

Organyltellurium-(IV) and -(II) Dithiocarbamates: Crystal and Molecular Structure of Dimethyldithiocarbamato(2-phenylazophenyl-*C,N'*)tellurium(II)†

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The synthesis of the (2-phenylazophenyl-*C,N'*)tellurium(II) dithiocarbamates $\text{Te}^{\text{II}}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})\text{(dte)}$ (dte = dimethyl-, diethyl-, or dibenzyl-dithiocarbamate) is reported. The corresponding series of tris compounds, $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dte})_3$ is also reported. ^{125}Te N.m.r. data indicate that the tris compounds dissociate to tellurium(II) compounds in solution and ^{125}Te Mössbauer data suggest that the tris compounds are better formulated as loose charge-transfer compounds $\text{Te}^{\text{II}}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dte})\cdot\text{R}'_2\text{NC}(\text{S})\text{S}-\text{S}(\text{S})\text{CNR}'_2$ ($\text{R}' = \text{Me, Et, or CH}_2\text{Ph}$). The crystal and molecular structure of dimethyldithiocarbamato(2-phenylazophenyl-*C,N'*)tellurium(II) has been determined. The compound crystallises in the monoclinic centrosymmetric space group $P2_1/n$ with $a = 6.225(5)$, $b = 12.133(9)$, $c = 21.784(14)$ Å, $\beta = 92.88(5)^\circ$, and $Z = 4$. The refinement converged to $R = 0.0517$. Tellurium is in a distorted planar environment with $\text{Te}-\text{C}$ 2.101(8), $\text{Te}-\text{N}$ 2.340(7), $\text{Te}-\text{S}$ 2.568(2), and $\text{Te}\cdots\text{S}$ 3.255(3) Å. Bond angles include STeS 60.9(1), STeC 89.8(2), CTeN 72.5(3), and NTeS 136.3(2)°. No significant intermolecular contacts are observed.

Structural investigations of tetrakis(dialkyldithiocarbamato)-tellurium(IV) compounds have shown them to be examples of eight-co-ordinate tellurium(IV),¹ having dodecahedral (D_{2d}) structures and with four sulphur atoms closer than the others; the lone pair of electrons has no apparent stereochemical role. Organyltellurium(IV) tris(dialkyldithiocarbamates) have been prepared by Foss² and $\text{TePh}(\text{S}_2\text{CNEt}_2)_3$ has been crystallographically characterised.³ In this compound a *trans* effect of the phenyl group significantly weakens the axial $\text{Te}-\text{S}$ bond (3.228 Å), but the equatorial TeS_3 group, which is almost planar, has $\text{Te}-\text{S}$ distances of ca. 2.715 Å; the lone pair is again stereochemically inactive. No attempts have been made to investigate the reaction of other Lewis bases with $\text{TeR}(\text{dte})_3$ (dte = dialkyldithiocarbamate); one possible approach is to select R to contain a donor group. The tellurated azobenzenes, which we have previously studied,^{4,5} are an appropriate choice (Figure 1). In addition, co-ordination should provide a means of stabilising organytellurium(II) dithiocarbamates, thus allowing a new series of compounds to be investigated. We report our findings in this paper.

Experimental

(a) *Preparations*.—Chloro(2-phenylazophenyl-*C,N'*)tellurium(II) and trichloro(2-phenylazophenyl-*C,N'*)tellurium(IV) were prepared as previously reported.^{4,5} Sodium dimethyldithiocarbamate, $\text{Na}(\text{dmdtc})$, and sodium diethyldithiocarbamate, $\text{Na}(\text{dedtc})$, were commercial specimens. Sodium dibenzylthiocarbamate $\text{Na}(\text{dbdte})$, was prepared by adding sodium hydroxide (3.2 g, 0.08 mol) in water (10 cm^3) to dibenzylamine (17.8 g, 0.08 mol) in ethanol (70 cm^3) with cooling and stirring. Carbon disulphide (6.0 g, 0.08 mol) was added gradually with continued cooling, the temperature being kept below 10 °C. Over a period of 30 min a heavy precipitate of $\text{Na}(\text{dbdte})$ formed.

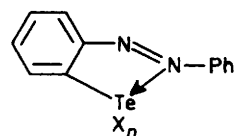


Figure 1. Tellurated azobenzene; X = anionic group, $n = 1$ or 3

*Synthesis of dialkyldithiocarbamato(2-phenylazophenyl-*C,N'*)tellurium(II)*. A solution of the appropriate sodium dialkyldithiocarbamate (1.03 mmol) in dry methanol (15 cm^3) was added with stirring, under dinitrogen, to a solution of chloro(2-phenylazophenyl-*C,N'*)tellurium(II) (0.35 g, 1 mmol) in dichloromethane (25 cm^3) at room temperature. The reaction mixture was stirred for a further 20 min after which the solvents were removed on a rotary film evaporator. Dichloromethane was added to the residue with vigorous stirring. The solution was filtered to remove sodium chloride and the solvent removed. Methanol (5 cm^3) was added to the product which was stirred well and filtered. The crude product was recrystallised from methanol. Yields were as follows: $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$, 85%, m.p. 155–156 °C; $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dbdte})$, 97%, m.p. 102–103 °C; $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dedtc})$, 48%, m.p. 113–115 °C. All three products are dark purple.

*Synthesis of tris(dialkyldithiocarbamato(2-phenylazophenyl-*C,N'*)tellurium(IV)*. To a solution of trichloro(2-phenylazophenyl-*C,N'*)tellurium(IV) (1.25 g, 3 mmol) in dichloromethane (200 cm^3) was added with stirring, under dinitrogen, a solution of the appropriate sodium dialkyldithiocarbamate (10 mmol) in dry methanol (100 cm^3) at room temperature. Stirring was continued for 30 min after which the solvents were removed on a rotary film evaporator. The residue was treated with dichloromethane (200 cm^3) and filtered to remove sodium chloride. Removal of dichloromethane and recrystallisation from methanol gave the purple products. Yields were as follows: $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})_3$, 92%, m.p. 124–125 °C; $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dbdte})_3$, 89%, m.p. 95 °C (decomp.); $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dedtc})_3$, 60%, m.p. 102–104 °C.

Reaction of $\text{Te}^{\text{II}}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$ with bromine. $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$ (0.43 g, 1 mmol) in boiling carbon

† Supplementary data available (SUP No. 56433, 3 pp.): anisotropic thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

tetrachloride (30 cm³) was treated with a solution of bromine (0.2 g) in carbon tetrachloride (10 cm³). The reaction mixture was heated for 10 min, filtered, and cooled to give orange crystals of m.p. 245 °C which on analysis proved to be tribromo(2-phenylazophenyl-*C,N'*)tellurium(IV) (Found: C, 26.2; H, 1.60; N, 5.10. C₁₀H₉Br₃N₂Te requires C, 26.3; H, 1.65; N, 5.10%). Lit.⁴ m.p., 245 °C.

Thermal stability of Te^{IV}(C₆H₄N₂Ph)(dte)₃. It was observed that the compounds were rather unstable in solution. Thus if solutions in methanol or chloroform were brought to boiling for in excess of 10 min, crystals of Te^{II}(C₆H₄N₂Ph)(dte) were obtained: these and the other product, the thiuram disulphide, were characterised by t.l.c.

Analytical data for the new complexes are given in Table 1, which were obtained *via* the Analytical Services Unit, Department of Chemistry, University of Aston.

(b) **Physical Measurements.**—Infrared spectra in the range 4 000–200 cm⁻¹ were obtained with a Perkin-Elmer 599B instrument. The compounds were examined as KBr or CsI discs. Mass spectra were recorded with an AEI MS9 mass spectrometer operating at 70 eV (1 eV = 1.60 × 10⁻¹⁹ J). ¹²⁵Te Mössbauer data were obtained with a ¹²⁵Sb/Rh source, absorbers were at 4 K. ¹²⁵Te N.m.r. spectra were recorded with a Bruker WH 90C spectrometer at the Université de Rouen, France. We thank Professeur P. Granger for these data. Physical data are given in Table 2.

(c) **Crystal and Molecular Structure of Dimethyldithiocarbamate(2-phenylazophenyl-*C,N'*)tellurium(II).**—Small, fine,

dark red-purple needle-shaped crystals of the title compound were obtained by recrystallisation from methanol. They were reasonably stable in the presence of air and light. The density (CHBr₃-CCl₄) was 1.71 + 0.03 g cm⁻³ at 20 °C.

X-Ray measurements. After preliminary oscillation and equi-inclination Weissenberg photographs had been taken, a crystal (0.03 × 0.03 × 0.83 mm) was mounted along its *z* axis on an Enraf-Nonius CAD-4 diffractometer. The automatic centring, indexing, and least-squares routines were applied to 25 reflections to obtain lattice parameters using graphite-mono-chromated Mo-*K_α* radiation. The intensity data were collected in the ω/2θ scan mode, the scan range (ω°) was calculated from (1.0 + 0.35 tan θ) and the scan speed varied in the range 0.3–1.3° min⁻¹ depending on the intensity. 4 189 Reflections were scanned in the range 2 < θ < 27° at room temperature. Three standard reflections were monitored every 2 h and the orientation of the crystal was checked every 100 reflections. No decomposition was observed. Lorentz and polarisation corrections were applied to the data and 2 135 independent observed reflections with *F* > 5σ(*F*) were used in the structure analysis. The crystals were monoclinic with no general absences, *h*0*l* present only when *h* + *l* = 2*n*, and 0*k*0 present only when *k* = 2*n*, consistent with the centrosymmetric space group *P*2₁/*n*. There were four formula weights in the unit cell.

Crystal data. C₁₅H₁₅N₃S₂Te, *M* = 428.6, monoclinic *a* = 6.225(5), *b* = 12.133(9), *c* = 21.784(14) Å, β = 92.88(5)°, *U* = 1 643.19 Å³, *D_m* = 1.71 g cm⁻³, *Z* = 4, *D_c* = 1.73 g cm⁻³, *F*(000) = 839.78, λ(Mo-*K_α*) = 0.710 69 Å, μ = 20.37 cm⁻¹.

Structure analysis and refinement. The atomic parameters for tellurium were found by direct methods using SHELX 76⁶ and confirmed by analysis of the Patterson map. The positions of the sulphur, nitrogen, and carbon atoms were found using difference maps. Anisotropic thermal parameters were calculated for all the non-hydrogen atoms. The positional and thermal parameters for tellurium, sulphur, nitrogen, and carbon were refined by three cycles of blocked full-matrix least-squares refinement, with hydrogen atoms included in their calculated positions. The weighting scheme used was *w* = 1.4559/σ²*F* + 0.002 47*F*² and the refinement converged to *R* = 0.0517 and *R'* = 0.0526. The fractional atomic co-ordinates are listed in Table 3, and bond distances, angles, and torsion angles in Table 4.

Discussion

The analytical data (Table 1) show the stoichiometries of the new compounds to be Te(C₆H₄N₂Ph)(dte) and Te(C₆H₄N₂Ph)(dte)₃ (dte = dialkyldithiocarbamate), but some properties

Table 1. Analytical data for new (2-phenylazophenyl-*C,N'*)tellurium dithiocarbamates

| Compound | Analysis* (%) | | | |
|---|----------------|----------------|----------------|----------------|
| | C | H | N | S |
| Te(C ₆ H ₄ N ₂ Ph)(dmdtc) | 42.1 (42.0) | 3.45 (3.50) | 9.65 (9.80) | 14.5 (14.9) |
| Te(C ₆ H ₄ N ₂ Ph)(dbdte) | 56.3 (55.8) | 3.80 (3.95) | 6.80 (7.25) | 11.2 (11.0) |
| Te(C ₆ H ₄ N ₂ Ph)(dedtc) | 45.0 (44.7) | 4.25 (4.15) | 9.35 (9.20) | |
| Te(C ₆ H ₄ N ₂ Ph)(dmdtc) ₃ | 38.1 (37.7) | 3.90 (4.05) | 10.3 (10.5) | 27.9 (28.7) |
| Te(C ₆ H ₄ N ₂ Ph)(dbdte) ₃ | 61.3 (60.8) | 4.60 (4.55) | 6.25 (6.20) | 17.0 (17.1) |
| Te(C ₆ H ₄ N ₂ Ph)(dedtc) ₃ | 42.5 (43.1) | 5.35 (5.20) | 9.05 (9.30) | |

* Calculated values are given in parentheses.

Table 2. Physical data for organyl-tellurium(II) and -tellurium(IV) compounds

| Compound TeRX | δ(¹²⁵ Te)/p.p.m. ^a | I.r. (cm ⁻¹) | | | ¹²⁵ Te Mössbauer | |
|--|---|--------------------------|-------|--------|------------------------------------|------------------------------------|
| | | ν(CN) | ν(CS) | ν(TeS) | δ ^b /mm s ⁻¹ | Δ ^c /mm s ⁻¹ |
| Te(C ₆ H ₄ N ₂ Ph)Cl | 1 486.5 ^d | — | — | — | 0.78 | 11.8 ^e |
| Te(C ₆ H ₄ N ₂ Ph)Cl ₃ | 1 278.2 | — | — | — | 0.89 | 8.1 |
| Te(C ₆ H ₄ N ₂ Ph)(dmdtc) | 1 228.6 | 1 485 | 980 | 295 | 0.90 | 12.6 |
| Te(C ₆ H ₄ N ₂ Ph)(dmdtc) ₃ | 1 225.4 | 1 485 | 980 | 295 | 0.99 | 11.4 |
| Te(C ₆ H ₄ N ₂ Ph)(dbdte) | 1 239.1 | 1 492 | 1 000 | 295 | — | — |
| Te(C ₆ H ₄ N ₂ Ph)(dbdte) ₃ | 1 239.6 | 1 492 | 1 000 | 295 | — | — |
| Te(C ₆ H ₄ N ₂ Ph)(dedtc) | — | 1 480 | 985 | 300 | — | — |
| Te(C ₆ H ₄ N ₂ Ph)(dedtc) ₃ | — | 1 500 | 990 | 300 | — | — |
| Te(C ₆ H ₄ N ₂ Ph)(SCN) ^f | — | — | — | — | 0.86 | 11.9 |
| Te(C ₆ H ₄ N ₂ Ph)(O ₂ CMe) ^f | — | — | — | — | 0.82 | 12.5 |

^a Versus TeMe₂; in CDCl₃ unless otherwise stated. ^b With respect to I/Cu; error ± 0.08 mm s⁻¹. ^c Error ± 0.2 mm s⁻¹. ^d In dimethyl sulphoxide. ^e See F. H. Musa, Ph.D. Thesis, University of Aston in Birmingham, 1978. ^f For synthesis see ref. 7.

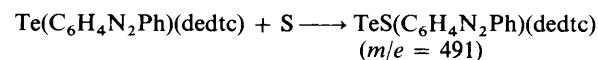
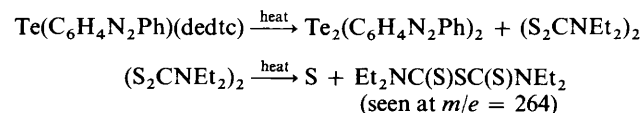
of the tris(dithiocarbamates) do raise questions as to whether they are correctly formulated as derivatives of tellurium(IV). The qualitative observation that the two series of compounds have the same colour is unexpected, although the great similarity of i.r. data (Table 2) is in line with what we⁷ and others^{8,9} have observed for the pair $\text{Te}(\text{dtc})_2$ and $\text{Te}(\text{dtc})_4$. Thus the i.r. data, being similar to those for compounds of known

structure in which the dithiocarbamate group is unsymmetrically bidentate, are consistent with the presence of similarly bonded dtc groups in the present series of compounds.

The mass spectrum of, for example $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dedtc})$ shows a molecular ion at $m/e = 459$ (^{130}Te , ^{12}C , ^1H , ^{14}N , ^{32}S) together with the expected fragmentation pattern. It is interesting that an ion with the characteristic isotope pattern of tellurium is seen at $(P + 32)$, i.e. $m/e = 491$. This suggests that, as is very common for organytellurium compounds, some pyrolysis has occurred (see below). The mass spectra of

Table 3. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$

| Atom | x | y | z |
|-------|------------|-----------|----------|
| Te | 2 356(1) | 1 868(0) | 976(0) |
| S(1) | 4 830(4) | 1 264(2) | 1 893(1) |
| S(2) | 6 119(5) | 3 509(2) | 1 480(2) |
| N(1) | -1 943(10) | 1 202(6) | 278(3) |
| N(2) | -557(10) | 1 962(5) | 256(3) |
| C(11) | -1 023(13) | 2 859(7) | -130(4) |
| C(12) | -3 133(15) | 3 092(9) | -345(5) |
| C(13) | -3 513(20) | 3 966(10) | -741(6) |
| C(14) | -1 831(18) | 4 604(9) | -934(5) |
| C(15) | 276(17) | 4 380(9) | -720(5) |
| C(16) | 655(14) | 3 513(8) | -314(5) |
| C(21) | -1 380(12) | 375(7) | 693(4) |
| C(22) | 536(13) | 423(7) | 1 064(4) |
| C(23) | 1 019(16) | -443(7) | 1 463(4) |
| C(24) | -394(17) | -1 325(8) | 1 494(5) |
| C(25) | -2 300(16) | -1 363(8) | 1 135(5) |
| C(26) | -2 809(15) | -514(8) | 731(4) |
| N(3) | 8 309(12) | 2 294(7) | 2 302(4) |
| C(31) | 6 574(12) | 2 382(7) | 1 914(4) |
| C(32) | 9 814(17) | 3 216(9) | 2 381(5) |
| C(33) | 8 781(18) | 1 299(9) | 2 670(5) |



$\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dtc})_3$ are all very similar and consist of the superposition of the spectra of $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dtc})$ and of $(\text{S}_2\text{CNR}')_2$ ($\text{R}' = \text{alkyl}$), indicating complete decomposition to tellurium(II) and the disulphide in the gas phase.

The lack of thermal stability of the tris compounds is further shown by experiments in which they are dissolved in boiling solvents such as methanol or chloroform when t.l.c. analysis shows decomposition to tellurium(II) and the disulphide. This led us to examine their nature in solution using ^{125}Te n.m.r. spectroscopy (Table 2). The mono- and tri-chlorides, both of which are crystallographically characterised,^{4,5} are included as an authentic Te^{II} , Te^{IV} pair. It is seen that a more positive chemical shift occurs for the tellurium(II) compound. The data

Table 4. Bond distances (Å), angles (°), and torsion angles (°) in $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$

| | | | |
|-----------------------|-----------|-----------------------|-----------|
| Te-S(1) | 2.568(2) | N(1)-C(21) | 1.384(10) |
| Te-S(2) | 3.225(3) | C(21)-C(22) | 1.408(11) |
| Te-N(2) | 2.340(7) | C(22)-C(23) | 1.387(12) |
| Te-C(22) | 2.101(8) | C(23)-C(24) | 1.389(14) |
| C(11)-C(12) | 1.401(12) | C(24)-C(25) | 1.389(14) |
| C(12)-C(13) | 1.380(14) | C(25)-C(26) | 1.381(14) |
| C(13)-C(14) | 1.384(16) | C(26)-C(21) | 1.403(12) |
| C(14)-C(15) | 1.396(15) | S(1)-C(31) | 1.736(9) |
| C(15)-C(16) | 1.387(13) | S(2)-C(31) | 1.679(9) |
| C(16)-C(11) | 1.387(13) | C(31)-N(3) | 1.342(11) |
| C(11)-N(2) | 1.396(10) | N(3)-C(32) | 1.464(12) |
| N(2)-N(1) | 1.265(9) | N(3)-C(33) | 1.470(13) |
| S(1)-Te-S(2) | 60.9(1) | N(1)-C(21)-C(26) | 117.1(7) |
| S(1)-Te-C(22) | 89.8(2) | C(22)-C(21)-C(26) | 121.3(8) |
| C(22)-Te-N(2) | 72.5(3) | C(21)-C(22)-C(23) | 118.7(8) |
| N(2)-Te-S(2) | 136.3(2) | Te-C(22)-C(23) | 126.0(6) |
| C(11)-N(2)-Te | 124.9(5) | Te-C(22)-C(21) | 115.3(6) |
| C(11)-N(2)-N(1) | 118.0(7) | C(22)-C(23)-C(24) | 119.7(9) |
| N(1)-N(2)-Te | 116.5(5) | C(23)-C(24)-C(25) | 121.5(9) |
| C(12)-C(11)-N(2) | 121.4(8) | C(24)-C(25)-C(26) | 119.8(9) |
| C(16)-C(11)-N(2) | 118.9(8) | C(25)-C(26)-C(21) | 119.0(8) |
| C(12)-C(11)-C(16) | 119.7(8) | Te-S(1)-C(31) | 98.5(3) |
| C(11)-C(12)-C(13) | 119.5(9) | Te-S(2)-C(31) | 77.8(3) |
| C(12)-C(13)-C(14) | 120.7(10) | S(1)-C(31)-S(2) | 122.3(5) |
| C(13)-C(14)-C(15) | 120.2(9) | S(1)-C(31)-N(3) | 115.9(7) |
| C(14)-C(15)-C(16) | 119.1(9) | S(2)-C(31)-N(3) | 121.8(7) |
| C(15)-C(16)-C(11) | 120.8(9) | C(31)-N(3)-C(32) | 120.2(8) |
| N(2)-N(1)-C(21) | 113.7(6) | C(31)-N(3)-C(33) | 122.7(8) |
| N(1)-C(21)-C(22) | 121.7(7) | C(32)-N(3)-C(32) | 117.0(8) |
| C(11)-N(2)-N(1)-C(21) | -177.2(7) | N(2)-N(1)-C(21)-C(26) | -178.2(7) |
| C(12)-C(11)-N(2)-N(1) | 18.5(6) | N(2)-N(1)-C(21)-C(22) | 2.1(7) |
| C(16)-C(11)-N(2)-N(1) | -159.9(6) | | |

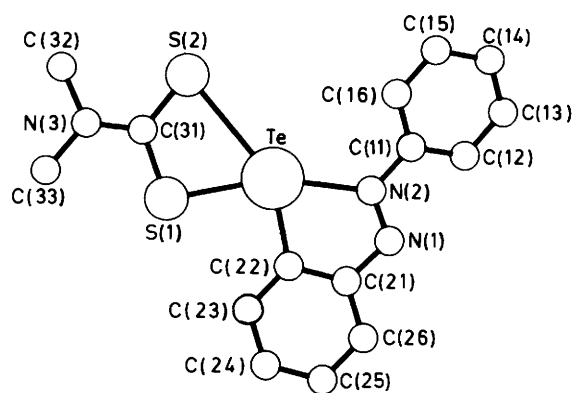


Figure 2. Molecular structure of $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$

for the dithiocarbamates show two features. First, the chemical shift of $\text{Te}^{\text{II}}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})\text{X}$ is sensitive to X, with the more electronegative group (Cl) giving the greater deshielding. Secondly, the oxidation state of tellurium in solution is the same for all the dithiocarbamate compounds; since $\text{Te}^{\text{II}}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$ has been crystallographically characterised (see later) it must be concluded that the relevant oxidation state is tellurium(II).

The instability of $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dtc})_3$ in solution frustrated our attempts to obtain suitable single crystals for X-ray analysis. We therefore turned to ^{125}Te Mössbauer spectroscopy as a means of probing the solid-state structures. Included in Table 2 for comparative purposes are data for $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})\text{X}$ (X = Cl, NCS, or O_2CMe) and $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})\text{Cl}_3$. Tellurium isomer shift data are generally insensitive and are subject to relatively large errors. However, it is to be expected that δ would become more positive from TeRX to TeRX_3 since the s electrons should be more deshielded in the tellurium(IV) case.¹⁰ Within the present series, comparison of $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})\text{Cl}$ with $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})\text{Cl}_3$ indicates that this is the case. However even for the monochloride the shift seems more positive than for other tellurium(II) species; indeed when other TeRX compounds from Table 2 are considered, it is noted that they are the most positive shifts observed for tellurium(II) compounds¹⁰ and, further, that the demarcation of δ for Te^{II} and Te^{IV} is blurred.

Previous work would predict the observation of values of quadrupole splittings for TeRX_3 ¹⁰ of $\sim 9.0 \text{ mm s}^{-1}$, and for TeRX^{II} of $\sim 14 \text{ mm s}^{-1}$. The value for $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})\text{Cl}_3$ is in accord with expectation, but those for $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})\text{X}$ (X = Cl, NCS, dtc, or O_2CMe) lie in the range $11.8\text{--}12.6 \text{ mm s}^{-1}$ and are thus lower than expected. One possibility is that tellurium p -electron density is delocalised into the heterocyclic $\text{C}=\text{C}-\text{N}=\text{N}-\text{Te}$ ring (N=N is longer and N-C shorter than in azobenzene for X = dmdtc, NCS,¹² and O_2CMe ¹²); if this were the case, further deshielding of the s electrons would occur and a more positive δ should result which is in line with observation.

The most interesting aspect of the data is the comparison of Δ for $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$ (12.6 mm s^{-1}) and $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})_3$ (11.4 mm s^{-1}). The values are significantly different and rule out the possibility that the tris complex should be formulated as a mixture of $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$ and the disulphide, $\text{Me}_2\text{NC}(\text{S})\text{S}-\text{SC}(\text{S})\text{NMe}_2$; however the observed value of Δ is more compatible with Te^{II} than with Te^{IV} . It is suggested that the tris compound may be formulated as a loose charge-transfer complex of $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$ and the disulphide. The removal of p -electron density from tellurium, which is reflected in the lowering of Δ from 12.6 to 11.4 mm s^{-1} is

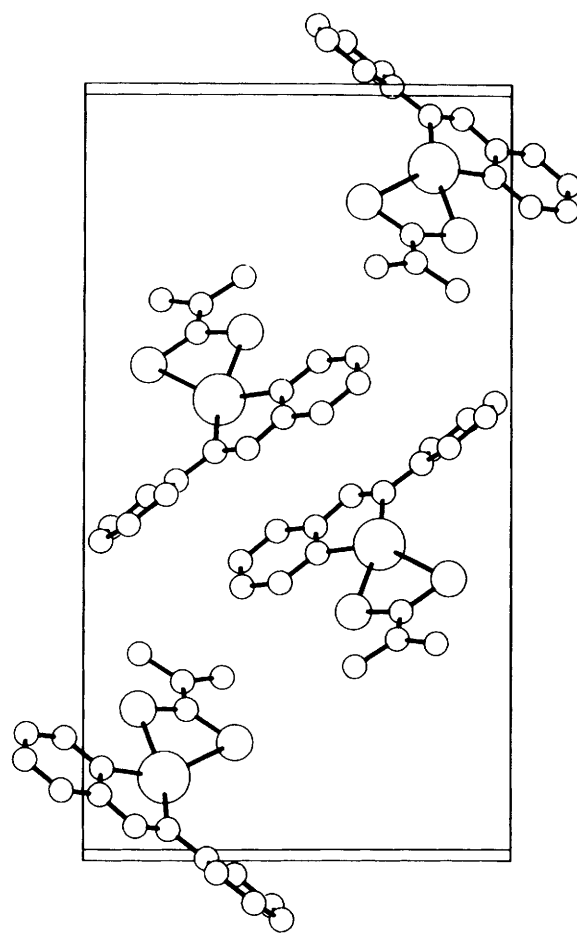


Figure 3. Unit cell of $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$

consistent with this formulation, which has also been suggested for $(p\text{-EtOC}_6\text{H}_4)\text{Te}(\text{CH}_2)\text{Te}(\text{C}_6\text{H}_4\text{OEt}-p)\text{-CH}_2\text{I}_2$.¹³ The suggestion is also compatible with the solution data, particularly the ^{125}Te n.m.r. data which imply ready dissociation to give $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})$. The large difference in temperature between the n.m.r. and Mössbauer measurements could reflect different regimes of stability.

It was of interest to note that attempts to prepare $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})(\text{dmdtc})\text{Br}_2$ gave the tribromo complex.

The Crystal and Molecular Structure of Dimethyldithiocarbamate(2-phenylazophenyl-C,N')tellurium(II).—The structure of the complex and the atom numbering is shown in Figure 2 and a unit-cell diagram in Figure 3. The structure consists of one discrete repeating molecule. The co-ordination about tellurium can be considered as essentially distorted square planar. The tellurium atom is bonded to carbon, nitrogen, and to two sulphur atoms with all five atoms being in approximately one plane (mean deviation 0.034 \AA). The description 'trapezoid planar' is preferred since it has been reported for many four-coordinate tellurium(II) complexes with bidentate ligands.¹ The phenyl ring is planar with a mean deviation of 0.004 \AA and with N(1) and N(2) lying slightly below it. The free phenyl ring, C(11)—C(16), is also planar (mean deviation = 0.006 \AA) but is twisted some 19° about the C(11)—N(2) bond away from planarity with the N(1)—N(2) bond. The free phenyl group makes an interplanar angle of 25° with the Te, N(2), N(1), C(21), C(22) ring which is itself tilted at an interplanar angle of 2.5° to the attached phenyl group. This five-membered nitrogen-

containing ring has an interplanar angle of 6.8° relative to the Te and the attached dithiocarbamate group [S(1), C(31), S(2), N(3), C(32), and C(33)]. The planes through Te, S(1), C(31), S(2) and C(31), N(3), C(32), C(33) are at an angle of 7.1° to one another. The dithiocarbamate group is planar (mean deviation = 0.028 \AA).

The distance Te–C(22) [$2.101(8) \text{ \AA}$] is in good agreement with the sum of the Pauling single-bond covalent radii¹⁴ of Te (1.37 \AA) and the sp^2 hybridised carbon (0.74 \AA), and with values in Te complexes: $^1\text{TePh}(\text{tu})_2\text{Cl}$, $[\text{NMe}_4][\text{TePh}(\text{ECN})_2]$ (E = S or Se), and $\text{TePh}(\text{tmsu})\text{Cl}$ (where tu = thiourea and tmsu = *N,N'*-trimethyleneselenourea) which lie in the range 2.10 – 2.104 \AA . The Te–N distance [$2.340(7) \text{ \AA}$] is larger than the sum of the covalent radii (2.07 \AA)¹⁴ and is also larger than in $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})\text{Cl}$, (2.23 \AA),⁴ but is comparable with the values in $\text{Te}(\text{C}_6\text{H}_4\text{N}_2\text{Ph})\text{Cl}_3$ (2.417 \AA)⁵ and $\text{Te}(\text{C}_9\text{H}_8\text{NO}_2\text{Cl}_3$ (2.402 \AA).¹⁵ The Te–S bonds differ in length [$2.568(2)$, $3.225(3) \text{ \AA}$]. The Te–S(1) bond is longer than the sum of the covalent radii¹⁴ (2.38 \AA), but similar to values found in other Te^{II} complexes¹ with bidentate sulphur ligands, e.g. $\text{Te}(\text{S}_2\text{COR}')_2$ ($R' = \text{Me}$ or Et), $\text{Te}(\text{S}_2\text{CNCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)_2$, and $\text{Te}(\text{S}_2\text{CNEt})_2$ which fall in the range 2.49 – 2.52 \AA . The Te–S(2) bond is within the van der Waals distance (4.05 ¹⁴ or 3.91 \AA ¹⁶) indicating a weak bond. Similar bonds have been found in the structures of $\text{Te}[\text{S}_2\text{P}(\text{OR}')_2]_2$ ¹ ($R' = \text{Me}$ or Et) and $\text{TePh}(\text{S}_2\text{CNEt}_2)_3$ which fall in the range 3.209 – 3.311 \AA .¹

An alternative view of the geometry of the molecule is to regard it as a ψ -trigonal bipyramidal structure with C(22) and two lone pairs making up the equatorial co-ordination with S(1) and N(2) axial. S(2) then makes a weak secondary interaction in the C(22), S(1), N(2) plane which bisects the angle between the lone pairs. Estimates have been made for the covalent radii of Te^{II} for axial and equatorial directions¹⁷ (taking the tellurium atom as effectively ellipsoidal). Thus the estimated Te–S(1) distance is 2.58 \AA [observed $2.568(2) \text{ \AA}$], and for Te–N(2) the estimate is 2.28 \AA and the observed $2.340(7) \text{ \AA}$. No significant intermolecular interactions are noted.

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