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The Crystal and Molecular Structure of Tris(diethyldithiocarbamato)phenyltellurium(IV)

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Tris(diethyldithiocarbamato)phenyltellurium(IV), $[Te(Et_2NCS_2)_3C_6H_5]$, forms transparent, yellow crystals belonging to the monoclinic space group $C_{2h}^5-P2_1/c$. The cell dimensions are $a=10.791(5)$ Å, $b=16.090(6)$ Å, $c=18.417(9)$ Å, $\beta=117.63(6)°$ and $Z=4$. The calculated and observed densities are 1.52 and 1.51 g/cm³, respectively. 4183 reflection intensities above background were collected on a Siemens AED-1 diffractometer using Mo$K\alpha$ radiation. Full-matrix least squares refinement of the structure has given a conventional R-value of 6.2 %.

The central tellurium atom is bonded to all six sulfur atoms in the molecule and to a carbon atom in the phenyl group in a distorted pentagonal, bipyramidal configuration. The axial Te–C bond length is 2.124(11) Å, while the axial Te–S bond length is 3.228(4) Å. The Te–C bond is nearly normal to the equatorial TeS_5 plane, but the angle between the two axial bonds is 144.6(2)°.

The five equatorial and nearly co-planar Te–S bonds have lengths ranging from 2.606 to 2.816 Å ($\sigma=0.003$ Å), and the Te–S bond angles between neighbouring bonds in the plane range from 64.76 to 79.56° ($\sigma=0.09°$).

Structures of tetravalent tellurium complexes with monodentate ligands are well known. The coordination number for tellurium is usually four or six.

In some octahedral, six-coordinated complexes like $[TeCl_6]^{2-}$, $[TeBr_6]^{2-}$, $[TeBr_4\{(Me_2N)_2C=S\}_2]$, the seventh electron pair on the tellurium atom is stereochemically inert.[1–3] Such an inert pair is found also in other elements in the lower, right hand corner of the periodic table.[4–8] The stereochemical inertness of the unshared electron pair in octahedral complexes has been explained as the result of the small overlap of the valency shell *ns* orbital with the ligand a_{1g} orbital.[9–11] Thus, according to Urch, the seventh electron pair goes into the a_{1g}* low energy antibonding MO. This MO is mostly localized on the ligands and thus electrons in this orbital do not disturb the octahedral arrangement of the six bonding pairs.[9]

Application of the VSEPR[12–14] theory predicts a pentagonal bipyramidal configuration for six-coordinated tetravalent tellurium with the lone pair

occupying one coordination position. The configuration of seven-coordinated tetravalent tellurium should, correspondingly, be based on a square antiprism or a dodecahedron with a lone pair occupying one coordination position.

Orgel has discussed the possibility of *sp* hybridization involving the *ns* orbital for such elements as discussed above, and has suggested several possible distortions from octahedral geometry due to the *ns* pair.[15] One such case of distortion has recently been found in $TeCl_4$ where tellurium is six-coordinated with three long Te – Cl distances *trans* to and co-linear with three short ones.[16]

On the basis of the molecular formula of tris(diethyldithiocarbamato)-phenyltellurium(IV), $[Te(Et_2NCS_2)_3C_6H_5]$, one may expect a coordination number for the central tellurium atom between four and seven. By analogy with divalent tellurium and trivalent arsenic dithiocarbamates,[17,18] one might expect rather large differences in the ligand to central atom bond lengths.

EXPERIMENTAL

Compounds of the type $[Te(R_2NCS_2)_3Ar]$, (Ar = aryl), were first prepared by Foss [19] either from the corresponding diarylditelluride and tetraalkylthiuramdisulphide:

$$(ArTe)_2 + 3(R_2NCS_2)_2 = 2Te(S_2CNR_2)_3Ar$$

or from the aryltellurium trichloride and sodium dialkyldithiocarbamate:

$$ArTeCl_3 + 3R_2NCS_2^- = Te(S_2CNR_2)_3Ar + 3Cl^-$$

The crystals used in the present investigation were kindly supplied by Prof. Foss, and were recrystallized from benzene solution. Upon heating, the greenish yellow colour of the solution changes reversibly to red. This is probably due to a reversible dissociation into the red ditelluride and the disulphide.[19]

The crystals are yellow with a greenish tinge, mostly in the form of irregular, truncated bipyramids, with the basal plane a parallelogram.

For recording of data, a Siemens automatic, off-line, single crystal diffractometer (AED-1) was used. The diffractometer was operated as a three-circle instrument using Mo$K\alpha$ radiation. A crystal with dimensons roughly $0.28 \times 0.26 \times 0.17$ mm^3 was mounted with the *ab* diagonal along the ϕ-axis of the instrument.

The crystal orientation and cell dimensions were first determined by measuring θ, χ, and ϕ for three non-co-planar reciprocal vectors. The rough setting angles for all reflections could then be calculated.

For determination of unit cell dimensions by least squares methods, the θ-angles of 20 reflections with high θ were measured. The cell data are $a = 10.791(5)$ Å, $b = 16.090(6)$ Å, $c = 18.417(9)$ Å and $\beta = 117.63(6)°$. There are four molecules per unit cell with density, calc. 1.52, found 1.51 g/cm^3. The systematic absences are $h0l$ for $l = 2n+1$ and $0k0$ for $k = 2n+1$, which give the space group $C_{2h}-P2_1/c$.

Intensity data were collected using a scintillation counter and $\theta - 2\theta$ scan technique. The scan speed was 0.5° per min, with automatic setting of greater speed for strong reflections. An attenuation filter was used to avoid counting losses, and the proper filter was automatically inserted in the primary beam. Each reflection was scanned between $\theta_1 = \theta - 0.50°$ and $\theta_2 = \theta + 0.50°$ where θ is the Bragg angle for the α_1 peak. The scan was performed by going from θ to θ_1, then from θ_1 to θ_2, and finally from θ_2 to θ.

The intensities for all three scans and their sum I_t were recorded. Likewise, background was measured for one-half the total scan time at both θ_1 and θ_2, and the respective intensities and their sum I_b were also recorded. The net intensity for a reflection, I_N, was put equal to $I_t - I_b$. This scan procedure also checks the setting angles.

Three reference reflections were measured at intervals of 50 reflections, and their setting checked by horizontal and vertical half shutters. The net intensities of the recorded reflections were brought to a common scale by means of the intensity variations of these reference reflections. The lower intensity limit for an observed reflection was put

equal to twice the standard deviation in net intensity. This standard deviation was defined as the square root of the sum of the total intensity and the intensity of the background. Unobserved reflections were assigned intensities equal to the lower intensity limit.

Out of 4924 possible reflections with $\sin\theta \leq 0.42$, 4183 were observed and measured. The data were corrected for Lorentz and polarization effects. No extinction or absorption corrections were found necessary ($\mu = 15.26$ cm^{-1}). The IBM 360/50H computer at the University of Bergen was used in all computations.

STRUCTURE ANALYSIS

A three-dimensional Patterson map established the coordinates of the tellurium atom in the asymmetric unit. Successive three-dimensional Fourier syntheses revealed the positions of all atoms except hydrogen.

Full-matrix least squares refinement was then begun, using a program (BDLS) which minimized the expression $r = \sum w(|F_o| - K|F_c|)^2$. Here K is a scale factor and w, the weight of a reflection, is the inverse of the variance of

Table 1. Atomic coordinates for tris(diethyldithiocarbamato)phenyltellurium(IV) in fractions of cell edges. Origin at a center of symmetry.

	x	y	z
Te	0.21565(6)	0.22043(4)	0.00900(4)
S1	0.0988(3)	0.3732(2)	−0.0260(2)
S2	−0.0702(3)	0.2238(2)	−0.1010(2)
S3	0.1323(3)	0.0573(2)	−0.0484(2)
S4	0.4113(3)	0.1051(2)	0.0809(2)
S5	0.4236(3)	0.3101(2)	0.1127(2)
S6	0.4254(3)	0.3065(2)	−0.0489(2)
N1	−0.1608(8)	0.3782(5)	−0.1489(5)
N2	0.3387(8)	−0.0508(5)	0.0318(5)
N3	0.5937(10)	0.4008(6)	0.0774(6)
C1	0.1674(9)	0.2070(6)	0.1079(5)
C2	0.1703(11)	0.2738(7)	0.1553(6)
C3	0.1438(13)	0.2647(8)	0.2249(7)
C4	0.1215(12)	0.1856(7)	0.2472(7)
C5	0.1187(12)	0.1166(7)	0.1992(7)
C6	0.1409(11)	0.1272(6)	0.1306(6)
C7	−0.0579(10)	0.3285(6)	−0.0980(5)
C8	−0.1484(11)	0.4695(7)	−0.1456(6)
C9	−0.0918(14)	0.4993(8)	−0.2044(8)
C10	−0.2926(11)	0.3408(7)	−0.2147(6)
C11	−0.4087(13)	0.3405(8)	−0.1903(8)
C12	0.2989(10)	0.0282(6)	0.0216(6)
C13	0.2393(11)	−0.1206(7)	−0.0091(6)
C14	0.2499(12)	−0.1491(7)	−0.0875(7)
C15	0.4845(11)	−0.0748(7)	0.0889(7)
C16	0.5003(14)	−0.0933(8)	0.1743(8)
C17	0.4886(11)	0.3412(6)	0.0473(6)
C18	0.6303(17)	0.4489(10)	0.1615(10)
C19	0.7343(21)	0.3994(13)	0.2127(12)
C20	0.6582(13)	0.4358(8)	0.0277(7)
C21	0.7776(15)	0.3811(9)	0.0400(9)

Table 2. Components of atomic vibration tensors, $U \times 10^3$, in Å^2, with standard deviations, referred to crystallographic axes. For Te and S, the expression is exp $\{-2\pi^2[h^2a^{-2}U_{11}+k^2b^{-2}U_{22}+l^2c^{-2}U_{33}+2hka^{-1}b^{-1}U_{12}+2klb^{-1}c^{-1}U_{23}+2hla^{-1}c^{-1}U_{13}]\}$. For the other atoms, the expression is exp $[-8\pi^2U(\sin^2\theta/\lambda^2)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Te	30.1(0.3)	36.7(0.4)	32.2(0.3)	−4.9(0.3)	−1.1(0.3)	10.4(0.3)
S1	40.8(1.5)	39.9(1.5)	44.2(1.5)	−3.6(1.2)	−2.5(1.2)	11.5(1.2)
S2	37.8(1.4)	41.7(1.5)	54.4(1.6)	−6.3(1.3)	1.8(1.4)	6.2(1.2)
S3	37.6(1.5)	39.0(1.6)	60.9(1.8)	−4.2(1.2)	−5.5(1.4)	4.9(1.3)
S4	33.6(1.4)	45.5(1.6)	46.4(1.5)	−3.2(1.2)	−4.8(1.3)	9.3(1.2)
S5	45.4(1.6)	59.7(1.8)	33.0(1.4)	−20.5(1.4)	−6.6(1.3)	14.5(1.2)
S6	49.3(1.6)	63.0(1.9)	40.4(1.5)	−13.7(1.4)	−9.7(1.3)	22.0(1.3)

	U		U		U		U
N1	46.8(2.1)	C4	61.4(3.2)	C10	51.4(2.8)	C16	76.4(3.8)
N2	41.5(1.9)	C5	60.0(3.2)	C11	72.2(3.5)	C17	45.8(2.6)
N3	66.1(2.8)	C6	49.3(2.7)	C12	40.5(2.4)	C18	100.0(5.0)
C1	39.0(2.3)	C7	36.8(2.3)	C13	51.9(2.9)	C19	134.4(6.8)
C2	54.3(2.7)	C8	52.0(2.8)	C14	62.8(3.2)	C20	66.7(3.4)
C3	64.3(3.2)	C9	74.9(3.8)	C15	54.8(2.9)	C21	86.8(4.2)

F_o. The variance of F_o is $\sigma^2(F_o)=F_o^2|I_t+I_b+k^2(I_t-I_b)^2|/4(I_t-I_b)$,[2] where k may be interpreted as the relative standard deviation in the scaling curve based on the variation in the intensities of the reference reflections. Non-observed reflections where $K|F_c|$ is larger than the observable limit are included in the refinement with F_o put equal to the limit.

After a few cycles of refinement based on isotropic temperature factors, the factor $R=\sum(||F_o|-|F_c||)/\sum|F_o|$ reached a value of 0.10. Anisotropic tem-

Table 3. Bond lengths with standard deviations in Å.

Te–S1	2.701(3)	N2–C13	1.493(13)
Te–S2	2.797(3)	N2–C15	1.482(12)
Te–S3	2.816(3)	C13–C14	1.569(19)
Te–S4	2.657(3)	C15–C16	1.531(21)
Te–S5	2.606(3)	S5–C17	1.725(14)
Te–S6	3.228(4)	S6–C17	1.672(11)
Te–C1	2.124(11)	C17–N3	1.389(14)
S1–C7	1.748(9)	N3–C18	1.608(21)
S2–C7	1.689(10)	N3–C20	1.493(20)
C7–N1	1.336(11)	C18–C19	1.342(23)
N1–C8	1.475(14)	C20–C21	1.488(21)
N1–C10	1.502(12)	C1–C2	1.376(15)
C8–C9	1.546(22)	C2–C3]	1.444(20)
C10–C11	1.515(22)	C3–C4	1.392(18)
S3–C12	1.721(9)	C4–C5	1.411(18)
S4–C12	1.722(9)	C5–C6	1.401(20)
C12–N2	1.327(13)	C1–C6	1.420(15)

Table 4. Bond angles with standard deviations in degrees.

Cl – Te – S1	91.4(0.3)	N1 – C8 – C9	109.8(1.0)
Cl – Te – S2	89.8(0.2)	C12 – S3 – Te	86.1(0.3)
Cl – Te – S3	93.7(0.3)	C12 – S4 – Te	91.3(0.3)
Cl – Te – S4	87.5(0.3)	S3 – C12 – S4	117.6(0.6)
Cl – Te – S5	84.2(0.2)	S4 – C12 – N2	120.8(0.6)
Cl – Te – S6	144.6(0.2)	S3 – C12 – N2	121.6(0.7)
S1 – Te – S2	64.76(0.09)	C12 – N2 – C13	122.6(0.7)
S1 – Te – S3	136.57(0.08)	C12 – N2 – C15	121.2(0.8)
S1 – Te – S4	158.35(0.08)	C13 – N2 – C15	116.1(0.8)
S1 – Te – S5	79.56(0.09)	N2 – C15 – C16	110.8(1.1)
S1 – Te – S6	81.47(0.10)	N2 – C13 – C14	110.0(1.0)
S2 – Te – S3	72.16(0.09)	C17 – S5 – Te	98.0(0.3)
S2 – Te – S4	136.81(0.09)	C17 – S6 – Te	78.3(0.5)
S2 – Te – S5	143.66(0.10)	S5 – C17 – S6	123.0(0.6)
S2 – Te – S6	117.32(0.09)	S5 – C17 – N3	116.3(0.8)
S3 – Te – S4	65.04(0.08)	S6 – C17 – N3	120.7(1.0)
S3 – Te – S5	143.86(0.09)	C17 – N3 – C18	120.5(1.2)
S3 – Te – S6	115.25(0.11)	C17 – N3 – C20	122.8(1.0)
S4 – Te – S5	78.82(0.09)	C18 – N3 – C20	115.6(1.0)
S4 – Te – S6	86.97(0.10)	N3 – C18 – C19	98.2(1.5)
S5 – Te – S6	60.45(0.11)	N3 – C20 – C21	107.5(1.1)
C7 – S1 – Te	89.2(0.3)	C2 – C1 – Te	121.5(0.8)
C7 – S2 – Te	87.3(0.3)	C6 – C1 – Te	120.5(0.8)
S1 – C7 – N1	118.9(0.7)	C1 – C2 – C3	121.9(1.1)
S2 – C7 – N1	123.2(0.7)	C2 – C3 – C4	119.1(1.2)
S1 – C7 – S2	118.0(0.5)	C3 – C4 – C5	119.4(1.3)
C7 – N1 – C10	119.6(0.8)	C4 – C5 – C6	120.4(1.1)
C7 – N1 – C8	122.5(0.7)	C5 – C6 – C1	121.2(1.0)
C8 – N1 – C10	117.8(0.7)	C2 – C1 – C6	117.9(1.0)
N1 – C10 – C11	111.5(1.0)		

perature factors were now introduced for tellurium and sulphur. However, one of the ethyl groups is probably disordered, as evidenced by the large temperature factors for atoms C18 and especially C19, and the large deviations from normal bond lengths and angles in the N3 – C18 – C19 group.

It is noteworthy that both methyl groups in the dithiocarbamate ligand involved in disorder point to the same side of the ligand plane. This was also the case when disorder was found in the same ligand in the diethyldithiocarbamate of divalent selenium.[20] Usually the two methyl groups for steric reasons point to different sides of the ligand plane.

Efforts were made to resolve the disorder by rotating the ethyl group around the N3 – C18 bond. However, refinement based on two different configurations of the ethyl group resulted in the original single configuration.

The gradients in a difference map calculated in the final stages of refinement indicated shifts in the atomic positions of C18 and C19 that would have given more reasonable bond lengths and angles, but on moving C18 and C19 to these new positions and refining, the original configuration again emerged. No other spurious peaks appeared in this map, where most hydrogen atoms showed up as maxima around 0.5 $e^-/Å^3$.

Due to the excessive computing time it would have required, hydrogen atoms were not included in the refinement. For the same reason, anisotropic

Table 5. Some intramolecular S–S distances in Å.

S1–S2	2.945(4)	S2–S3	3.306(4)
S3–S4	2.946(4)	S4–S5	3.342(5)
S5–S6	2.986(6)	S1–S5	3.396(4)
S1–S6	3.890(5)	S3–S6	5.110(5)
S2–S6	5.151(5)	S4–S6	4.071(5)

temperature factors for the light atoms were not introduced. The structure was refined to a final R-value of 0.062.

Observed and calculated structure factors following the last refinement cycle can be obtained from the author Steinar Husebye upon request. Atomic scattering factors for tellurium, sulphur, nitrogen, and carbon listed in the *International Tables* [21] were used. The atomic scattering factors for tellurium were corrected for anomalous dispersion, using f' and f'' values from the *International Tables*.[22] Final atomic parameters are listed in Table 1 and components of atomic vibration tensors are listed in Table 2. Interatomic distances and angles are listed in Tables 3–6.

Table 6. Intermolecular distances in Å. The left column represents distances from an atom in the original molecule (Table 1) to an atom in a molecule whose transformation from the original one is listed in the next column.

S2–C13	$-x, -y, -z$	3.69
C5–C14	»	3.57
C6–C13	»	3.65
C4–C14	»	3.76
C6–C14	»	3.93
C5–C13	»	3.83
C5–C9	$x, \frac{1}{2}-y, \frac{1}{2}+z$	3.94
S2–C19	$-1+x, \frac{1}{2}-y, -\frac{1}{2}+z$	3.67
N1–C21	$-1+x, y, z$	3.83
C11–C21	»	3.81
C7–C21	»	3.81
C10–C14	$-x, \frac{1}{2}+y, -\frac{1}{2}-z$	3.88
S6–C4	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	3.67
S1–C8	$-x, 1-y, -z$	3.89
C2–C9	»	3.95
C3–C9	»	3.83
C5–C18	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$	3.84
C6–C18	»	3.94
C5–C19	»	3.87
C16–C19	»	3.96
S6–C11	$1+x, y, z$	3.82
S4–C14	$1-x, -y, -z$	3.67
C14–C21	»	3.88
S4–C15	»	3.81
C12–C15	»	3.82
S5–C16	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	3.94
S4–C10	$1+x, \frac{1}{2}-y, \frac{1}{2}+z$	3.74
S4–C11	»	3.84
N3–C20	$1-x, 1-y, -z$	3.63
C9–C21	»	3.85
C20–C20	»	3.71
C17–C20	»	3.91
C18–C20	»	3.90

RESULTS AND DISCUSSION

The crystals are built up of monomeric tris(diethyldithiocarbamato)-phenyltellurium(IV) complexes, as shown in Fig. 1, which represents the contents of the unit cell. Figs. 3 and 4 illustrate the coordination around the central tellurium atom. This is best described as distorted pentagonal bipyramidal, with tellurium bonded to the phenyl group and to all six sulphur atoms in the molecule. The least squares plane through the equatorial TeS_5 group (Table 7) passes within 0.13 Å of all six atoms of the plane. The five nearly co-planar Te – S bond lengths range from 2.606 to 2.816 Å ($\sigma = 0.003$ Å), while the corresponding interbond angles between neighbouring bonds range from 64.76 to 79.56° ($\sigma = 0.09°$). Almost perpendicular to the above plane one finds the $Te - C_1$ bond with length 2.124(11) Å. Roughly *trans* to this bond there is a weak Te – S6 bond with a length of 3.228(4) Å. This may be compared to 2.41 Å, the sum of the respective covalent radii and 4.05 Å, the sum of the corresponding van der Waals radii. The C1 – Te – S6 interbond angle is 144.6(2)°. This deviation from linearity represents the greatest distortion

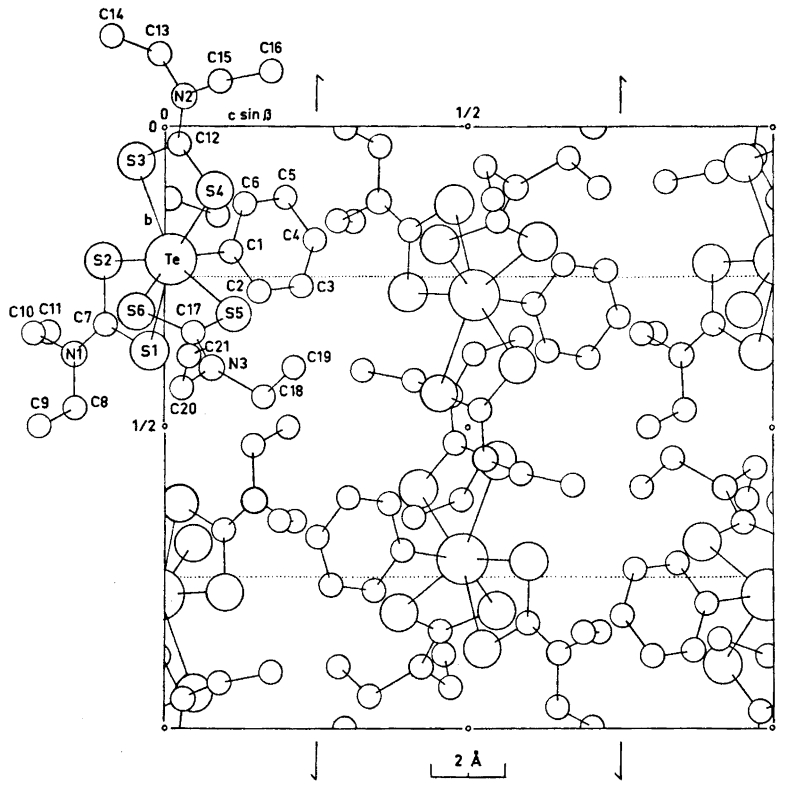

Fig. 1. The arrangement of molecules in the unit cell as seen along the *a*-axis.

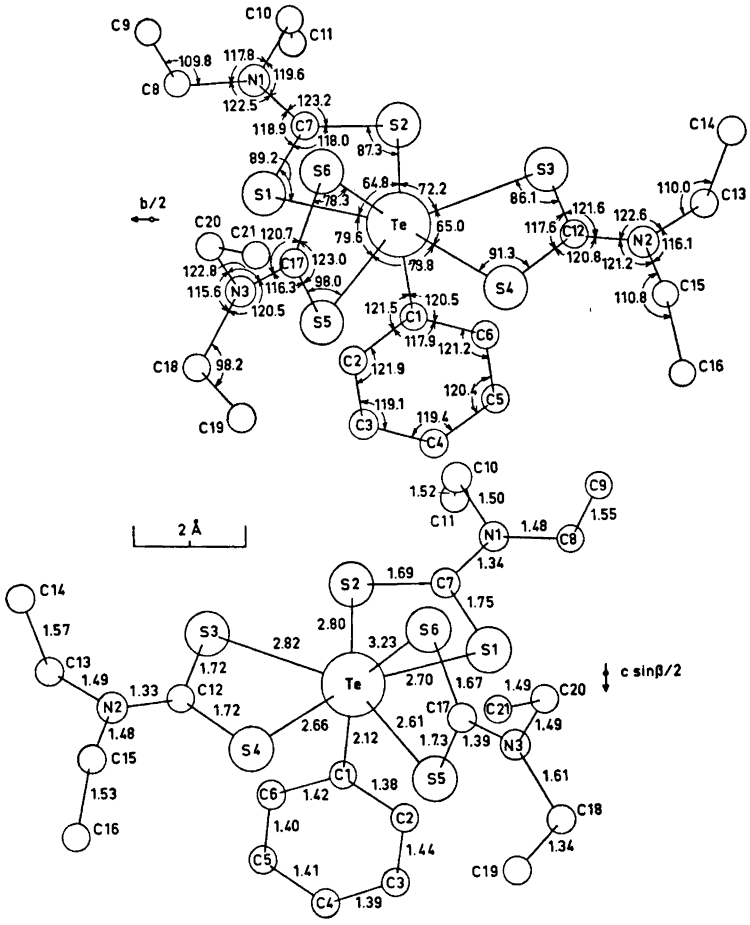

Fig. 2. A pair of tris(diethyldithiocarbamato)phenyltellurium(IV) molecules as seen along the *a* axis with bond lengths and angles indicated. The two molecules are related by a glide plane.

from pentagonal bipyramidal symmetry in the complex. The TeS_6C group, representing the central tellurium atom and atoms bonded to it, has near, mirror plane symmetry, the "mirror plane" passing through Te, C1, S5, and S6.

All three dithiocarbamate ligands are nearly planar, except for the hydrogen atoms and the methyl groups (Table 7). From Table 7 it can be seen that two ligands are nearly co-planar with the equatorial TeS_5 plane, while the third, which forms the long Te – S bond, is nearly at right angles to that plane. The phenyl group forms an angle of 96.5° with the equatorial TeS_5 plane.

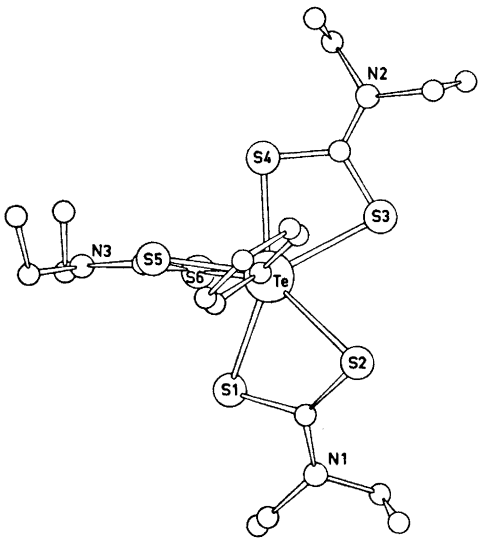

Fig. 3. The molecule seen down the normal to the plane through Te, S4, and S5. Unlabelled spheres represent carbon atoms.

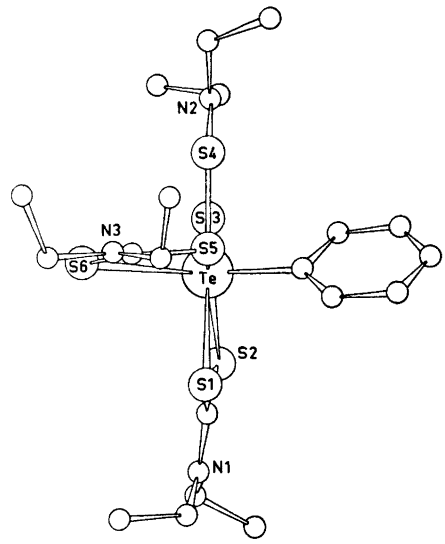

Fig. 4. The molecule seen at right angles to the normal to the plane through Te, S4, and S5. Unlabelled spheres represent carbon atoms.

Table 7. Least squares planes in the molecule.

No. of plane	Atoms included	Equation of planes based on coordinates in Å. (Axes along a, b, and c)
1	Te, S1, S2, S3, S4, S5	$-0.682\,X-0.131\,Y+0.954\,Z+1.859=0$
2	C1, C2, C3, C4, C5, C6	$0.804\,X-0.127\,Y+0.142\,Z-1.310=0$
3	S1, S2, C7, N1, C8, C10	$0.765\,X-0.030\,Y-0.925\,Z-1.049=0$
4	S3, S4, C12, N2, C13, C15	$-0.687\,X-0.088\,Y+0.958\,Z+1.853=0$
5	S5, S6, C17, N3, C18, C20	$0.601\,X-0.697\,Y+0.067\,Z+0.636=0$

Distance of atoms from planes in Å

Plane	1		2		3		4		5
Te	−0.034	C1	0.000	S1	0.031	S3	−0.062	S5	0.043
S1	−0.110	C2	0.012	S2	−0.014	S4	0.084	S6	−0.103
S2	0.131	C3	−0.017	N1	−0.019	N2	−0.025	N3	0.086
S3	−0.086	C4	0.010	C7	−0.014	C12	−0.021	C17	0.036
S4	0.031	C5	0.002	C8	−0.017	C13	0.089	C18	−0.113
S5	0.068	C6	−0.007	C10	0.033	C15	−0.064	C20	0.051
S6	−2.776	Te	0.132	C9	1.438	C14	−1.333	C19	1.180
C1	2.086			C11	−1.341	C16	1.351	C21	1.454

The role of the lone pair is difficult to assess. From the above it is reasonable to regard the central tellurium atom as being seven-coordinated. From the VSEPR theory, it then follows that the eight valence electron pairs should be arranged at the corners of a square antiprism or a dodecahedron, with one position occupied by the lone pair. This is not in accord with the found structure. But then six-coordinated complexes such as $[TeX_6]^{2-}$ and $[TeX_4(tmtu)_2]$ where X is halogen and tmtu is tetramethylthiourea, do not have structures based on the VSEPR arrangement of seven valence electron pairs of tellurium either.[1–3] There, the seventh electron pair on tellurium is stereochemically inert, and the result is octahedral structures based on the most probable distribution on the six bonding electron pairs only. Assuming the eighth electron pair to be inert in the present case, one should expect the structure to be based on the most likely distribution of the seven bonding electron pairs, which is a pentagonal bipyramidal arrangement.

In tris(diethyldithiocarbamato)phenyltellurium(IV) there is, as mentioned above, some deviation from this symmetry. First the C1 – Te bond is rather short, only 2.124 Å, corresponding to a tellurium radius of 1.38 Å, which is much smaller than 1.54 – 1.56 Å, the value proposed for the octahedral radius of tellurium.[24] However, the C1 – Te bond length value is close to the values found in other tetravalent tellurium compounds with Te – C bonds, and also in divalent tellurium compounds with such bonds.[24,25] In these compounds the phenyl group was found to have a large *trans* effect, virtually expelling the ligand *trans* to it. This effect then partly accounts for the weak axial Te – S6 bond. The deviation from linearity of about 35° in the C1 – Te – S6 system may be explained from geometrical reasons. The narrow S – S bite in a dithiocarbamate ligand makes it impossible for it to span an equatorial plus an axial coordination position in a regular pentagonal bipyramidal complex with a large central atom like tellurium, without violating the regular geometry. And the most weakly bonded ligand atom, here S6, may then move somewhat away from its most likely position, as found. In this manner the geometry of the molecule is explained without necessarily involving stereochemical activity of the lone pair.

In several four- and six-coordinate tellurium compounds, the 5*s* electron pair is stereochemically active in the sense that it distorts the regular symmetry.[15,26] In the three complex ions with $(n-1)d^{10}ns^2$ central atoms, trioxalatoantimonate(III) [28] (I), tri(ethylxanthato)plumbate(II) [28] (II) and tris(*O*,*O*-diisopropylphosphorodithioato)plumbate(II) [29] (III), the lone pair in I and II occupies axial and in III equatorial positions in the pentagonal bipyramidal coordination polyedra.

The structure of II is very similar to that of tris(diethyldithiocarbamato)phenyltellurium(IV). But then Pb(II) and Te(IV) both have a $(n-1)d^{10}$ ns^2 electron configuration. Here, the lone pair of Pb(II) can be said to exert the stereochemical role of the phenyl ligand in Te(IV) where the lone pair is regarded as inert. There is, in II, even a short intermolecular Pb···S contact of 3.68 Å, roughly in the direction of the axial position presumably occupied by the lone pair.[28] This contact may be compared to the weak intramolecular Te – S6 bond of 3.23 Å in the present structure. One may, therefore, alternatively regard the structure of tris(diethyldithiocarbamato)phenyltellu-

rium(IV) as being based upon six-coordination with a stereochemically active lone pair occupying the seventh, axial position in the resulting pentagonal bipyramid. S6 would in this case be regarded as not bonded to tellurium in spite of the short Te – S6 distance of 3.23 Å. The angle S5 – C17 – S6 and the distance S5 – S6 are significantly larger than the corresponding angles and distances in the two other ligands. This indicates that S6 is pushed away from tellurium, for instance by the lone pair. The two sulphur atoms S2 and S3 form significantly longer bonds to tellurium than the other three sulphur atoms (Table 3) in the TeS_5 plane, indicating that the *5s* lone pair may be located between S2, S3, and S6. The real situation may well be somewhere in between the two alternatives outlined here. Thus, in the present structure, the stereochemical effect of the lone pair is not quite clear, but it is probably small.

The average Te – S bond length in tris(diethyldithiocarbamato)phenyltellurium(IV) is 2.800 Å. Exclusion of the weak axial Te – S bond of 3.228 Å gives an average of 2.715 Å for the five equatorial Te – S bonds. This latter value is nearly the same as 2.707(10) and 2.699(8) Å, the values found for such a bond in *trans*-tetrabromo- and *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV), respectively.[3] These values are significantly higher than 2.59 Å, the sum of the octahedral radius of tellurium [24] and the covalent radius of sulphur. Work in progress in this laboratory on the structure of tetrakis(diethyldithiocarbamato)tellurium(IV), however, shows an even greater average Te – S bond length (2.74 Å) in this eight-coordinate complex where Te – S bonds at the initial stage of refinement vary between 2.61 and 2.88 Å.[31] The long Te – S bonds in these compounds are probably due to the antibonding character of the lone pair [9,29] and to increasing *d*-character with increasing coordination number of the tellurium atom. Steric factors may also play a role,[14] especially in tetrakis(diethyldithiocarbamato)tellurium(IV) where the crowding around tellurium is large.

The intraligand angles S1 – Te – S2 and S2 – Te – S4 are 64.75(9) and 65.04(8)°, respectively, in good agreement with corresponding values found in divalent tellurium and selenium dithiocarbamates.[17,20,30] The angle S5 – Te – S6 in the third ligand is only 60.45(11)°. This is due to the great asymmetry in the S – Te bonds formed by that ligand.

The ligand C – S distances range from 1.672 to 1.748 Å with σ values ranging from 0.009 to 0.014 Å, the average being 1.714 Å, which seems to be normal in dithiocarbamates. This gives a π-bond order of 0.24 based on Pauling's bond order-bond length relationship with parameters used by Merlino.[32] In the three dithiocarbamate ligands, the C7 – N1, C12 – N2, and C17 – N3 bonds are 1.34(1), 1.33(1), and 1.39(1) Å, all significantly shorter than a single bond. The two first values are in good agreement with corresponding distances found in other dithiocarbamates. The high value for the C17 – N3 bond length, 1.39 Å, may be due to the possible disorder in the C18 – C19 ethyl group.

The π-bond order for a C – N bond length of 1.34 Å is 0.31. Bond angles on the nitrogen atoms and on carbon atoms bonded to sulphur are in good agreement with sp^2 hybridization on these atoms. Another feature of these angles is that their relative values correspond well with those predicted on the basis of the VSEPR theory.

The other C–N and C–C bond lengths and their bond angles also correspond to normal values within error limits, except for those in the disordered ethyl group.

There are no especially short intermolecular contacts between the molecules. The shortest C–C and C–S separations are found equal to 3.57 and 3.67 Å, respectively. The packing of the molecules is shown in Fig. 1 and intermolecular contacts are listed in Table 6.

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