# 2-Pyridyl- and Quinolin-2-yl-functionalised Organyltellurium Ligands. The Stabilisation of Diorganyl Tritellurides. The Crystal and Molecular Structures of 2-(2-Pyridyl)phenyltellurium(IV) Tribromide, Dimethyldithiocarbamato[2-(2-pyridyl)phenyl]tellurium(II), and *p*-Ethoxyphenyl 2-(2-Pyridyl)phenyl Telluride*

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The syntheses and spectroscopic data ($^{13}C$ n.m.r.) for some new organyltellurium ligands are described. Thus *trans* metallation of 2-(2-pyridyl)phenyl- (R) or 2-(quinolin-2-yl)phenyl- (R′) mercury(II) chloride with $TeBr_4$ gives the organyltellurium tribromides $RTeBr_3$ and $R'TeBr_3$, which may be reduced to the organyltellurium bromides RTeBr and R′TeBr, some metathesis reactions of which are described; or, in the presence of excess hydrazine, to diorganyl ditellurides, $R_2Te_2$ and $R'_2Te_2$. Reduction of $RTeBr_3X$ with $NaBH_4$ gave a novel tritelluride, $R_2Te_3$; a method of preparation for $R'_2Te_3$ was also devised. Syntheses of the tellurides $R_2Te$, $R'_2Te$, and $RTe(C_6H_4OEt\text{-}p)$ were developed and the intermediacy of ionic compounds $[R_2TeBr][HgClBr_2]$ and $[R_2TeCl][HgCl_3]$ noted. The crystal structures of 2-(2-pyridyl)phenyltellurium(IV) tribromide, (**1**), dimethyldithiocarbamato[2-(2-pyridyl)phenyl]tellurium(II), (**2**), and *p*-ethoxyphenyl 2-(2-pyridyl)phenyltelluride, (**3**), have been determined from three-dimensional *X*-ray counter data. Complex (**1**) is triclinic, space group $P\bar{1}$ with $a = 6.953(6)$, $b = 8.382(1)$, $c = 12.133(2)$ Å, $\alpha = 78.68(1)$, $\beta = 82.87(4)$, $\gamma = 87.14(4)°$, and $Z = 2$; $R = 0.0735$ for 1 963 observed reflections. The co-ordination about Te is octahedral with a vacant equatorial position, two Br atoms apical, the third Br and the organic group equatorial [Te–C, 2.110(19); Te–N, 2.244(14) Å]. The compound is essentially monomeric, with a weak association between Te and Br [3.596(3) Å] in a neighbouring molecule. Complex (**2**) is triclinic, space group $P\bar{1}$ with $a = 8.809(3)$, $b = 9.032(5)$, $c = 10.727(4)$ Å, $\alpha = 83.06(4)$, $\beta = 86.49(3)$, $\gamma = 63.68(4)$, and $Z = 2$; $R = 0.0417$ for 2 502 observed reflections. The co-ordination about Te is trigonal bipyramidal, C(1) and two lone pairs of Te comprising the equatorial co-ordination and the S(1) atom together with the pyridyl-N atom axial [Te–C, 2.111(5); Te–N, 2.354(4) Å]. No significant intermolecular contacts occur. Complex (**3**) is monoclinic, space group $P2_1/c$ with $a = 13.422(2)$, $b = 16.469(3)$, $c = 7.711(3)$ Å, $\beta = 91.01(2)°$, and $Z = 4$; $R = 0.0415$ for 2 014 observed reflections. The Te atom is bonded to two C atoms. The N atom of the pyridyl ring is twisted away from Te [Te–N, 2.695(4) Å] by rotation of the pyridyl ring about the pyridyl–phenyl bond by 23.2(3)°, a manifestation of the *trans* effect of the Te–C(ethoxyphenyl) covalent bond.

Current objectives include the synthesis of ligands which are bidentate or multidentate containing only tellurium atoms[1] and also the preparation of ligands which, in addition to tellurium, contain a harder donor atom, *e.g.* oxygen or nitrogen. We have reported briefly on our synthesis of organyltellurides functionalised with imino groups[2] and in this paper describe the syntheses of 2-pyridyl- and quinolin-2-yl-functionalised organyltellurium compounds. These materials constitute a new class of ligand, although a few related organylselenium compounds and their complexes are known, *e.g.* bis[2-(2-pyridyl)ethyl] selenide (L),[3] a terdentate ligand which forms complexes $[Cu(L)X_2]$ (X = Cl, Br, $NO_3$, or $ClO_4$). The preparation of 2-(2-pyridyl)benzo[*b*]selenophene (L′) has been reported together with the palladium(II) complex, $[Pd(L')Cl_2]$.[4] Amongst known selenium ligands containing a quinoline nucleus may be listed 8-methylselenoquinoline[5] and quinoline-8-selenol.[6]

During the course of the preparative work novel tritellurides were isolated, a preliminary account of which has appeared;[7] full preparative details are given here. Following that earlier structural study[7] of bis[2-(2-pyridyl)phenyl] tritelluride in which a short Te–N [2.554(7) Å] interaction occurs, we now also report the crystal structures of 2-(2-pyridyl)phenyltellurium(IV) tribomide, (**1**), dimethyldithiocarbamato[2-(2-pyridyl)phenyl]tellurium(II), (**2**), and *p*-ethoxyphenyl 2-(2-pyridyl)phenyl telluride, (**3**). We examine the effect of tellurium oxidation state and ligand type *trans* to nitrogen on the Te–N interaction.

## Experimental

*Synthesis of New Organyltellurium Compounds.*—(a) *2-Pyridyl derivatives. 2-(2-Pyridyl)phenylmercury*(II) *chloride.* 2-Phenylpyridine (7.81 g, 50 mmol) and mercury(II) acetate (15.93 g, 50 mmol) were mixed in absolute ethanol (100 $cm^3$) and refluxed for 24 h, after which LiCl (4.4 g) in absolute ethanol (100 $cm^3$) was added with vigorous stirring; the thick mixture was heated

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

for a further 15 min. The reaction mixture was poured into distilled water (300 cm$^3$) and filtered. The filtrate was left to stand at room temperature whereupon a white crystalline compound formed which was filtered off, washed with cold methanol, and oven dried at 60 °C; yield 35.5%, m.p. 138—140 °C.

*2-(2-Pyridyl)phenyltellurium*(IV) *tribomide*, (**1**). A solution of 2-(2-pyridyl)phenylmercury(II) chloride (3.9 g, 10 mmol) in dry 1,4-dioxane (20 cm$^3$) was added to tellurium tetrabromide (4.47 g, 10 mmol) dissolved in dry 1,4-dioxane (15 cm$^3$). The mixture was refluxed under dry dinitrogen for 2 h during which time a yellow compound precipitated. The hot mixture was filtered and the yellow product washed with pure ethanol and recrystallised from acetonitrile–methanol (1:1) to give yellow crystals; yield 77%, m.p. 283—285 °C.

*2-(2-Pyridyl)phenyltellurium*(II) *bromide*. 2-(2-Pyridyl)phenyltellurium(IV) tribromide (1.04 g, 2 mmol) was suspended in absolute ethanol. Hydrazine hydrate (0.1 g, 2 mmol) was added to the stirred mixture under dinitrogen. The solid dissolved at the completion of the addition and the solution was refluxed for 15 min and set aside to cool to room temperature. Yellow crystals deposited which were filtered off and washed with ethanol; yield 65%, m.p. 178—180 °C.

*Bis*[*2-(2-pyridyl)phenyl*] *ditelluride*. 2-(2-Pyridyl)phenyltellurium(IV) tribomide (1.04 g, 2 mmol) was dissolved in acetonitrile–ethanol (2:1) (30 cm$^3$) and treated with excess hydrazine hydrate (0.6 g, 12 mmol) in ethanol (10 cm$^3$) and then refluxed for 20 min. The precipitate so formed was filtered off and recrystallised from benzene to give yellow-orange crystals; yield 60%, m.p. 150—152 °C.

*Bis*[*2-(2-pyridyl)phenyl*] *tritelluride*. 2-(2-Pyridyl)phenyltellurium(IV) tribomide (2.6 g, 5 mmol) was suspended in absolute ethanol (60 cm$^3$) and treated dropwise under dinitrogen with a solution of sodium tetrahydroborate (1.1 g, 30 mmol) in ethanol. The solid dissolved as the addition proceeded, then a black precipitate of tellurium formed; this then redissolved to give, finally, a red solution. The solution was heated for 10 min, filtered hot and allowed to cool to room temperature. A red-brown solid appeared which was filtered off and recrystallised from benzene–toluene; yield 90% (based on Te content of the tribromide), m.p. 165—166 °C.

*Reaction of bis*[*2-(2-pyridyl)phenyl*] *tritelluride with copper metal*. Bis[2-(2-pyridyl)phenyl] tritelluride (1.38 g, 2 mmol) dissolved in 1,4-dioxane (15 cm$^3$) was treated with copper powder (0.38 g, 6 mmol). The mixture was refluxed for 24 h and then filtered. Removal of the solvent *in vacuo* gave a residue which, on recrystallisation from ethanol gave golden yellow crystals of bis[2-(2-pyridyl)phenyl] ditelluride (by analysis, m.p., and mixed m.p.).

*Bis*[*2-(2-pyridyl)phenyl*] *telluride*. 2-(2-Pyridyl)phenyltellurium(IV) tribromide (1.04 g, 2 mmol) and 2-(2-pyridyl)phenylmercury(II) chloride (0.78 g, 2 mmol) were dissolved in dry 1,4-dioxane (20 cm$^3$) and refluxed for 3 h. The white solid thus formed was filtered off and washed with dry methanol, followed by recrystallisation from nitromethane, m.p. 235—238 °C. Analysis indicated the composition $C_{22}H_{16}Br_3ClHgN_2Te$ (Found: C, 29.3; H, 1.80; N, 3.10. $C_{22}H_{16}Br_3ClHgN_2Te$ requires C, 29.0; H, 1.75; N, 3.05%). The white solid (0.91 g, 1 mmol) was suspended in ethanol, stirred, and treated dropwise with a solution of hydrazine hydrate (0.2 g, 5 mmol) in ethanol (5 cm$^3$) after which it was heated. Elemental mercury deposited and the solution became yellow. After filtering, water was added to the filtrate to precipitate a yellow compound which was filtered off, washed with water, and recrystallised from ethanol; yield 65%, m.p. 102—103 °C.

*Bis*[*2-(2-pyridinio)phenyl*]*tellurium*(II) *diperchlorate*. Bis[2-(2-pyridyl)phenyl] telluride (0.44 g, 1 mmol) was dissolved in hot methanol (30 cm$^3$) and treated with an excess of perchloric acid. The solution was heated with stirring for 30 min and filtered. The filtrate was set aside and, over a period of time, a yellow crystalline compound formed which was filtered off, washed with ethanol, and air dried; m.p. 270 °C (decomp.).

p-*Ethoxyphenyl 2-(2-pyridyl)phenyl telluride*, (**3**). 2-(2-Pyridyl)phenylmercury(II) chloride (1.95 g, 5 mmol) and *p*-ethoxyphenyltellurium(IV) trichloride[8] (1.28 g, 5 mmol) were dissolved in dry 1,4-dioxane (20 cm$^3$) and refluxed for 2 h. The white product was filtered from the hot solution, washed with methanol, and oven dried at 100 °C (Found: C, 30.4; H, 2.50; N, 1.60. $C_{19}H_{17}Cl_4NOTe$ requires C, 30.6; H, 2.30; N, 1.85%). The white compound was suspended in ethanol (30 cm$^3$) and treated dropwise with an excess of hydrazine hydrate and stirred for 15 min. Water (50 cm$^3$) was added and the reaction mixture filtered. The solid obtained was recrystallised from ethanol–acetone (1:1) to give a pale yellow crystalline compound; yield 67%, m.p. 124—126 °C.

*Dimethyldithiocarbamato*[*2-(2-pyridyl)phenyl*]*tellurium*(II) (**2**). 2-(2-Pyridyl)phenyltellurium(II) bromide (0.36 g, 1 mmol) in acetonitrile (15 cm$^3$) was treated with an acetonitrile solution (15 cm$^3$) of sodium dimethyldithiocarbamate [Na(dmdtc)] (0.18 g, 1 mmol); the mixture was then heated for 30 min. The solution was filtered and the filtrate left to cool to afford a yellow crystalline material; 75% yield, m.p. 165—167 °C.

(b) *Quinolin-2-yl derivatives*. *2-(Quinolin-2-yl)phenylmercury*(II) *chloride*. 2-Phenylquinoline[9] (m.p. 84—85 °C, lit.,[9] 85—86 °C) (10.25 g, 50 mmol) and mercury(II) acetate (15.93 g, 50 mmol) were mixed and refluxed in absolute ethanol (100 cm$^3$). After 7 h, LiCl (4.4 g) in methanol (30 cm$^3$) was added after which the procedure was identical to that for the 2-pyridyl derivative. The white product had m.p. 180—182 °C and yield 34%.

*2-(Quinolin-2-yl)phenyltellurium*(IV) *tribromide*, *2-(quinolin-2-yl)phenyltellurium*(II) *bromide, and bis*[*2-(quinolin-2-yl)-phenyl*] *ditelluride*. These compounds (m.p. 340, 150, and 220—222 °C respectively) were all prepared by methods analogous to those developed for the 2-(2-pyridyl)phenyl derivatives.

*Bis*[*2-(quinolin-2-yl)phenyl*] *telluride*. Bis[2-(quinolin-2-yl)-phenyl] ditelluride (1.33 g, 2 mmol) and copper powder (0.38 g, 6 mmol) were stirred under reflux in 1,4-dioxane (15 cm$^3$) for 24 h. The mixture was filtered and the solvent removed *in vacuo*. The residue was recrystallised from ethanol to give a yellow crystalline compound; yield 70%, m.p. 187—189 °C.

*Bis*[*2-(quinolin-2-yl)phenyl*] *tritelluride*. Sodium tetrahydroborate reduction of 2-(quinolin-2-yl)phenyltellurium(IV) tribromide gave only the ditelluride; also no precipitated tellurium was seen during the reaction. The following method was therefore adopted: 2-(quinolin-2-yl)phenyltellurium(IV) tribromide (2.28 g, 4 mmol) was suspended in ethanol (25 cm$^3$), tellurium powder (0.26 g, 4 mmol) was then added and the mixture stirred under argon. Sodium tetrahydroborate (1.1 g) in ethanol (20 cm$^3$) was then introduced slowly until all the tellurium had dissolved, the resulting red solution was refluxed for 30 min and then set aside to cool. An orange product formed which was filtered and recrystallised from benzene to give an 80% yield of an orange-brown compound, m.p. 211—212 °C.

*Dimethyldithiocarbamato*[*2-(quinolin-2-yl)phenyl*]*tellurium*(II). This compound, m.p. 206 °C, was prepared by the method used for the 2-pyridyl analogue.

Analytical data for the compounds are given in Table 1. The Scheme summarises the syntheses and interconversions within the 2-(2-pyridyl)phenyl series.

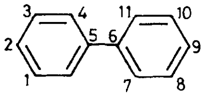
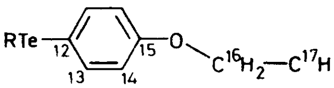
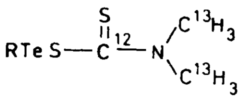
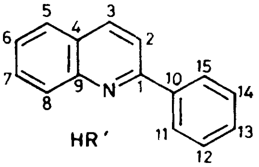
*Physical Measurements*.—Melting points (uncorrected) were determined with a Gallenkamp electrically heated apparatus. The molar conductance ($10^{-3}$ mol dm$^{-3}$ solutions) was measured at room temperature with a Mullard bridge and dip cell with bright platinum electrodes (type E7591/B).

**Table 1.** Analytical data for new organyltellurium compounds; R = 2-(2-pyridyl)phenyl, R′ = 2-(quinolin-2-yl)phenyl, dmdtc = dimethyldithiocarbamate

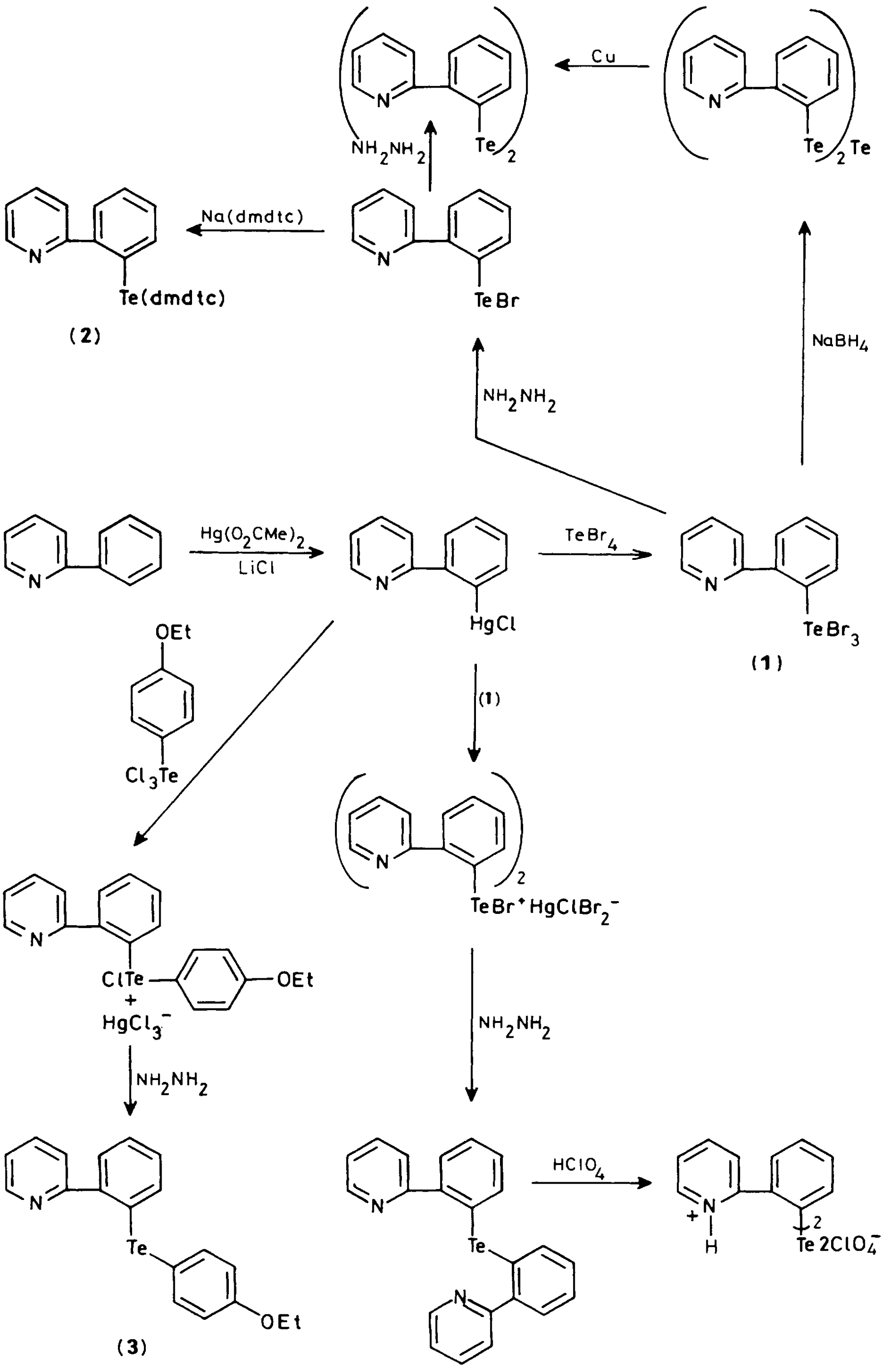
| | | Found (%) | | | | | Calc. (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Colour | C | H | N | Br | Te | C | H | N | Br | Te |
| RHgCl | White | 33.7 | 2.00 | 3.50 | | | 33.8 | 2.10 | 3.60 | | |
| $RTeBr_3$ | Yellow | 25.7 | 1.40 | 2.80 | 46.3 | | 25.3 | 1.60 | 2.70 | 46.0 | |
| RTeBr | Yellow | 37.0 | 2.20 | 3.80 | 22.3 | | 36.5 | 2.20 | 3.85 | 22.1 | |
| $R_2Te_2$ | Yellow-orange | 46.6 | 3.00 | 5.20 | | 45.4 | 46.9 | 2.90 | 5.00 | | 46.0 |
| $R_2Te_3$ | Brown-red | 39.0 | 2.30 | 3.90 | | 55.6 | 38.2 | 2.30 | 4.00 | | 55.4 |
| $R_2Te$ | Yellow | 60.5 | 3.70 | 6.30 | | 28.5 | 60.6 | 3.70 | 6.40 | | 29.2 |
| $[(HR)_2Te][ClO_4]$[a] | Dull yellow | 41.6 | 2.60 | 4.10 | | | 41.5 | 2.50 | 4.40 | | |
| $R(C_6H_4OEt\text{-}p)$ | Pale yellow | 56.5 | 4.10 | 3.40 | | 31.1 | 56.6 | 4.30 | 3.45 | | 31.7 |
| RTe(dmdtc) | Yellow | 42.0 | 3.50 | 7.00 | < 1 | | 41.8 | 3.50 | 6.95 | 0.0 | |
| HR′ | White | 87.2 | 5.20 | 6.80 | | | 87.8 | 5.40 | 6.80 | | |
| R′HgCl | White | 40.9 | 2.10 | 2.90 | | | 40.9 | 2.30 | 3.20 | | |
| $R'TeBr_3$ | Bright yellow | 31.3 | 1.70 | 2.60 | 41.9 | | 31.2 | 1.75 | 2.45 | 41.9 | |
| R′TeBr | Yellow | 43.9 | 2.30 | 3.20 | 19.3 | | 43.8 | 2.45 | 3.40 | 19.4 | |
| $R'_2Te_2$ | Orange | 54.1 | 2.90 | 3.90 | | 38.1 | 54.3 | 3.04 | 4.20 | | 38.5 |
| $R'_2Te$ | Yellow | 67.5 | 3.50 | 4.90 | | 23.6 | 67.2 | 3.75 | 5.20 | | 23.8 |
| $R'_2Te_3$ | Orange-brown | 45.8 | 2.30 | 3.50 | | 47.5 | 45.5 | 2.55 | 3.55 | | 48.4 |
| R′Te(dmdtc) | Yellow | 48.0 | 3.30 | 6.40 | | | 47.8 | 3.55 | 6.20 | | |
| $[R_2TeBr][HgClX_2]$[b] | White | 29.3 | 1.80 | 3.10 | | | 29.0 | 1.75 | 3.05 | | |
| $[R_2TeCl][HgCl_3]$[c] | White | 30.4 | 2.50 | 1.60 | | | 30.6 | 2.30 | 1.85 | | |

[a] $\Lambda(CH_3CN)$, 251 ohm$^{-1}$ cm$^2$ mol$^{-1}$. [b] $\Lambda(CH_3NO_2)$, 73.7 ohm$^{-1}$ cm$^2$ mol$^{-1}$. [c] $\Lambda(Me_2SO)$, 33.6 ohm$^{-1}$ cm$^2$ mol$^{-1}$.

**Table 2.** Some $^{13}C$ n.m.r. data for organylmercury and organyltellurium derivatives of 2-phenylpyridine (HR) and 2-phenylquinoline (HR′)

| Compound (solvent) | $^{13}C$ Chemical shifts (p.p.m.) relative to $SiMe_4$ | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C^1$ | $C^2$ | $C^3$ | $C^4$ | $C^5$ | $C^6$ | $C^7$ | $C^8$ | $C^9$ | $C^{10}$ | $C^{11}$ | |
| <br>HR<br>$(CDCl_3)$ | 149.1 | 119.9 | 136.2 | 121.5 | 156.7 | 138.8<br>139.6[a] | 126.3<br>127.1[a] | <br>128.7[a] | 128.1<br>129[a] | <br>128.7[a] | 126.3<br>127.1[a] | |
| RHgCl<br>$(Me_2SO)$ | 149.5 | 120.9 | 138.3 | 123.4 | 155.9 | 141.3<br>136.5[b] | 147.9<br>151[b] | 137.8<br>136.5[b] | 128.2<br>127.9[b] | 129.2<br>127.6[b] | 127.1<br>127.9[b] | |
| $RTeBr_3$<br>$(Me_2SO)$ | 145.1 | 122.7 | 133.6 | 126.4 | 151.5 | | 144.3 | 132.2 | 129.3 | 131.1 | 127.9 | |
| <br>$(CDCl_3)$ | | 145.7<br>109.7<br>$(C^{12})$ | 119.9<br>141.3<br>$(C^{13})$ | 134.4<br>115.7<br>$(C^{14})$ | 121.7<br>159.7<br>$(C^{15})$ | 142.1<br>63.2<br>$(C^{16})$ | 115.3<br>14.7<br>$(C^{17})$ | 136.8 | 128.9 | 132.2 | 127 | |
| <br>$(CDCl_3)$ | 142.9 | 119.9 | 134.6 | 122.2 | 154.1 | 134.9 | 130.1 | 137.9 | 126.3 | 130.3 | 126.1 | 44.7<br>$(C^{13})$ |
| $R_2Te_3$<br>$(CDCl_3)$ | 146 | 119 | 137.2 | 122.3 | | 140.2 | 120.4 | 140.7 | 129.5 | 125.6 | 126.8 | |
| <br>HR′<br>$(Me_2SO)$ | 156.2<br>128.9<br>$(C^{12})$ | 118.8<br>129.1<br>$(C^{13})$ | 137.2 | 127.8 | 127.2 | 126.5 | 129.6 | 129.9 | 147.6 | 138.7 | 127 | |
| R′HgCl<br>$(Me_2SO)$ | 156<br>130.0<br>$(C^{13})$ | 119.1<br>128.2<br>$(C^{14})$ | 135<br>127.4<br>$(C^{15})$ | <br>138.2<br>$(C^{12})$ | 127.9 | 126.8 | | 130.4 | 146.3 | 141.1 | 150 | |
| $R'TeBr_3$<br>$(Me_2SO)$ | 150.9<br>131.3<br>$(C^{13})$ | 118.9 | 132.7<br>127.8<br>$(C^{15})$ | <br>134.4<br>$(C^{12})$ | 128.5 | 124.5 | 129.6 | 131.8 | 144.7 | 140.8 | | |

[a] Data for 2,4,6-triphenylpyridine. [b] Data for phenylmercury(II) chloride.[18]



**Scheme.** Synthesis and interconversions of 2-pyridyl-functionalised organyltellurium compounds

I.r. spectra were determined for KBr discs with a Perkin-Elmer 599B instrument. $^1H$ And $^{13}C$ n.m.r. spectra were obtained with a JEOL FX 90Q spectrometer at 90 and 22.5 MHz respectively; $SiMe_4$ was the internal standard in both cases.

Analysis for tellurium was by a literature method,[10] other analyses were provided by the Analytical Services Unit, Department of Molecular Sciences, Aston University.

$^{13}C$ N.m.r. data are given in Table 2.

*Structural Investigations*.—Crystal samples of (**1**), (**2**), and (**3**) were subjected to preliminary study by photographic methods, but the final cell dimensions and reflection intensities were measured with graphite-monochromated Mo-$K_\alpha$ radiation on an Enraf–Nonius CAD-4 diffractometer, operating in the ω–2θ scan mode. Three standard reflections were monitored at regular intervals to check the stability of the system. Lorentz and polarisation factors were applied, and also empirical absorption corrections in the case of compound (**1**);[11] range of transmission factors 0.524—1.083. Details of crystal and experimental parameters are given in Table 3.

The tellurium and bromine atoms of (**1**) were located by direct methods. For (**2**) and (**3**) the tellurium atom was located

**Table 3**. Crystal and experimental parameters

| Complex | **(1)** | **(2)** | **(3)** |
|---|---|---|---|
| Molecular formula | $C_{11}H_8Br_3NTe$ | $C_{14}H_{14}N_2S_2Te$ | $C_{19}H_{17}NOTe$ |
| $M$ | 521.5 | 402.0 | 402.9 |
| Crystal size (mm) | 0.4 × 0.2 × 0.1 | 0.6 × 0.25 × 0.075 | 0.55 × 0.25 × 0.125 |
| $a$/A | 6.953(6) | 8.809(3) | 13.422(2) |
| $b$/A | 8.382(1) | 9.032(5) | 16.469(3) |
| $c$/A | 12.133(2) | 10.727(4) | 7.711(3) |
| $\alpha$/° | 78.68(1) | 83.06(4) | 90.00 |
| $\beta$/° | 82.87(4) | 86.49(3) | 91.01(2) |
| $\gamma$/° | 87.14(4) | 63.68(4) | 90.00 |
| $U$/A$^3$ | 687.8 | 759.4 | 1 704.2 |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ |
| $Z$ | 2 | 2 | 4 |
| $F(000)$ | 476 | 392 | 792 |
| $D_c$/g cm$^{-3}$ | 2.519 | 1.759 | 1.571 |
| $\mu$(Mo-$K_\alpha$) mm$^{-1}$ | 11.453 | 2.282 | 1.813 |
| Data collection range, $\theta$/° ($\lambda$ = 0.710 69 A) | 2—25 | 2—25 | 2—22.5 |
| Unique data measured | 2 697 | 2 940 | 3 356 |
| Significant data [$I > 2.5\sigma(I)$] | 1 963 | 2 502 | 2 014 |
| Least-squares weight, $K$ [$w = [\sigma^2(F) + KF^2]^{-1}$] | 0 | 0.0025 | 0.0015 |
| Maximum shift error in final least-squares cycle | 0.15 | 0.01 | 0.01 |
| Final $R$ | 0.0735 | 0.0417 | 0.0415 |
| Final $R'$ | 0.1085 | 0.0636 | 0.0539 |

**Table 4.** Bond lengths (A) and angles (°) for compound (**1**) with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Te–Br(1) | 2.673(3) | C(5)–C(6) | 1.410(25) |
| Te–Br(2) | 2.658(3) | C(6)–C(1) | 1.438(25) |
| Te–Br(3) | 2.589(3) | C(6)–C(7) | 1.415(28) |
| Te–C(1) | 2.110(19) | C(8)–C(9) | 1.435(34) |
| Te–N(1) | 2.244(14) | C(8)–C(7) | 1.441(25) |
| C(2)–C(3) | 1.312(29) | C(9)–C(10) | 1.312(35) |
| C(2)–C(1) | 1.373(29) | C(10)–C(11) | 1.397(28) |
| C(3)–C(4) | 1.471(29) | C(11)–N(1) | 1.295(25) |
| C(4)–C(5) | 1.357(30) | N(1)–C(7) | 1.407(21) |
| | | | |
| Br(1)–Te–Br(2) | 172.4(1) | C(5)–C(6)–C(7) | 121.7(16) |
| Br(1)–Te–Br(3) | 93.5(2) | C(1)–C(6)–C(7) | 121.2(17) |
| Br(2)–Te–Br(3) | 92.8(1) | Te–C(1)–C(2) | 125.4(16) |
| Br(1)–Te–C(1) | 87.5(5) | Te–C(1)–C(6) | 112.8(14) |
| Br(2)–Te–C(1) | 88.1(5) | C(2)–C(1)–C(6) | 121.7(18) |
| Br(3)–Te–C(1) | 92.5(6) | C(9)–C(8)–C(7) | 117.4(20) |
| Br(1)–Te–N(1) | 88.4(4) | C(8)–C(9)–C(10) | 120.2(21) |
| Br(2)–Te–N(1) | 84.7(4) | C(9)–C(10)–C(11) | 119.2(23) |
| Br(3)–Te–N(1) | 170.4(4) | C(10)–C(11)–N(1) | 123.4(22) |
| C(1)–Te–N(1) | 78.2(7) | Te–N(1)–C(11) | 126.8(14) |
| C(3)–C(2)–C(1) | 118.9(21) | Te–N(1)–C(7) | 113.0(11) |
| C(2)–C(3)–C(4) | 122.9(21) | C(11)–N(1)–C(7) | 120.3(17) |
| C(3)–C(4)–C(5) | 117.0(20) | C(6)–C(7)–C(8) | 127.1(17) |
| C(4)–C(5)–C(6) | 121.5(19) | C(6)–C(7)–N(1) | 114.7(15) |
| C(5)–C(6)–C(1) | 117.0(17) | C(8)–C(7)–N(1) | 117.8(18) |

**Table 5.** Bond lengths (Å) and angles (°) for compound (**2**) with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Te–S(1) | 2.518(1) | C(1)–C(6) | 1.406(7) |
| Te–N(1) | 2.354(4) | C(2)–C(3) | 1.375(8) |
| Te–C(1) | 2.111(5) | C(3)–C(4) | 1.367(9) |
| S(1)–C(12) | 1.764(4) | C(4)–C(5) | 1.398(8) |
| S(2)–C(12) | 1.676(5) | C(5)–C(6) | 1.373(7) |
| N(1)–C(7) | 1.332(7) | C(6)–C(7) | 1.464(6) |
| N(1)–C(11) | 1.333(7) | C(7)–C(8) | 1.410(7) |
| N(2)–C(12) | 1.319(6) | C(8)–C(9) | 1.353(9) |
| N(2)–C(13) | 1.478(7) | C(9)–C(10) | 1.395(10) |
| N(2)–C(14) | 1.464(7) | C(10)–C(11) | 1.372(8) |
| C(1)–C(2) | 1.400(6) | | |
| | | | |
| S(1)–Te–N(1) | 167.6(1) | C(3)–C(4)–C(5) | 120.7(5) |
| S(1)–Te–C(1) | 95.0(1) | C(4)–C(5)–C(6) | 119.7(5) |
| N(1)–Te–C(1) | 74.4(2) | C(1)–C(6)–C(5) | 119.5(5) |
| Te–S(1)–C(12) | 109.6(1) | C(1)–C(6)–C(7) | 118.1(4) |
| Te–N(1)–C(7) | 113.8(3) | C(5)–C(6)–C(7) | 122.4(5) |
| Te–N(1)–C(11) | 125.2(4) | N(1)–C(7)–C(6) | 115.8(4) |
| C(7)–N(1)–C(11) | 120.9(5) | N(1)–C(7)–C(8) | 119.8(5) |
| C(12)–N(2)–C(13) | 121.8(5) | C(6)–C(7)–C(8) | 124.4(5) |
| C(12)–N(2)–C(14) | 123.4(5) | C(7)–C(8)–C(9) | 119.0(5) |
| C(13)–N(2)–C(14) | 114.8(4) | C(8)–C(9)–C(10) | 120.5(5) |
| Te–C(1)–C(2) | 122.0(4) | C(9)–C(10)–C(11) | 117.7(5) |
| Te–C(1)–C(6) | 118.0(3) | N(1)–C(11)–C(10) | 122.0(5) |
| C(2)–C(1)–C(6) | 120.1(4) | S(1)–C(12)–S(2) | 122.3(3) |
| C(1)–C(2)–C(3) | 119.3(5) | S(1)–C(12)–N(2) | 115.1(4) |
| C(2)–C(3)–C(4) | 120.7(5) | S(2)–C(12)–N(2) | 122.7(4) |

**Table 6.** Bond lengths (Å) and angles (°) for compound (**3**) with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Te–C(1) | 2.138(6) | C(6)–C(7) | 1.468(9) |
| Te–C(12) | 2.144(6) | C(7)–C(8) | 1.394(10) |
| O(1)–C(15) | 1.368(8) | C(8)–C(9) | 1.359(11) |
| O(1)–C(18) | 1.430(9) | C(9)–C(10) | 1.364(12) |
| N(1)–C(7) | 1.325(8) | C(10)–C(11) | 1.384(11) |
| N(1)–C(11) | 1.331(9) | C(12)–C(13) | 1.372(10) |
| C(1)–C(2) | 1.387(9) | C(12)–C(17) | 1.393(10) |
| C(1)–C(6) | 1.415(9) | C(13)–C(14) | 1.382(10) |
| C(2)–C(3) | 1.380(10) | C(14)–C(15) | 1.380(10) |
| C(3)–C(4) | 1.382(11) | C(15)–C(16) | 1.372(10) |
| C(4)–C(5) | 1.346(10) | C(16)–C(17) | 1.408(10) |
| C(5)–C(6) | 1.410(9) | C(18)–C(19) | 1.463(12) |
| | | | |
| C(1)–Te–C(12) | 94.8(2) | C(7)–C(8)–C(9) | 119.5(8) |
| C(15)–O(1)–C(18) | 118.1(6) | C(8)–C(9)–C(10) | 120.2(8) |
| C(7)–N(1)–C(11) | 118.9(7) | C(9)–C(10)–C(11) | 117.4(7) |
| Te–C(1)–C(2) | 120.2(5) | N(1)–C(11)–C(10) | 123.2(8) |
| Te–C(1)–C(6) | 119.8(4) | Te–C(12)–C(13) | 119.8(5) |
| C(2)–C(1)–C(6) | 120.0(6) | Te–C(12)–C(17) | 121.9(5) |
| C(1)–C(2)–C(3) | 120.6(7) | C(13)–C(12)–C(17) | 118.3(6) |
| C(2)–C(3)–C(4) | 119.4(7) | C(12)–C(13)–C(14) | 122.2(7) |
| C(3)–C(4)–C(5) | 121.1(7) | C(13)–C(14)–C(15) | 119.2(7) |
| C(4)–C(5)–C(6) | 121.5(7) | O(1)–C(15)–C(14) | 116.2(7) |
| C(1)–C(6)–C(5) | 117.3(6) | O(1)–C(15)–C(16) | 123.3(7) |
| C(1)–C(6)–C(7) | 122.2(6) | C(14)–C(15)–C(16) | 120.5(7) |
| C(5)–C(6)–C(7) | 120.5(6) | C(15)–C(16)–C(17) | 119.6(7) |
| N(1)–C(7)–C(6) | 115.7(6) | C(12)–C(17)–C(16) | 120.2(7) |
| N(1)–C(7)–C(8) | 120.8(6) | O(1)–C(18)–C(19) | 109.2(8) |
| C(6)–C(7)–C(8) | 123.5(6) | | |

from a Patterson synthesis. In each of the three crystal structures the remaining non-hydrogen atoms were located by Fourier-difference syntheses. With the exception of the ring hydrogens of (**2**), which were located from a difference synthesis, H atoms were placed in calculated positions (C–H, 1.08 Å) and allowed to 'ride' on their respective carbon atoms in the subsequent least-squares refinements. Bond lengths and angles for (**1**), (**2**), and (**3**) are given in Tables 4—6 respectively and atomic co-ordinates in Tables 7—9 respectively.

Computations were carried out on the Birmingham University Honeywell computer with SHELX.[12] Stereoscopic views were drawn using PLUTO[13] at the University of Manchester regional computer centre.

**Table 7.** Fractional atomic co-ordinates ( × 10$^4$) for compound (**1**) with e.s.d.s in parentheses

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Te | −1 148(2) | 4 702(1) | 6 901(1) |
| Br(1) | 373(3) | 3 242(3) | 8 772(2) |
| Br(2) | −2 577(4) | 6 522(3) | 5 122(2) |
| Br(3) | −3 547(4) | 2 395(3) | 7 016(3) |
| N(1) | 504(22) | 6 926(16) | 6 923(14) |
| C(1) | −3 102(29) | 5 931(23) | 7 944(17) |
| C(2) | −4 963(30) | 5 475(22) | 8 358(19) |
| C(3) | −5 976(34) | 6 289(29) | 9 061(19) |
| C(4) | −5 318(34) | 7 810(27) | 9 306(19) |
| C(5) | −3 481(28) | 8 252(22) | 8 884(16) |
| C(6) | −2 333(29) | 7 402(20) | 8 135(17) |
| C(7) | −467(27) | 7 924(21) | 7 633(16) |
| C(8) | 423(33) | 9 423(21) | 7 677(23) |
| C(9) | 2 327(35) | 9 709(22) | 7 082(25) |
| C(10) | 3 045(40) | 8 803(25) | 6 354(24) |
| C(11) | 2 176(31) | 7 331(28) | 6 366(18) |

**Table 8.** Fractional atomic co-ordinates for compound (**2**) ( × 10$^5$ for Te, × 10$^4$ for others) with e.s.d.s in parentheses

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Te | 105 314(3) | 13 542(3) | 33 091(3) |
| S(1) | 9 013(2) | 1 518(2) | 1 346(1) |
| S(2) | 5 995(2) | 3 887(2) | 2 727(1) |
| N(1) | 12 174(5) | 1 562(5) | 4 869(4) |
| N(2) | 5 861(5) | 2 549(6) | 713(4) |
| C(1) | 10 496(5) | 3 713(5) | 2 887(4) |
| C(2) | 9 645(6) | 4 791(6) | 1 842(5) |
| C(3) | 9 632(7) | 6 328(7) | 1 632(6) |
| C(4) | 10 470(7) | 6 795(6) | 2 417(6) |
| C(5) | 11 331(7) | 5 731(6) | 3 463(5) |
| C(6) | 11 368(6) | 4 187(5) | 3 690(4) |
| C(7) | 12 295(6) | 2 992(6) | 4 743(4) |
| C(8) | 13 305(8) | 3 254(7) | 5 579(5) |
| C(9) | 14 156(9) | 2 030(10) | 6 489(6) |
| C(10) | 14 017(7) | 540(8) | 6 609(5) |
| C(11) | 13 012(7) | 361(7) | 5 768(5) |
| C(12) | 6 811(6) | 2 680(5) | 1 556(4) |
| C(13) | 3 998(8) | 3 513(9) | 714(6) |
| C(14) | 6 548(9) | 1 467(10) | −296(6) |

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

## Discussion

2-Phenylpyridine and 2-phenylquinoline have both been directly *ortho*-palladated when treated with $Na_2[PdCl_4]$ in ethanol.[14] Although the direct telluration of azobenzene with tellurium tetrachloride can proceed under forcing conditions,[15] generally a *trans* metallation route must be used for the synthesis of *ortho*-tellurated bases.[16] The mercuration of 2-phenylpyridine and 2-phenylquinoline was achieved *via* mercury(II) acetate, generally considered a stronger electrophile than mercury(II) chloride.[17] A method similar to that for the mercuration of azobenzene[18] was adopted and gave moderate, but adequate yields, of the mercurated products. The telluration was achieved by *trans* metallation with $TeBr_4$ (which is less readily hydrolysed than $TeCl_4$ and gives fewer problems with protonated by-products) or with (*p*-ethoxyphenyl)tellurium(IV) trichloride (Table 1 and Scheme).

Reduction of the tribromides with the stoicheiometric quantity of hydrazine hydrate affords the organyltellurium bromides which are stabilised by co-ordination of the heterocyclic nitrogen atom; these materials undergo metathesis with sodium dimethyldithiocarbamate to give the organyltellurium(II) dithiocarbamates (see later).

**Table 9.** Fractional atomic co-ordinates for compound (**3**) ( × 10$^5$ for Te, × 10$^4$ for others) with e.s.d.s in parentheses

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Te | 12 013(3) | −2 182(3) | −13 169(5) |
| O(1) | 3 726(4) | 1 292(3) | 4 833(6) |
| N(1) | 445(4) | −1 079(4) | −4 005(7) |
| C(1) | 2 325(4) | −1 013(4) | −2 275(8) |
| C(2) | 3 301(5) | −944(4) | −1 675(8) |
| C(3) | 4 041(5) | −1 425(5) | −2 353(10) |
| C(4) | 3 803(6) | −1 975(5) | −3 648(10) |
| C(5) | 2 858(5) | −2 068(5) | −4 222(9) |
| C(6) | 2 075(5) | −1 595(4) | −3 562(8) |
| C(7) | 1 049(5) | −1 707(4) | −4 209(7) |
| C(8) | 708(6) | −2 422(5) | −4 983(10) |
| C(9) | −256(6) | −2 471(6) | −5 548(11) |
| C(10) | −880(6) | −1 825(6) | −5 362(10) |
| C(11) | −496(6) | −1 138(5) | −4 562(10) |
| C(12) | 2 110(5) | 246(4) | 773(8) |
| C(13) | 2 428(5) | 1 037(5) | 739(9) |
| C(14) | 2 966(5) | 1 380(4) | 2 097(9) |
| C(15) | 3 208(5) | 911(5) | 3 525(9) |
| C(16) | 2 912(6) | 114(5) | 3 606(10) |
| C(17) | 2 357(6) | −224(5) | 2 220(9) |
| C(18) | 3 971(6) | 835(6) | 6 357(10) |
| C(19) | 4 596(8) | 1 331(6) | 7 514(13) |

The reduction of both tribromides with an excess of hydrazine hydrate gives the corresponding ditellurides. In principle, the reduction of a ditelluride with sodium tetrahydroborate under mildly alkaline conditions should give the sodium organyltellurate, a useful nucleophile. Attempts were made to eliminate intermediate stages of the synthesis by reacting the tribromides directly with sodium tetrahydroborate. For the 2-phenylquinoline series only the ditelluride was isolated; however in the 2-phenylpyridine series an initial precipitate of tellurium redissolved during the course of the reaction. Work-up gave a novel diorganyl tritelluride the nature of which was confirmed by *X*-ray crystallography.[7] Although triselenides have been known for some time,[19] and Zingaro and co-workers[20,21] have reported a range of diorganyltellurium selenides, the tritellurides reported here, together with $(Me_3Si)_3CTeTeTeC(SiMe_3)_2$[22] constitute the first well characterised examples of diorganyl tritellurides.

The stabilisation of bis[tris(trimethylsilyl)methyl] tritelluride[22] has been attributed to the bulk of the organic group. The compounds in this paper owe their stability to co-ordination of the heterocyclic nitrogen atom to the terminal tellurium atoms (Te–N, 2.554 Å; *cf.* van der Waals distance of 3.61 Å). The Te–Te bond length (2.776 Å) is longer than that for some ditellurides, *e.g.* $Ph_2Te_2$ (2.712 Å),[23] $(p\text{-}CH_3C_6H_4)_2Te_2$ (2.697 Å),[24] and $(p\text{-}MeOC_6H_4)_2Te_2$ (2.72 Å)[25] and it is also longer by 0.066 Å than the Te–Te distance in bis[tris(trimethylsilyl)methyl] tritelluride.[22] It is likely that a wide range of diorganyl polytellurides may be stabilised by co-ordination of the terminal tellurium atoms.

Reduction of 2-(2-pyridyl)phenyltellurium(IV) tribromide, (**1**), with an excess of hydrazine hydrate gave bis[2-(2-pyridyl)phenyl] ditelluride (Scheme); also treatment of the tritelluride with copper powder gave the same ditelluride. The observation that an initial precipitate of tellurium seemed responsible for the formation of the tritelluride on $NaBH_4$ reduction of (**1**) led us deliberately to add tellurium powder in a repeat of the tetrahydroborate reduction of 2-(quinolin-2-yl)phenyltellurium(IV) tribromide. This procedure gave the corresponding tritelluride in good yield. Two possible mechanisms, (**1**) and (**2**), may be considered for the formation of tritellurides [R = 2-(2-pyridyl)phenyl or 2-(quinolin-2-yl)phenyl].

$$\begin{tikzcd} 2RTeBr_3 \arrow[r, "BH_4^-"] & 2RTeBr + Te^{2-} \arrow[r] & R_2Te_3 + 2Br^- \quad (1) \\ & Te \arrow[u, "BH_4^-"'] & \end{tikzcd}$$

$$RTeBr_3 \xrightarrow{BH_4^-} RTe^- + Te \longrightarrow RTeTe^- \xrightarrow{O_2} R_2Te_3 \quad (2)$$

Mechanism (2) has been favoured by others,[22] but (1) may be applicable here given our practice of excluding air from our preparations. If this is so, we speculate that it may be possible to synthesise higher polytellurides, *e.g.* by reaction of a co-ordination stabilised organyltellurium halide with the ditelluride anion.

Reactions of 2-(2-pyridyl)phenyltellurium(IV) tribromide and of *p*-ethoxyphenyltellurium(IV) trichloride with 2-(2-pyridyl)phenylmercury(II) chloride were carried out. It was anticipated that diorganyltellurium(IV) dihalides would be formed but the products contained both tellurium and mercury; further they were 1 : 1 electrolytes (see Table 1). The conductivities, together with the stoicheiometries, strongly suggest ionic structures $[R_2TeBr][HgClBr_2]$ and $[RR'TeCl][HgCl_3]$ respectively [R = 2-(2-pyridyl)phenyl, R′ = *p*-$EtOC_6H_4$]. It is interesting that the tellurium atom should bond to one pyridyl nitrogen atom rather than to the second halogen. For $[RR'TeCl]$-$[HgCl_3]$, a strong i.r. band at 287 $cm^{-1}$ is reasonably assigned as ν(TeCl).[26] Both compounds may be cleanly reduced to tellurides (Scheme). Bis[2-(2-pyridyl)phenyl] telluride may be converted to a diperchlorate salt.

*Spectroscopic Studies.*—I.r. and $^1H$ n.m.r. data were useful in confirming the metallation of 2-phenylpyridine and of 2-phenylquinoline; however, the $^{13}C$ n.m.r. data are generally more directly indicative of the position of metallation and the data in Table 2 are therefore worthy of brief comment. Mercuration of the bases causes a downfield shift of *ca.* 22 p.p.m. for one phenyl *ortho* carbon atom; similar observations are made for other mercurated species;[15,16,27] in this instance the rather limited solubility prevented the observation of $^{199}Hg$–$^{13}C$ coupling constants. The tellurium compounds are even less soluble, however spectra were obtained which confirmed the telluration of the bases, although the downfield shift of the metallated carbon is not quite so great. It is interesting that the resonances of the carbons *ortho* and *para* to nitrogen in the pyridine ring are more sensitive to the presence of tellurium than of mercury. This may reflect a stronger N–Te than N–Hg interaction. The spectrum of bis[2-(2-pyridyl)phenyl] tritelluride is of interest. The resonance of the tellurated carbon atom has shifted some 24 p.p.m. to higher field than in the corresponding mercurated derivative and than in the organyltellurium(IV) tribromide, (**1**). There is no value for the chemical shift of a similar carbon in the literature to provide a basis for comparison, however Zingaro and co-workers[20] have reported values of 123—125 p.p.m. for *ipso* carbons of some diorganyltellurium selenides. Again, a high-field (*ca.* 3 p.p.m.) shift for C(1) (adjacent to nitrogen, see Table 2) is seen which we take to be indicative of the relatively short Te ··· N contact of 2.55 Å in $R_2Te_3$.[7]

The spectra of other compounds in Table 2 have been assigned following our previous work and the literature.[28,29]

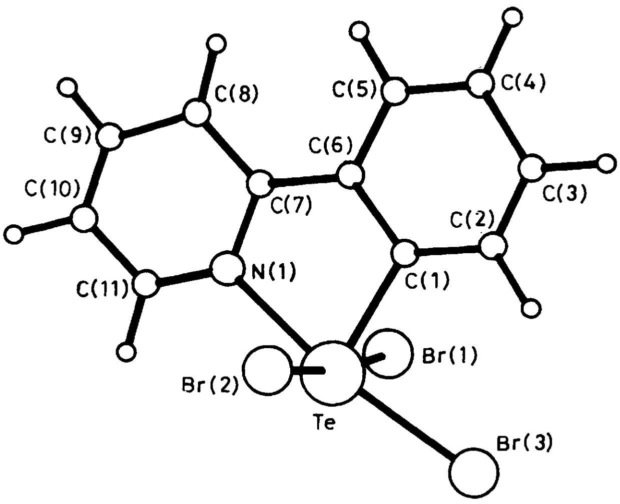


**Figure 1.** View of complex (**1**) showing the atom numbering

*Structural Investigations.*—The structure of $RTeBr_3$ (**1**) [R = 2-(2-pyridyl)phenyl] is shown in Figure 1. The co-ordination about tellurium can be considered as essentially pseudo-octahedral, with a lone pair of electrons occupying the forth equatorial site. The whole molecule, apart from the apical bromine atoms, Br(1) and Br(2), is planar to within ±0.15 Å. Br(1) and Br(2) lie 2.739(5) and 2.575(3) Å on either side of the Te–N(1)–C(1)–Br(3) plane. The angle of 6.2(3)° between the mean planes of the pyridyl and phenyl rings illustrates the slight deviation from planarity of the organic ligand.

The distortion of the co-ordination geometry from ideal octahedral angles (90 and 180°), particularly N(1)–Te–Br(3) [170.4(4)°] can be explained in terms of a lone pair of electrons occupying an equatorial position between N(1) and Br(3). The small value of the angle N(1)–Te–C(1) [78.2(7)°] is due to the constraint of the five-membered chelate ring. The axial atoms are displaced from the lone pair electrons reducing the Br(1)–Te–Br(2) angle to 172.4(1)°. These values are analogous to those found in the crystal structure of (2-phenylazophenyl-*C,N′*)tellurium(IV) trichloride.[15]

The distance Te–C(1) [2.110(19) Å] is in excellent agreement with the sum of the Pauling[30] single bond covalent radii of Te (1.37 Å) and *sp*$^2$ hybridised carbon (0.74 Å) and with values in the crystal structures of the analogous compounds (pap)-$TeCl_3$ (pap = 2-phenylazophenyl),[15] (bip)$TeBr_3$ (bip = 2-biphenylyl),[31] and $C_4H_8STeBr_2$[32] in which Te–C is in the range 2.11—2.16 Å. The Te–N distance of 2.244(14) Å is longer than the sum of the covalent radii (2.07 Å),[30] but shorter than that reported for (2-phenylazophenyl-*C,N′*)tellurium(IV) trichloride,[15] 2.417 Å, and for (dapy)$TeCl_3$ (dapy = 2,6-diacetylpyridine), 2.402 Å,[33] indicating a stronger interaction in this case. The interaction between Te and the pyridyl nitrogen atom holds the organic ligand in an essentially planar geometry. The Te–Br distances [2.589(3) Å equatorial, 2.673(3) and 2.658(3) Å axial] are in good agreement with the sum of the covalent radii (equatorial Te–Br, 2.51 Å and axial Te–Br, 2.67 Å[30,34]) and fall within the range commonly found for Te–Br covalent bonds.[31,32,35] There is a weak secondary[36] intermolecular interaction between centrosymmetrically related molecules Te ··· Br of 3.596(3) Å, which is a feature noted in the structures of (bip)$TeBr_3$ (Te ··· Br, 3.71 Å)[31] and $C_4H_8STeBr_2$ (Te ··· Br, 3.59 Å).[32]

The structure of RTe(dmdtc) (**2**) [R = 2-(2-pyridyl)phenyl] is shown in Figure 2. The co-ordination about tellurium can be considered as essentially pseudo-trigonal bipyramidal, with C(1) and the lone pairs making up the equatorial co-ordination, and S(1)

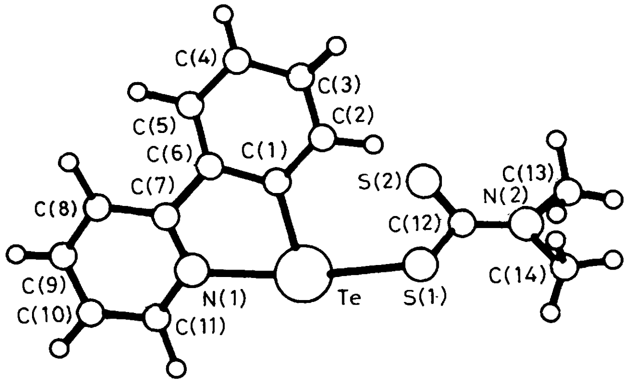


**Figure 2.** View of complex (**2**) showing the atom numbering

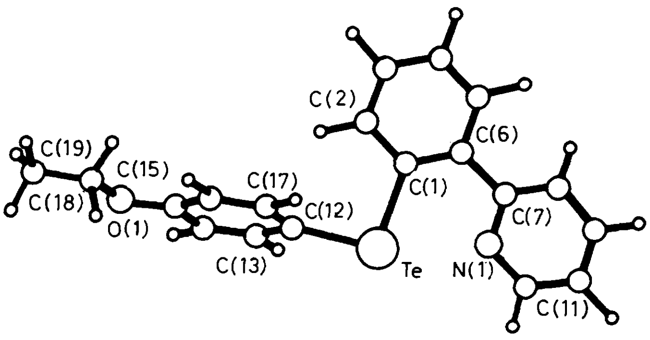


**Figure 3.** View of complex (**3**) showing the atom numbering

and N(1) axial. The position *trans* to the bonded carbon atom is unoccupied and the compound is almost 'T'-shaped.[34] The 2-(2-pyridyl)phenyl ligand is planar to within ±0.06 Å, with the Te atom displaced 0.03 Å from the plane, and the S(1) atom also displaced 0.30 Å. The dimethyldithiocarbamato group is planar to within ±0.04 Å and is orientated at an angle of 72.7(2)° to the Te–R plane. The distortion of the co-ordination geometry from ideal pseudo-trigonal bipyramidal values, particularly the N(1)–Te–C(1) angle of 74.4(2)°, is again due to constraints arising from the five-membered chelate ring.

The distance Te–C(1) [2.111(5) Å] is in good agreement with the sum of the Pauling covalent single bond radii[30] and with typical values in $Te^{II}$ complexes, *e.g.* $PhTe(tu)_2Cl$,[37] PhTe(tmsu)Cl,[37] and (pap)Te(dmdtc)[38] (where tu = thiourea and tmsu = *N,N'*-trimethyleneselenourea), which lie in the range 2.097—2.102 Å. The Te–N distance, 2.354(4) Å, is longer than the sum of the covalent radii (2.24 Å for axial Te–N)[30,34] and is also longer than in (pap)Te(SCN), 2.243 Å,[39] and in (pap)TeCl, 2.23 Å,[40] but is comparable with that reported for (pap)Te(dmdtc), 2.340 Å.[35] The Te–N interaction holds the organic ligand is an almost planar geometry, with only an angle at 4.4(2)° between the mean planes of the pyridyl and phenyl rings. The Te–S(1) bond, 2.518(1) Å, is in good agreement with the sum of the S and Te axial covalent radii,[30,34] 2.58 Å, and similar to values found in other tellurium(II) complexes with sulphur ligands,[37] *e.g.* $Te(S_2COR)_2$ (R = Me or Et), $Te(S_2CNCH_2CH_2OCH_2CH_2)_2$, and $Te(S_2CNEt_2)_2$, which fall in the range 2.49—2.52 Å. The Te–S(2) distance of 3.667(1) Å, although within the sum of the van der Waals radii (4.05[30] or 3.86 Å[41]), indicates only an extremely weak interaction. By contrast, dimethyldithiocarbamato(2-phenylazophenyl-*C,N'*)-tellurium(II) has both sulphur atoms essentially coplanar with the tellurium atoms and the bonded C and N atoms of the organic ligand and the Te–S(2) distance of 3.225(3) Å clearly shows a significantly stronger interaction in the case of the tellurated azobenzene derivative.

The arrangement of the molecules in the unit cell reveals that almost planar organic ligands related by centres of symmetry overlie one another, with an interplanar distance of 3.50(1) Å. No unusually short intermolecular contacts occur.

The structure of $RTe(C_6H_4OEt\text{-}p)$ [R = 2-(2-pyridyl)-phenyl] is shown in Figure 3. The tellurium atom is bonded to two carbon atoms with Te–C(1) 2.138 (6) and Te–C(12) 2.144(6) Å, in good agreement with the sum of the Pauling[30] single bond covalent radii and with values in the crystal structures of analogous compounds, *e.g.* $R_2Te_3$ [R = 2-(2-pyridyl)phenyl],[7] 1,6-bis(2-butyltellurophenyl)-2,5-diazahexa-1,5-diene[2] and in complexes (**1**) and (**2**) above, which lie in the range 2.10—2.13 Å. The Te–N distance of 2.695(4) Å is much greater than the sum of the covalent radii[30] and much greater than the comparable distance in (**1**) and (**2**) above. The occurrence of a Te–C covalent bond *trans* to the Te • • • N vector thus significantly weakens the Te–N interaction. A similar Te • • • N distance of 2.773 Å occurs in a previously reported bis-telluride.[2] The weakening of the Te–N interation allows the rings in the 2-(2-pyridyl)phenyl moiety to twist by 23.2(2)° relative to each other, unlike in (**1**) and (**2**) where the stronger Te–N bonding holds the corresponding organic ligand in a near-planar geometry. Within the *p*-ethoxyphenyl ligand, the ethoxy group is orientated at 4.3(1)° to the phenyl ring. No unusually short intermolecular contacts occur.

Vikane[42] has noted, with reference to organyltellurium bromide complexes, that only long weak interactions are found *trans* to a Te–C bond. A similar effect has been noted in organyltellurium(IV) bromides and iodides;[31,32,35] strong Te–halogen interactions are never *trans* to a Te–C bond. It is also true of complexes (**1**), (**2**), and (**3**) that no strong bonds are seen *trans* to a Te–C covalent bond.

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