

The Crystal and Molecular Structure of Tetrakis-(diethyldithiocarbamato)tellurium(IV)

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Tetrakis(diethyldithiocarbamato)tellurium(IV), $[\text{Te}(\text{Et}_2\text{NCS}_2)_4]$, forms flat, prismatic, orange crystals belonging to the orthorhombic space group $C_{2v}^9 - Pn2_1a$. The unit cell dimensions are $a = 19.805(2)$ Å, $b = 35.178(4)$ Å, and $c = 9.371(2)$ Å. There are eight formula units per cell; the density, found and calculated, is 1.46 g/cm³.

The structure is based on 4477 intensities above background, collected on a Siemens AED-1 diffractometer using $\text{CuK}\alpha$ radiation. The structure was solved by conventional heavy atom methods, and full-matrix least squares refinement has given a conventional R -value of 0.05.

There are two crystallographically independent but very similar molecules in the asymmetric unit. The central tellurium atom is bonded to all eight sulphur atoms in each molecule in a slightly distorted dodecahedral configuration. The Te-S bond lengths vary between 2.631 and 2.845 Å with an average of 2.744 Å.

The solution of this structure is part of a study of the configuration in complexes with central atoms¹⁻³ possessing an $(n-1) d^{10} ns^2$ electronic configuration. Earlier work on Te(IV) complexes shows that the ns^2 lone pair is sometimes stereochemically inert^{1,4-6} and sometimes active.⁷⁻¹¹

For Te(IV), most of the known structures are of complexes with monodentate ligands. The solution of the structure of tetrakis(diethyldithiocarbamato)tellurium(IV) represents the first structural work on a Te(IV) complex with bidentate ligands only.

IR, UV, and NMR spectra have been obtained for tetrakis(diethyldithiocarbamato)tellurium(IV), $\text{Te}(\text{dtc})_4$, by Nikolov *et al.*¹² In the NMR spectrum, two types of CH_2 quartets were found: one centered almost at the position of the CH_2 quartet of tetraethylthiuram disulphide and the other shifted 0.2 ppm to lower magnetic fields. The first quartet should then be due to monodentate ligands, the latter to bidentate. In the latter the electron shift from nitrogen to the sp^2 carbon atom is expected to be greatest, hence the deshielding of the CH_2 protons should be greater in bidentate than in unidentate (and asymmetric) ligands.¹²⁻¹⁴ Both CH_2 quartets have the same area, thus an

octahedral Te(dtc), complex with two monodentate and two bidentate ligands is expected.¹² The recent structure determination of tetrakis(diethyldithiocarbamato)tin(IV) represents an example of an octahedral complex with two monodentate and two bidentate diethyldithiocarbamate ligands.¹⁵

The NMR spectrum is obtained in solution, and the structures in solution and in the crystalline phase may be different.

In the complex, tris(diethyldithiocarbamato)phenyltellurium(IV), Te(dtc)₃Ph, the coordination number of Te(IV) is seven.^{2,3} It was therefore felt that tellurium in the present structure might have as high a coordination number as eight in the solid state.

The IR spectrum of Te(dtc)₄ in CHCl₃ solution is also interpreted in terms of both mono- and bidentate ligands.¹² An IR spectrum based on KBr mulls was reported to give the same information as the corresponding spectrum in solution.¹⁷

EXPERIMENTAL

The crystals used in this investigation were made by Nikolov *et al.*¹² They were prepared by adding a 10 % solution of sodium diethyldithiocarbamate to a 0.1 M solution of K₂TeO₆, buffered to pH 8.4 by a phosphate-borate buffer. The precipitate was dried in vacuum and recrystallized from benzene. The crystals used in the structural work were flat orange prisms.

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 CuK α radiation. A crystal, elongated along *c*, with dimensions 0.21 \times 0.04 \times 0.17 mm³ was mounted along the *c* axis. The crystal orientation and rough cell dimensions were first determined by measuring θ , χ , and ϕ for three non-coplanar reciprocal vectors. The rough setting angles for all reflections were then calculated.

For determination of accurate unit cell dimensions by least squares methods, the θ angles of 16 reflections with high values of θ were measured. The cell dimensions are $a = 19.805(2)$ Å, $b = 35.178(4)$ Å, and $c = 9.371(2)$ Å. There are eight formula units per cell, with density, calculated and found, 1.46 g/cm³. The systematic absences are $hk0$ for $h = 2n + 1$, and $0kl$ for $k + l = 2n + 1$ in the orthorhombic crystals. Thus the space group is either *Pnma* or *Pna2*₁.

Intensity data were collected using a scintillation counter and $\theta - 2\theta$ scan technique. The scan speed was 0.5°/min, with automatic setting of greater speed for strong reflections. Attenuation filters were used to avoid counting losses, and the correct filter was automatically inserted in the primary beam. The reflections were scanned between $\theta_1 = \theta - 0.40^\circ$, and $\theta_2 = \theta + 0.32 + 0.19 \text{ tg } \theta$, where θ is the Bragg angle for the α_1 peak. The scanning 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 the background was measured for 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.

Two reference reflections were measured at intervals of 100 reflections. The intensity variations for these reflections were used to scale the net intensities of the recorded 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 background intensity. Unobserved reflections were assigned intensities equal to the lower intensity limit.

Of 5 378 reflections with $\sin \theta \leq 0.891$, 4477 were observed and measured. The data were corrected for Lorentz, polarization, absorption¹⁶ ($\mu = 122.3 \text{ cm}^{-1}$) and secondary extinction effects. The University of Bergen's IBM 360/50H computer was used in all computations.

STRUCTURE ANALYSIS

The structure analysis was started with the assumption that the space group was $Pnma$. This space group would result in a Te—Te vector giving a maximum in the Patterson function at $0, \frac{1}{2} - 2y, 0$. In the three-dimensional Patterson map no such peak could be found, unless it coincided with the origin peak. Assuming the latter to be the case, this in turn leads to a y -coordinate of $1/4$ for tellurium, *i.e.* that tellurium is located on a mirror plane in four-fold special positions. Since there are eight formula units in a cell, it follows that there is either a binuclear complex present or there are two crystallographically non-equivalent molecules in the asymmetric unit. Since the tellurium atoms in the y -direction then must be $b/2$, or 17.6 Å apart, packing considerations seem to rule out $Pnma$ as the correct space group. Also two prominent peaks in the map could not be explained on the basis of this space group.

Attention was therefore shifted to the other possible space group, the non-centric $Pna2_1$. In order to preserve the labeling of axes and the reflection indices based on $Pnma$, the setting $Pn2_1a$ was chosen. This is then equivalent to an interchange of b and c axes relative to $Pna2_1$. Since this space group has four equivalent positions, there must be two tellurium atoms in the asymmetric unit.

Both tellurium positions were then found from the map. Their x -coordinates were close to 0.0 and 0.25 in agreement with semi-extinctions found from films. In the y -direction, Te1 was arbitrarily assigned the coordinate 0.000, which was kept constant throughout the later refinements. Successive Fourier syntheses revealed the positions of all atoms, except hydrogen, in the two crystallographically non-equivalent molecules in the asymmetric unit.

Full-matrix least squares refinement was then started using a program (BDLS) which minimizes 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 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 with $K|F_c|$ 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 for all atoms except tellurium (anisotropic), the factor $R = \sum (||F_o| - |F_c||) / \sum |F_o|$ reached a value of 0.14. After corrections for absorption, the R -value was reduced to 0.08. After introducing anisotropic temperature factors for the sulphur atoms and correcting the intensities for secondary extinction effects, the R -value reached its final value of 0.050.

Observed and calculated structure factors following the last refinement cycle can be obtained from the author St. H. upon request. Atomic scattering factors were taken from the *International Tables*.⁷ The atomic scattering factors for tellurium and sulphur were corrected for anomalous dispersion, using f' and f'' values calculated by Cromer.¹⁸ Final atomic parameters are listed in Table 1, and components of atomic vibration tensors in Tables 2 and 3. Inter-atomic distances and angles are listed in Tables 4–7, while least squares planes through groups of atoms are listed in Tables 8–10.

Table 1. Final atomic coordinates in fractions of cell edges, with standard deviations in brackets.

| | <i>x</i> | <i>y</i> | <i>z</i> |
|------|-------------|------------|-------------|
| Te1 | 0.00516(7) | 0 | 0.17889(19) |
| Te2 | 0.25219(7) | 0.28604(5) | 0.17501(17) |
| S11 | -0.0487(3) | -0.0597(2) | 0.0451(8) |
| S12 | 0.0873(3) | -0.0623(2) | 0.1669(9) |
| S13 | -0.0688(3) | 0.0350(2) | -0.0303(8) |
| S14 | 0.0748(3) | 0.0153(2) | -0.0549(8) |
| S15 | 0.0300(5) | 0.0750(4) | 0.2537(8) |
| S16 | 0.1323(4) | 0.0163(3) | 0.2995(10) |
| S17 | -0.0259(3) | -0.0298(2) | 0.4478(8) |
| S18 | -0.1253(5) | 0.0128(4) | 0.2781(9) |
| S21 | 0.1990(3) | 0.3444(2) | 0.0403(9) |
| S22 | 0.3347(3) | 0.3466(2) | 0.1612(9) |
| S23 | 0.1779(3) | 0.2500(2) | -0.0364(8) |
| S24 | 0.3224(3) | 0.2672(2) | -0.0552(8) |
| S25 | 0.2728(5) | 0.2092(4) | 0.2588(7) |
| S26 | 0.3790(4) | 0.2679(3) | 0.2940(10) |
| S27 | 0.2205(3) | 0.3150(2) | 0.4417(8) |
| S28 | 0.1229(5) | 0.2711(4) | 0.2703(8) |
| N11 | 0.0342(6) | -0.1200(4) | 0.0187(13) |
| N12 | 0.0019(9) | 0.0489(6) | -0.2609(14) |
| N13 | 0.1590(6) | 0.0905(4) | 0.2834(14) |
| N14 | -0.1539(6) | -0.0166(4) | 0.5309(14) |
| N21 | 0.2811(6) | 0.4036(4) | 0.0181(14) |
| N22 | 0.2564(9) | 0.2326(6) | -0.2622(14) |
| N23 | 0.4050(6) | 0.1939(4) | 0.3061(16) |
| N24 | 0.0933(6) | 0.3019(4) | 0.5226(14) |
| C11 | 0.0256(7) | -0.0855(4) | 0.0700(16) |
| C111 | -0.0191(8) | -0.1398(5) | -0.0589(18) |
| C112 | -0.0128(13) | -0.1333(9) | -0.2254(23) |
| C113 | 0.1003(7) | -0.1400(5) | 0.0355(18) |
| C114 | 0.1036(10) | -0.1623(6) | 0.1722(25) |
| C12 | 0.0047(6) | 0.0352(4) | -0.1296(17) |
| C121 | -0.0563(8) | 0.0651(5) | -0.3315(21) |
| C122 | -0.0798(10) | 0.1053(7) | -0.2829(23) |
| C123 | 0.0704(9) | 0.0517(5) | -0.3400(21) |
| C124 | 0.1071(12) | 0.0901(8) | -0.3043(29) |
| C13 | 0.1107(8) | 0.0642(5) | 0.2830(19) |
| C131 | 0.1446(9) | 0.1304(6) | 0.2638(19) |
| C132 | 0.1511(11) | 0.1412(7) | 0.1084(26) |
| C133 | 0.2318(8) | 0.0792(5) | 0.2909(20) |
| C134 | 0.2566(10) | 0.0795(6) | 0.4479(22) |
| C14 | -0.1055(7) | -0.0125(4) | 0.4271(16) |
| C141 | -0.1369(8) | -0.0376(6) | 0.6680(22) |
| C142 | -0.1673(10) | -0.0771(6) | 0.6624(24) |
| C143 | -0.2253(8) | -0.0043(5) | 0.5075(17) |
| C144 | -0.2327(9) | 0.0356(6) | 0.5727(21) |
| C21 | 0.2727(7) | 0.3685(4) | 0.0696(16) |
| C211 | 0.2267(9) | 0.4231(5) | -0.0706(20) |
| C212 | 0.2301(12) | 0.4144(8) | -0.2303(20) |
| C213 | 0.3475(8) | 0.4245(5) | 0.0342(19) |
| C214 | 0.3478(10) | 0.4480(7) | 0.1753(27) |
| C22 | 0.2514(7) | 0.2479(5) | -0.1276(18) |
| C221 | 0.1909(9) | 0.2215(6) | -0.3377(22) |

Table 1. Continued.

| | | | |
|------|------------|-----------|-------------|
| C222 | 0.1809(10) | 0.1789(7) | -0.3119(27) |
| C223 | 0.3203(9) | 0.2294(5) | -0.3400(21) |
| C224 | 0.3480(12) | 0.1885(8) | -0.2978(29) |
| C23 | 0.3575(7) | 0.2227(5) | 0.2827(17) |
| C231 | 0.4802(9) | 0.2025(6) | 0.3160(23) |
| C232 | 0.4980(10) | 0.2109(6) | 0.4757(22) |
| C233 | 0.3871(8) | 0.1516(6) | 0.3034(22) |
| C234 | 0.3884(8) | 0.1386(5) | 0.1426(20) |
| C24 | 0.1405(6) | 0.2967(4) | 0.4236(15) |
| C241 | 0.1053(8) | 0.3194(5) | 0.6619(21) |
| C242 | 0.0753(9) | 0.3617(6) | 0.6564(24) |
| C243 | 0.0237(7) | 0.2847(5) | 0.5040(17) |
| C244 | 0.0160(10) | 0.2438(6) | 0.5644(20) |

Table 2. Components of atomic vibration tensors for Te and S, $U \times 10^3$, in \AA^2 with standard deviations, referred to crystallographic axes. The expression used is $\exp\{-2\pi^2[h^2a^{-2}U_{11} + k^2b^{-2}U_{22} + l^2c^{-2}U_{33} + 2hka^{-1}b^{-1}U_{12} + 2klb^{-1}c^{-1}U_{23} + 2hla^{-1}c^{-1}U_{13}]\}$.

| | | | | |
|-----|------------|------------|------------|----------------------------|
| Te1 | 33.6(0.8) | 36.9(0.7) | 42.8(1.0) | (U_{11}, U_{22}, U_{33}) |
| | 2.8(0.7) | 3.6(1.3) | 0.1(0.8) | (U_{12}, U_{23}, U_{13}) |
| Te2 | 33.5(0.8) | 37.5(0.7) | 41.4(1.0) | |
| | -3.8(0.7) | -1.7(1.3) | 0.6(0.9) | |
| S11 | 39.4(3.8) | 46.8(4.3) | 69.3(5.8) | |
| | 0.5(3.4) | -5.7(4.1) | -7.7(3.7) | |
| S12 | 48.9(4.0) | 48.5(4.1) | 71.6(5.7) | |
| | 9.3(3.5) | -10.5(4.4) | -21.8(4.1) | |
| S13 | 41.0(3.9) | 66.5(5.0) | 50.5(5.1) | |
| | 11.3(3.6) | 14.3(4.3) | 4.0(3.5) | |
| S14 | 38.7(3.6) | 69.4(5.0) | 50.1(4.7) | |
| | 6.6(3.6) | 7.3(4.3) | 7.4(3.4) | |
| S15 | 39.3(5.5) | 35.1(6.0) | 85.3(9.7) | |
| | 3.5(4.9) | -0.4(3.4) | -2.9(3.3) | |
| S16 | 47.3(4.1) | 43.0(4.1) | 67.1(5.2) | |
| | 5.0(3.4) | 4.6(5.7) | -9.6(4.7) | |
| S17 | 52.5(4.5) | 62.4(5.0) | 58.1(5.4) | |
| | 11.9(4.0) | 16.0(4.4) | -0.6(3.7) | |
| S18 | 46.5(4.8) | 77.6(7.7) | 55.6(5.1) | |
| | 13.9(4.9) | 28.4(5.7) | 13.1(3.9) | |
| S21 | 35.5(3.6) | 48.2(4.4) | 75.1(6.0) | |
| | 2.0(3.4) | 5.0(4.2) | -9.4(3.7) | |
| S22 | 46.7(3.7) | 50.2(4.2) | 68.9(6.0) | |
| | -15.0(3.3) | 11.3(4.5) | -15.7(3.9) | |
| S23 | 37.9(3.5) | 60.0(4.6) | 54.3(5.1) | |
| | -8.2(3.5) | -12.7(4.2) | 4.8(3.2) | |
| S24 | 38.0(3.5) | 75.2(5.3) | 53.6(5.0) | |
| | -9.6(3.8) | -3.7(4.4) | 6.6(3.3) | |
| S25 | 32.9(5.2) | 51.3(7.5) | 59.3(7.5) | |
| | -10.0(5.2) | 1.5(3.5) | -2.9(3.0) | |
| S26 | 41.3(3.9) | 43.1(3.9) | 72.6(5.5) | |
| | -8.1(3.3) | 7.5(5.5) | -8.2(4.4) | |
| S27 | 49.5(4.4) | 68.7(5.2) | 52.6(5.2) | |
| | -9.4(4.0) | -19.3(4.4) | 2.8(3.7) | |
| S28 | 37.2(4.4) | 63.3(6.8) | 55.6(5.5) | |
| | -7.4(4.5) | -12.4(4.7) | 3.0(3.4) | |

Table 3. Final isotropic vibration tensors ($\times 10^3$) in \AA^2 for N and C. The expression used is $\exp[-8\pi^2 U(\sin^2 \theta/\lambda)]$.

| | <i>U</i> | | <i>U</i> |
|------|------------|------|------------|
| N11 | 46.1(3.2) | N21 | 52.8(3.5) |
| N12 | 53.3(5.7) | N22 | 51.5(5.7) |
| N13 | 49.8(3.6) | N23 | 51.8(3.3) |
| N14 | 57.1(3.6) | N24 | 54.4(3.5) |
| C11 | 41.0(3.6) | C21 | 47.3(4.0) |
| C111 | 60.6(4.8) | C211 | 68.7(5.4) |
| C112 | 90.8(8.6) | C212 | 73.0(7.4) |
| C113 | 54.7(4.4) | C213 | 60.7(4.8) |
| C114 | 87.5(6.2) | C214 | 93.8(6.6) |
| C12 | 43.0(3.8) | C22 | 49.6(4.2) |
| C121 | 69.3(5.0) | C221 | 74.1(5.4) |
| C122 | 86.0(6.7) | C222 | 101.7(7.0) |
| C123 | 72.8(5.3) | C223 | 70.9(5.2) |
| C124 | 109.3(7.9) | C224 | 114.7(8.4) |
| C13 | 49.8(4.7) | C23 | 37.1(3.9) |
| C131 | 65.6(5.8) | C231 | 71.8(5.1) |
| C132 | 107.9(7.7) | C232 | 83.1(6.0) |
| C133 | 60.2(4.8) | C233 | 61.7(4.7) |
| C134 | 88.2(6.3) | C234 | 69.2(5.3) |
| C14 | 48.9(4.1) | C24 | 42.2(3.7) |
| C141 | 73.1(5.3) | C241 | 67.4(5.0) |
| C142 | 87.8(6.3) | C242 | 90.2(6.5) |
| C143 | 60.0(4.4) | C243 | 56.2(4.1) |
| C144 | 79.0(5.5) | C244 | 88.8(6.4) |

Table 4. Bond lengths with standard deviations, in \AA .

| | | | |
|----------|-----------|----------|-----------|
| Te1-S11 | 2.669(7) | Te2-S21 | 2.631(8) |
| Te1-S12 | 2.732(7) | Te2-S22 | 2.689(7) |
| Te1-S13 | 2.740(7) | Te2-S23 | 2.774(7) |
| Te1-S14 | 2.644(7) | Te2-S24 | 2.651(7) |
| Te1-S15 | 2.774(13) | Te2-S25 | 2.845(14) |
| Te1-S16 | 2.819(8) | Te2-S26 | 2.821(8) |
| Te1-S17 | 2.797(8) | Te2-S27 | 2.771(8) |
| Te1-S18 | 2.782(9) | Te2-S28 | 2.763(9) |
| S11-C11 | 1.74(2) | S21-C21 | 1.71(2) |
| S12-C11 | 1.73(2) | S22-C21 | 1.68(2) |
| S13-C12 | 1.73(2) | S23-C22 | 1.69(2) |
| S14-C12 | 1.70(2) | S24-C22 | 1.70(2) |
| S15-C13 | 1.67(2) | S25-C23 | 1.76(2) |
| S16-C13 | 1.75(2) | S26-C23 | 1.65(2) |
| S17-C14 | 1.70(2) | S27-C24 | 1.72(1) |
| S18-C14 | 1.70(2) | S28-C24 | 1.73(2) |
| C11-N11 | 1.32(2) | C21-N21 | 1.34(2) |
| C12-N12 | 1.32(2) | C22-N22 | 1.37(2) |
| C13-N13 | 1.33(2) | C23-N23 | 1.40(2) |
| C14-N14 | 1.37(2) | C24-N24 | 1.33(2) |
| N11-C111 | 1.46(2) | N21-C211 | 1.53(2) |
| N11-C113 | 1.49(2) | N21-C213 | 1.51(2) |
| N12-C121 | 1.45(2) | N22-C221 | 1.53(2) |

Table 4. Continued.

| | | | |
|-----------|---------|-----------|---------|
| N12—C123 | 1.55(2) | N22—C223 | 1.47(2) |
| N13—C131 | 1.44(2) | N23—C231 | 1.52(2) |
| N13—C133 | 1.50(2) | N23—C233 | 1.53(2) |
| N14—C141 | 1.52(2) | N24—C241 | 1.46(2) |
| N14—C143 | 1.49(2) | N24—C243 | 1.51(2) |
| C111—C112 | 1.58(3) | C211—C212 | 1.53(3) |
| C113—C114 | 1.50(3) | C213—C214 | 1.56(3) |
| C121—C122 | 1.56(3) | C221—C222 | 1.53(3) |
| C123—C124 | 1.57(3) | C223—C224 | 1.59(3) |
| C131—C132 | 1.51(3) | C231—C232 | 1.57(3) |
| C133—C134 | 1.55(3) | C233—C234 | 1.58(3) |
| C141—C142 | 1.52(3) | C241—C242 | 1.60(3) |
| C143—C144 | 1.54(3) | C243—C244 | 1.55(3) |

Table 5. Non-bonded S—S distances in the $\text{Te}(\text{dtc})_4$ molecules, in Å.

| | | | |
|---------|-----------|---------|-----------|
| S11—S12 | 2.928(10) | S21—S22 | 2.917(9) |
| S13—S14 | 2.936(9) | S23—S24 | 2.930(9) |
| S15—S16 | 2.925(14) | S25—S26 | 2.967(15) |
| S17—S18 | 2.939(13) | S27—S28 | 2.950(13) |
| S12—S16 | 3.158(11) | S22—S26 | 3.160(12) |
| S13—S18 | 3.200(12) | S23—S28 | 3.163(11) |
| S11—S15 | 5.358(15) | S21—S25 | 5.381(15) |
| S14—S17 | 5.356(11) | S24—S27 | 5.346(11) |
| S11—S13 | 3.431(11) | S21—S23 | 3.423(12) |
| S11—S14 | 3.719(10) | S21—S24 | 3.762(10) |
| S11—S17 | 3.944(11) | S21—S27 | 3.924(11) |
| S11—S18 | 3.684(14) | S21—S28 | 3.684(14) |
| S12—S13 | 4.970(10) | S22—S23 | 4.961(10) |
| S12—S14 | 3.441(11) | S22—S24 | 3.460(11) |
| S12—S17 | 3.642(11) | S22—S27 | 3.641(11) |
| S12—S18 | 5.078(13) | S22—S28 | 5.070(12) |
| S15—S13 | 3.590(12) | S25—S23 | 3.640(12) |
| S15—S14 | 3.682(12) | S25—S24 | 3.713(13) |
| S15—S17 | 4.256(15) | S25—S27 | 4.228(16) |
| S15—S18 | 3.781(16) | S25—S28 | 3.684(16) |
| S16—S13 | 5.084(11) | S26—S23 | 5.083(10) |
| S16—S14 | 3.512(12) | S26—S24 | 3.458(12) |
| S16—S17 | 3.791(11) | S26—S27 | 3.811(11) |
| S16—S18 | 5.107(12) | S26—S28 | 5.079(12) |

Table 6. Bond angles with standard deviations, in degrees.

| | | | |
|-------------|------------|-------------|------------|
| S11—Te1—S12 | 65.6(0.2) | S21—Te2—S22 | 66.5(0.2) |
| S13—Te1—S14 | 66.1(0.2) | S23—Te2—S24 | 65.3(0.2) |
| S15—Te1—S16 | 63.1(0.3) | S25—Te2—S26 | 63.2(0.3) |
| S17—Te1—S18 | 63.6(0.3) | S27—Te2—S28 | 64.4(0.3) |
| S12—Te1—S16 | 69.3(0.2) | S22—Te2—S26 | 70.0(0.2) |
| S13—Te1—S18 | 70.8(0.3) | S23—Te2—S28 | 69.7(0.2) |
| S11—Te1—S15 | 159.8(0.3) | S21—Te2—S25 | 158.7(0.3) |
| S14—Te1—S17 | 159.6(0.2) | S24—Te2—S27 | 160.9(0.2) |
| Te1—S11—C11 | 90.5(0.5) | Te2—S21—C21 | 88.2(0.6) |

Table 6. Continued.

| | | | |
|---------------|------------|---------------|------------|
| Tel-S12-C11 | 88.8(0.5) | Te2-S22-C21 | 86.7(0.6) |
| Tel-S13-C12 | 86.3(0.6) | Te2-S23-C22 | 85.7(0.6) |
| Tel-S14-C12 | 90.0(0.6) | Te2-S24-C22 | 89.5(0.6) |
| Tel-S15-C13 | 89.7(0.8) | Te2-S25-C23 | 85.2(0.7) |
| Tel-S16-C13 | 86.6(0.6) | Te2-S26-C23 | 87.9(0.6) |
| Tel-S17-C14 | 88.1(0.6) | Te2-S27-C24 | 88.9(0.6) |
| Tel-S18-C14 | 88.7(0.6) | Te2-S28-C24 | 89.0(0.6) |
| S11-C11-N11 | 122.6(0.9) | S21-C21-N21 | 120.5(1.0) |
| S12-C11-N11 | 122.4(0.9) | S22-C21-N21 | 120.9(1.0) |
| S13-C12-N12 | 117.8(1.1) | S23-C22-N22 | 122.9(1.1) |
| S14-C12-N12 | 124.5(1.1) | S24-C22-N22 | 117.6(1.1) |
| S15-C13-N13 | 122.1(1.2) | S25-C23-N23 | 117.8(1.1) |
| S16-C13-N13 | 119.6(1.1) | S26-C23-N23 | 120.9(1.0) |
| S17-C14-N14 | 121.9(1.0) | S27-C24-N24 | 121.8(1.0) |
| S18-C14-N14 | 118.5(1.0) | S28-C24-N24 | 120.5(0.9) |
| S11-C11-S12 | 114.9(0.7) | S21-C21-S22 | 118.6(0.8) |
| S13-C12-S14 | 117.7(0.8) | S23-C22-S24 | 119.4(0.8) |
| S15-C13-S16 | 118.1(1.0) | S25-C23-S26 | 121.0(0.9) |
| S17-C14-S18 | 119.5(0.8) | S27-C24-S28 | 117.6(0.7) |
| C11-N11-C111 | 121.9(1.1) | C21-N21-C211 | 121.6(1.1) |
| C11-N11-C113 | 120.5(1.1) | C21-N21-C213 | 121.5(1.1) |
| C12-N12-C121 | 127.1(1.3) | C22-N22-C221 | 117.7(1.3) |
| C12-N12-C123 | 115.6(1.3) | C22-N22-C223 | 123.2(1.3) |
| C13-N13-C131 | 122.3(1.3) | C23-N23-C231 | 121.5(1.2) |
| C13-N13-C133 | 120.6(1.3) | C23-N23-C233 | 123.0(1.1) |
| C14-N14-C141 | 119.7(1.1) | C24-N24-C241 | 124.4(1.1) |
| C14-N14-C143 | 121.7(1.1) | C24-N24-C243 | 120.3(1.1) |
| C111-N11-C113 | 117.6(1.1) | C211-N21-C213 | 116.7(1.2) |
| C121-N12-C123 | 117.0(1.3) | C221-N22-C223 | 119.0(1.3) |
| C131-N13-C133 | 116.9(1.3) | C231-N23-C233 | 115.0(1.2) |
| C141-N14-C143 | 118.4(1.1) | C241-N24-C243 | 114.7(1.1) |
| N11-C111-C112 | 111.5(1.4) | N21-C211-C212 | 114.4(1.4) |
| N11-C113-C114 | 111.9(1.2) | N21-C213-C214 | 110.3(1.3) |
| N12-C121-C122 | 117.5(1.5) | N22-C221-C222 | 106.7(1.5) |
| N12-C123-C124 | 111.0(1.5) | N22-C223-C224 | 104.1(1.5) |
| N13-C131-C132 | 110.5(1.5) | N23-C231-C232 | 108.4(1.4) |
| N13-C133-C134 | 110.4(1.3) | N23-C233-C234 | 107.2(1.4) |
| N14-C141-C142 | 109.2(1.4) | N24-C241-C242 | 107.6(1.4) |
| N14-C143-C144 | 107.2(1.2) | N24-C243-C244 | 114.6(1.2) |

Table 7. Some short, intermolecular interatomic separations, in Å. The left column represents distances from an atom in one of the two original molecules (Table 1), to an atom in a molecule whose transformation from one of the two original ones is listed in the next column.

| | | |
|----------|---|---------|
| S11-C211 | $-x, y - \frac{1}{2}, -z$ | 3.58(2) |
| S12-C213 | $\frac{1}{2}-x, y - \frac{1}{2}, \frac{1}{2}+z$ | 3.71(2) |
| S14-C214 | $\frac{1}{2}-x, y - \frac{1}{2}, z - \frac{1}{2}$ | 3.79(2) |
| S15-C234 | $x - \frac{1}{2}, y, \frac{1}{2}-z$ | 3.72(2) |
| S18-C133 | » | 3.73(2) |
| S21-C111 | $-x, \frac{1}{2}+y, -z$ | 3.61(2) |
| S22-C113 | $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ | 3.77(2) |
| S22-C112 | » | 3.75(3) |
| S25-C131 | x, y, z | 3.76(2) |
| S25-C132 | » | 3.68(3) |

Table 7. Continued.

| | | |
|-------------|--|---------|
| N11 - C242 | $-x, y - \frac{1}{2}, 1 - z$ | 3.79(2) |
| N14 - C121 | $x, y, 1 + z$ | 3.70(2) |
| N24 - C221 | » | 3.67(2) |
| C11 - C242 | $-x, y - \frac{1}{2}, 1 - z$ | 3.74(3) |
| C121 - C14 | $x, y, z - 1$ | 3.68(2) |
| C121 - C144 | » | 3.75(2) |
| C123 - C13 | » | 3.65(3) |
| C112 - C142 | » | 3.79(3) |
| C122 - C224 | $x - \frac{1}{2}, y, -z - \frac{1}{2}$ | 3.34(3) |
| C122 - C234 | » | 3.62(3) |
| C124 - C222 | x, y, z | 3.45(4) |
| C124 - C134 | $x, y, z - 1$ | 3.78(3) |
| C142 - C21 | $-x, y - \frac{1}{2}, 1 - z$ | 3.79(3) |
| C221 - C24 | $x, y, z - 1$ | 3.60(2) |
| C221 - C244 | » | 3.67(3) |
| C223 - C23 | » | 3.62(2) |
| C224 - C232 | » | 3.74(3) |
| C212 - C242 | » | 3.74(3) |

Table 8. Least squares planes. The following planes were calculated:

| | | | | | | |
|----------|------|------|------|------|-------|------|
| Plane 1 | Te1, | S11, | S12, | S15, | S16 | |
| Plane 2 | Te1, | S13, | S14, | S17, | S18 | |
| Plane 3 | Te2, | S21, | S22, | S25, | S26 | |
| Plane 4 | Te2, | S23, | S24, | S27, | S28 | |
| Plane 5 | S11, | S12, | C11, | N11, | C111, | C113 |
| Plane 6 | S13, | S14, | C12, | N12, | C121, | C123 |
| Plane 7 | S15, | S16, | C13, | N13, | C131, | C133 |
| Plane 8 | S17, | S18, | C14, | N14, | C141, | C143 |
| Plane 9 | S21, | S22, | C21, | N21, | C211, | C213 |
| Plane 10 | S23, | S24, | C22, | N22, | C221, | C223 |
| Plane 11 | S25, | S26, | C23, | N23, | C231, | C233 |
| Plane 12 | S27, | S28, | C24, | N24, | C241, | C243 |

Equation of planes, based on the cell axes and coordinates in fractions of cell edges.

| | |
|----------|--|
| Plane 1 | $-7.661x - 8.690y + 8.325z - 1.310 = 0$ |
| Plane 2 | $5.579x + 30.723y + 3.723z - 0.659 = 0$ |
| Plane 3 | $-7.399x + 9.472y + 8.318z - 2.174 = 0$ |
| Plane 4 | $5.401x - 30.632y + 3.834z + 6.718 = 0$ |
| Plane 5 | $-6.932x - 13.746y + 7.978z - 1.553 = 0$ |
| Plane 6 | $4.345x + 31.528y + 3.612z - 0.648 = 0$ |
| Plane 7 | $-1.802x + 3.116y + 9.295z - 2.588 = 0$ |
| Plane 8 | $5.179x + 30.303y + 4.080z - 0.833 = 0$ |
| Plane 9 | $-7.174x + 13.831y + 7.919z - 3.674 = 0$ |
| Plane 10 | $3.259x - 31.754y + 3.726z + 7.561 = 0$ |
| Plane 11 | $-2.646x + 0.659y + 9.285z - 1.856 = 0$ |
| Plane 12 | $5.886x - 30.001y + 4.023z + 6.358 = 0$ |

RESULTS AND DISCUSSION

The two molecules in the asymmetric unit with atoms labeled are shown in Fig. 1, as seen along the c axis. From the figure it may be seen that the molecules are near to being mirror images of each other, the direction of the

Table 9. Distances in Å from atoms listed to least squares planes. (Input coordinates in fractions of cell edges give distances in Å.)

| Plane 1 | | Plane 2 | | Plane 3 | |
|----------|---------|----------|---------|----------|---------|
| Te1 | 0.1400 | Te1 | 0.0356 | Te2 | 0.1258 |
| S11 | -0.0418 | S13 | -0.0791 | S21 | -0.0482 |
| S12 | -0.0477 | S14 | 0.0243 | S22 | -0.0253 |
| S15 | -0.0791 | S17 | -0.0507 | S25 | -0.0579 |
| S16 | 0.0286 | S18 | 0.0698 | S26 | 0.0056 |
| Plane 4 | | Plane 5 | | Plane 6 | |
| Te2 | -0.0105 | Te1 | -0.1614 | Te1 | 0.0203 |
| S23 | -0.1189 | S11 | -0.0340 | S13 | 0.0483 |
| S24 | 0.0630 | S12 | 0.0299 | S14 | -0.0387 |
| S27 | -0.0479 | C11 | 0.0038 | C12 | 0.0126 |
| S28 | 0.1142 | N11 | 0.0097 | N12 | -0.0420 |
| | | C111 | 0.0314 | C121 | -0.0383 |
| | | C113 | -0.0408 | C123 | 0.0581 |
| | | C112 | -1.4297 | C122 | 1.3041 |
| | | C114 | 1.3341 | C124 | 1.5574 |
| Plane 7 | | Plane 8 | | Plane 9 | |
| Te1 | -0.9341 | Te1 | -0.0768 | Te2 | -0.1406 |
| S15 | -0.0498 | S17 | -0.0423 | S21 | -0.0183 |
| S16 | 0.0087 | S18 | 0.0397 | S22 | -0.0034 |
| C13 | 0.0434 | C14 | -0.0148 | C21 | 0.0181 |
| N13 | 0.0418 | N14 | 0.0328 | N21 | 0.0350 |
| C131 | 0.0101 | C141 | 0.0442 | C211 | -0.0075 |
| C133 | -0.0542 | C143 | -0.0595 | C213 | -0.0238 |
| C132 | -1.4128 | C142 | -1.3334 | C212 | -1.4170 |
| C134 | 1.3608 | C144 | 1.3782 | C214 | 1.4159 |
| Plane 10 | | Plane 11 | | Plane 12 | |
| Te2 | -0.0475 | Te2 | -0.7097 | Te2 | -0.0349 |
| S23 | 0.0663 | S25 | -0.0370 | S27 | -0.0187 |
| S24 | -0.0786 | S26 | 0.0475 | S28 | 0.0358 |
| C22 | 0.0344 | C23 | -0.0306 | C24 | -0.0109 |
| N23 | 0.0339 | N23 | 0.0423 | N24 | -0.0473 |
| C221 | -0.1093 | C231 | -0.0592 | C241 | 0.0575 |
| C223 | 0.0533 | C233 | 0.0369 | C243 | -0.0165 |
| C222 | 1.3078 | C232 | 1.3826 | C242 | -1.4082 |
| C224 | 1.5993 | C234 | -1.4686 | C244 | 1.4090 |

Table 10. Interplanar angles.

| | |
|-----------------|-------|
| Plane 1-Plane 2 | 88.4° |
| Plane 3-Plane 4 | 88.5° |

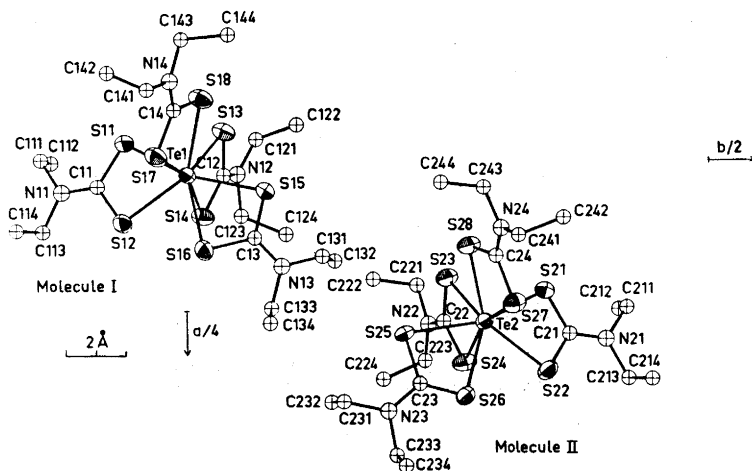


Fig. 1. The two molecules in the asymmetric unit seen along c .

“mirror plane” being roughly parallel to the ac plane. Thus in both molecules only one ligand has both methyl groups pointing to the same side relative to the ligand plane. Most corresponding bond lengths and angles are also nearly equal in the two molecules; only a few are significantly different. As can be seen from the figure, and Table 4, all eight sulphur atoms in each molecule are bonded to the central tellurium atom. This is presumably the first time tellurium has been shown to have as high a coordination number as eight. For a better view of the configuration around tellurium, a stereoscopic pair of one of the crystallographically independent molecules is shown in Fig. 2.

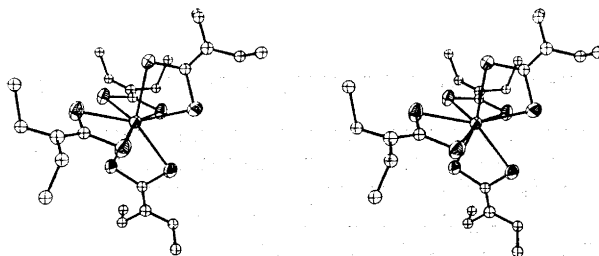


Fig. 2. Stereo drawing of molecule I.

The configurations around the central atoms in the molecules are distorted dodecahedral. In the tellurium valency shell there are eight bonded electron pairs plus the $5s$ lone pair. Assuming that the lone pair does not occupy a position in the coordination polyhedron, being essentially inert, as in the hexahalotellurate(IV) complex ions,⁴⁻⁶ the configuration should be based on the most energetically favourable distribution of the eight bonding pairs.^{19,20}

This is either at the vertices of a dodecahedron as found here, or a square antiprism.²¹ Several metal complexes of the type $M(dtc)_4$ where $M = Th, Np,$ and Ti , show both types of configuration.²²⁻²⁴

A regular dodecahedron can be visualized as two interleaving planar trapezoids at right angles to each other.^{25,26} In $Te(dtc)_4$ such trapezoids are defined by S11, S12, S15, S16 and S13, S14, S17, S18 for molecule I, and by S21, S22, S25, S26 and S23, S24, S27, S28 for molecule II. The average coordination within such a trapezoid is shown in Fig. 3. Least squares planes through

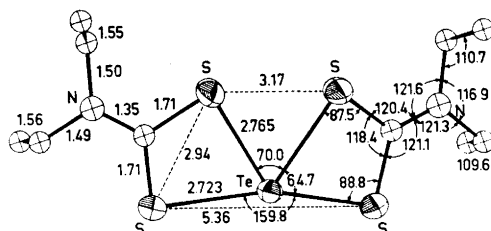
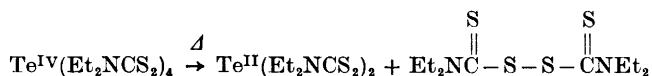


Fig. 3. Average bond lengths and angles. The figure is based on the Te1, S11, S12, S15, and S16 trapezoid.

the TeS_4 groups in such trapezoids show that the groups are nearly planar, the maximum deviation of atoms from planes being 0.14 Å. The average interplanar angle between the two trapezoids in a $Te(dtc)_4$ molecule is 88.5° , leading to some distortion from D_{2d} symmetry, in the TeS_8 group.

Such a $Te^{IV}S_4$ group as mentioned above is not very different from the $Te^{IV}S_4$ group found in trapezoid planar tellurium bis(dialkyldithiocarbamates).^{27,28} On heating $Te(dtc)_4$ in solution, an equi-molecular mixture of $Te(dtc)_2$ and the corresponding disulphide is produced.²⁹



Thus the formation of disulphide may result when two of the ligand sulphur atoms lying closest to each other in one trapezoid form an S-S bond, while the four Te-S bonds in the same trapezoid are broken.

The remaining two ligands then presumably form $Te(dtc)_2$ with relatively small rearrangement of bond lengths and angles.

Hoard and Silverton have studied both dodecahedral and square antiprismatic configurations in some detail.²⁶ In a dodecahedron, the eight corners are not equivalent. In $Te(dtc)_4$ the chelation is along edges m ; S12, S13, S16, and S18 in molecule I, and S22, S23, S26, and S28 in molecule II are at dodecahedral corners of type A. The other sulphur atoms, then, are at corners of type B, which are not equivalent with those of type A.

A dodecahedral complex can be described by several parameters, among which are θ_A , θ_B and MA/MB.²⁶ $\theta_A(\theta_B)$ represents the angle between bonds from the central atom, M, to ligand atoms of type A(B) and the unique axis

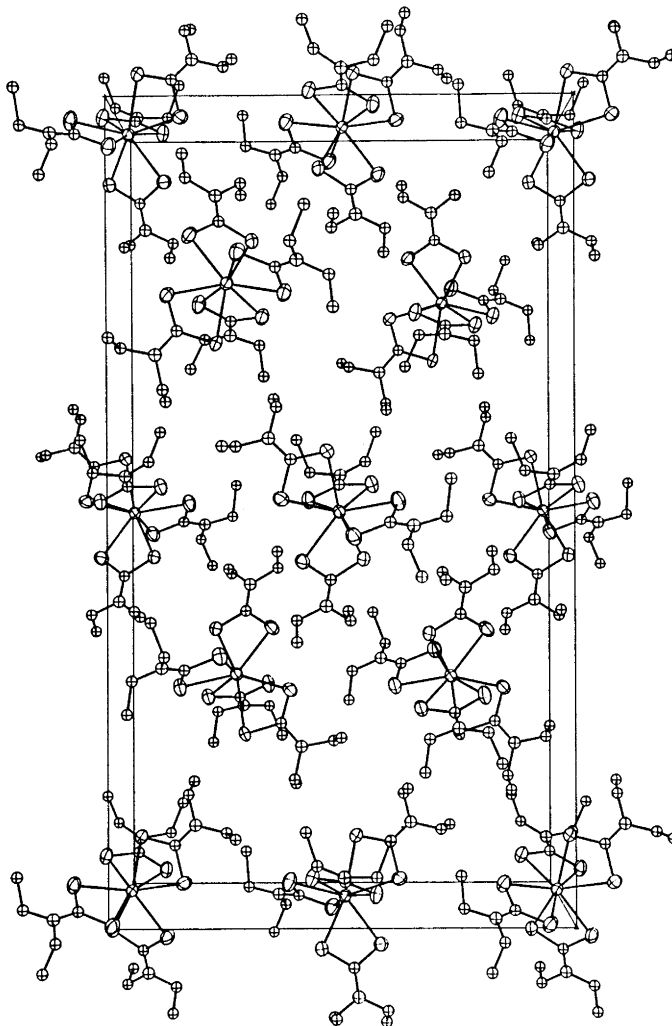


Fig. 4. The contents of the unit cell, seen parallel to c towards the center of the cell.

passing through the midpoints of the A–A(B–B) contacts in the two trap-
ezoids. MA and MB are the bond lengths MA and MB. The “most favour-
able” D_{2d} dodecahedron is characterized by the following values:²⁶

$$\theta_A = 35.2^\circ \quad \theta_B = 73.5^\circ \quad \text{MA/MB} = 1.03$$

For $\text{Te}(\text{dte})_4$, the values are

$$\theta_A = 35.1^\circ \quad \theta_B = 79.9^\circ \quad \text{MA/MB} = 1.016 \text{ for molecule I,}$$

$$\text{and } \theta_A = 34.9^\circ \quad \theta_B = 79.8^\circ \quad \text{MA/MB} = 1.014 \text{ for molecule II.}$$

For comparison, the values for a square antiprism, where A and B are
equivalent, are $\theta_A = \theta_B = 57.3^\circ$, MA/MB = 1.

From the above, it is clear that the configurations for the $\text{Te}(\text{dte})_4$ molecules are distorted dodecahedral. From inspection of Tables 4–6, there appears to be no systematic distortion toward nine-coordination with the lone pair playing a stereochemically active role in the two molecules. Such a stereochemically inert pair is found in several complexes with central atoms from the lower right hand corner of the periodic table. Examples are the well known octahedral $[\text{TeCl}_6]^{2-}$,⁴ $[\text{SeCl}_6]^{2-}$,⁴ $[\text{SeCl}_6]^{2-}$,³⁰ $[\text{SbCl}_6]^{3-}$,³¹ $[\text{BiCl}_6]^{3-}$,³² and hexathiourealead(II)³³ complex ions. For such complexes, according to Urch,³⁴ the lone pair of electrons may go into a low lying antibonding a^*_{1g} molecular orbital, mostly localized on the ligands, thus being stereochemically inert. According to Gillespie, the ns lone pair is forced inside the valency shell because of ligand-ligand repulsions, when ligand size and coordination numbers are large.²⁰

In the solid phase, the configuration around the tellurium atoms in TeCl_4 (tetramers) is distorted octahedral, with three short $\text{Te}-\text{Cl}$ bonds *trans* to and nearly collinear with three long $\text{Te}\cdots\text{Cl}$ bonds with average lengths of 2.311 Å and 2.929 Å, respectively.⁷ A corresponding configuration is found for the addition compound $\text{TeCl}_3^+\text{AlCl}_4^-$.⁸ In these compounds, the lone pair is presumably located between the long $\text{Te}\cdots\text{Cl}$ bonds. Such distortions are also found in complexes of $\text{Pb}(\text{II})$ and $\text{Tl}(\text{I})$ and are probably due to mixing of s and p orbitals.³⁵

The $\text{Te}-\text{S}$ bond lengths in $\text{Te}(\text{dte})_4$ vary from 2.63 to 2.85 Å, with an average of 2.744 Å. The average standard deviation is 0.008 Å. These bond lengths are much larger than 2.37 Å, the sum of the covalent radii corrected for bond polarity. They are also significantly larger than 2.59 Å, the sum of the octahedral radius of tellurium and the covalent radius of sulphur.

However, for $\text{TeX}_4(\text{tmtu})_2$ ($X = \text{Cl}$ or Br , $\text{tmtu} = \text{tetramethylthiourea}$) the average $\text{Te}-\text{S}$ bond length is 2.71 Å.¹ For $\text{Te}(\text{dte})_3\text{Ph}$ the average $\text{Te}-\text{S}$ bond length, excluding a long $\text{Te}-\text{S}$ bond weakened by the *trans*-effect of the phenyl group, is 2.714 Å.^{2,3} These latter values are more in agreement with the value 2.744 Å found in the present investigation. The increase in bond length going from $\text{TeX}_4(\text{tmtu})_2$ to $\text{Te}(\text{dte})_4$ is probably due to the stronger ligand-ligand repulsion following the increase in coordination number, and to increasing use of high energy d -orbitals. From the theory of Urch,³⁴ one should expect such bonds to be relatively weak in the hexahalotellurates, because of the weak bonding capacity of the electrons in the a_{1g} bonding orbital, and the antibonding nature of the lone pair in the a^*_{1g} orbital. This line of reasoning must also be valid for $\text{Te}(\text{dte})_3\text{Ph}$ and $\text{Te}(\text{dte})_4$.

The structure of another dithiocarbamate of tetravalent tellurium, tetrakis-(4-morpholinecarbodithioato)tellurium(IV), has just been solved in this laboratory. At the present stage of refinement ($R = 0.09$) the average $\text{Te}-\text{S}$ bond length is 2.74 Å, the same as found in the present investigation. The configuration around the central tellurium atom is again dodecahedral, but the distortion from D_{2d} symmetry is probably smaller than that found for the diethyldithiocarbamate.

In hexahydroxotellurium(VI), $\text{Te}(\text{OH})_6$, tellurium has no $5s$ lone pair of electrons. The average $\text{Te}-\text{O}$ bond length in this octahedral complex is 1.916 Å as compared to 1.91 Å, the sum of the covalent radii of tellurium and

oxygen corrected for bond polarity. This seems to indicate that the stereochemically inert lone pair above has a bond lengthening effect. However, the possibility of π -bonding in $\text{Te}(\text{OH})_6$,³⁶ and also the smaller size of oxygen as compared to the heavier halogens and sulphur, and the smaller radius and larger charge of $\text{Te}(\text{VI})$ as compared to $\text{Te}(\text{IV})$, may all be important factors contributing to a strong tellurium-oxygen bond.

In the dithiocarbamate complexes of divalent tellurium,^{27,28} the average $\text{Te}-\text{S}$ bond length is close to 2.68 Å, but the weak average bonds found in such compounds are probably due to three-center four-electron bonding.^{27,28}

Since there are many heavy atoms in the tetrakis(diethyldithiocarbamate) tellurium(IV) molecules, the bond lengths involving light atoms are determined with relatively small accuracy.

In the ligands, the $\text{C}-\text{S}$ bond lengths vary between 1.65 and 1.76 Å, the average being 1.71 Å corresponding to a π -bond order³ close to 0.25. In $\text{Te}(\text{dtc})_3\text{Ph}$, the average is 1.713 Å.^{2,3} These values agree well with values found in other dithiocarbamates.

For the $\text{C}=\text{N}$ bonds, the average bond length is 1.35 Å, corresponding to a π -bond order³ of 0.27, which seems to be normal for dithiocarbamate complexes. The other interatomic bonds are normal within the error limits.

The average $\text{S}-\text{Te}-\text{S}$ angle, where both sulphur atoms come from the same ligand, is 64.7°, which seems to be normal for intraligand $\text{S}-\text{Te}-\text{S}$ angles. The two $\text{S}-\text{Te}-\text{S}$ angles, where the sulphur atoms come from different ligands in one trapezoid, are 70.0 and 159.8° respectively. These may be compared to 80.1(1) and 147.8(1)° found for the corresponding angles in $\text{Te}(\text{dtc})_2$.²⁸ This difference in angles may be due to steric factors. In $\text{Te}(\text{dtc})_4$, where two TeS_4 trapezoids are interleaved at almost right angles, the large interligand $\text{S}-\text{Te}-\text{S}$ angles in a trapezoid has to open up in order to accommodate atoms from the other trapezoid. As the trapezoids remain planar and the intraligand $\text{S}-\text{Te}-\text{S}$ angles are nearly constant, the other interligand $\text{S}-\text{Te}-\text{S}$ angle in a trapezoid must decrease relative to that found in $\text{Te}(\text{dtc})_2$. As this bond angle is reduced, the corresponding $\text{Te}-\text{S}$ bond lengths increase relative to those in $\text{Te}(\text{dtc})_2$ in order to minimize $\text{S}\cdots\text{S}$ repulsion.

The $\text{Te}-\text{S}-\text{C}$ angles vary from 85.2 to 90.5°, indicating that p -orbitals on the sulphur atoms are used for bonding to tellurium. The angles on sp^2 hybridized carbon and nitrogen are near 120°, the variation mostly following the pattern predicted from VSEPR theory;²⁰ *i.e.* that the electron density in a double bond has a greater repulsion effect than that in a single bond.

Least squares planes through various parts of the molecules are shown in Tables 8–10. The ligands, except for methyl carbon atoms and hydrogen atoms, are nearly planar.

The intermolecular distances are normal except for two $\text{C}-\text{C}$ distances of 3.34 and 3.45 Å. The other $\text{C}-\text{C}$ distances are all above 3.60 Å. The short interactions may in this case, where such large molecules are involved, be due to packing effects.

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