1)–Te–S(4) and S(2)–Te–S(3) would be the two (*3c–4e*) bonds, the fifth T–S contact being then essentially ionic. The two lone pairs would occupy the remaining *p* and *s* orbitals. This model would justify the planarity of the TeS_4 group, as well as the lengthening of the Te–S bonds with respect to the sum of the covalent radii, since of the four electrons involved in each linear S–Te–S system, only two are bonding. The absence of linearity in the two (*3c–4e*) bonds [the angles S(1)–Te–S(4) and S(2)–Te–S(3) are 145·5 (1) and 146·4 (1)° respectively] can be explained by considering the rigidity of the four-membered TeS_2C rings. It is more difficult to explain the difference in the lengths of the two *trans* Te–S bonds in each three-centre system and especially, the value of the angle S(1)–Te–S(3), which is much less than 90°.

A further explanation of the observed results is provided by the full hybridization theory (Cotton & Wilkinson, 1966), by considering the approximately planar TeS_5 system formed by the tellurium atom and by the sulphur atoms which approach it. With this assumption there would be fourteen electrons (seven pairs) in the valence shell of tellurium, four from tellurium(II), and a total of ten from the sulphur atoms. The stereochemical arrangement of these seven pairs, of which five are bonding and two are lone pairs, requires the use of a set of sp^3d^3 hybrid orbitals of the metal. On the basis of the simple electron pair repulsion model of Sidgwick & Powell (1940) and Gillespie & Nyholm (1957), the five bonding pairs should be in the equatorial and the two lone pairs in the axial positions of a pentagonal bipyramid. In Fig. 3 an ideal model is given representing the geometry of the TeS_5 system according to the full hybridization theory.

Obviously the observed structure does not conform to any of the models discussed; each of these theories represents an extreme, which is a drastic over-simplification. Therefore none can be expected to be entirely adequate, but each has its merits in rationalizing the structural results found in tellurium(I) bis-(*N*,*N*-diethyldithiocarbamate).

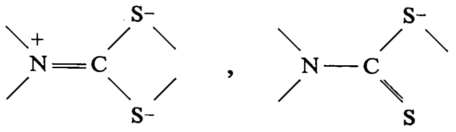
The structure of lead(II) bis-(*O*,*O*-diisopropylphosphorodithioate) (Guzy, Raynor & Stodulsky, 1969) constitutes an example for which the model proposed by the full hybridization theory seems to be the more adequate. In fact the Pb–S distances have a relatively small range (2·76 to 3·22 Å), and the large size of the central atom allows the angles S–Pb–S, in the plane of the bipyramid, to be nearer to the ideal value.

An example for which the three-centre bond theory is better is given by the structure of selenium(II) bis-(*N*,*N*-diethyldithiocarbamate), (Husebye & Helland-Madsen, 1970). As a consequence of the smaller size of selenium, the two three-centre S–Se–S bonds become more linear, and the angle between them becomes nearer to 90°. In this compound only four Se–S contacts occur.

These structures provide examples where one theory is preferred over the others, whilst the case of tellurium(II) bis-(*N*,*N*-diethyldithiocarbamate) is intermediate and both theories have their merits.

The ligand

Apart from the terminal methyl groups each ligand molecule is essentially planar. All bond lengths and angles within the ligand molecules are normal; from the values of the C–S and C(sp^2)–N bond lengths, it can be seen that the canonical forms



make the more important contributions to the ground state of the $[Te(S_2CNEt_2)_2]$ molecule.

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