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The crystal and molecular structure of chloro-*p*-ethoxyphenyl-2-(2-pyridyl)phenyltelluronium(IV) trichloromercurate(II), a novel telluronium salt

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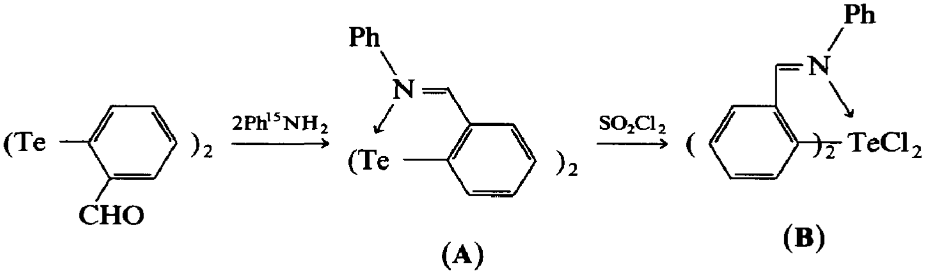
Abstract

The title compound is a novel telluronium salt, $RR'TeCl^+HgCl_3^-$ (R = 2-(2-pyridyl)phenyl, R′ = *p*-ethoxyphenyl) stabilised by intramolecular coordination. It consists of discrete ions, and the cation has tellurium in a ψ-trigonal bipyramidal environment with axial Te–Cl (2.43(1) Å) and Te–N (2.31(2) Å) bonds.

We recently reported [1] that the reaction of *p*-ethoxyphenyltellurium(IV) trichloride with 2-(2-pyridyl)phenylmercury(II) chloride gave a material $[RR'TeCl][HgCl_3]$ (R′ = *p*-ethoxyphenyl, R = 2-(2-pyridyl)phenyl) which was formulated on the basis of elemental analysis and conductivity data. Since the proposed formulation involved a new type of telluronium ion stabilised by intramolecular coordination of the pyridyl-nitrogen atom, it seemed desirable to place the structural assignment on a firmer foundation, and we describe here the crystal structure of the compound, as well as some aspects of its solution chemistry. We note that Russian workers [2] have recently described the following reaction sequence:



in which intramolecular coordination of nitrogen in both **A** and **B** was demonstrated by the observation of ^{125}Te–^{15}N spin–spin coupling (61 Hz for **A**, 122 Hz for **B**).

Experimental

The title compound was prepared by the reported method [1] and recrystallised from methyl cyanide; m.p. 220–225 °C, anal. found: C, 30.5; H, 2.20; N, 1.80. $C_{19}H_{17}Cl_4HgNOTe$ calcd.: C, 30.6; H, 2.30; N, 1.85%.

NMR spectra (^{1}H, ^{13}C, ^{125}Te, and ^{199}Hg) were obtained for dmso-d_6 solutions with a Bruker AC 300 spectrometer operating at 300, 75.4, 94.7, and 53.7 MHz, respectively. References were tetramethylsilane (^{1}H, ^{13}C), bis(*p*-ethoxyphenyl) ditelluride (with ^{125}Te chemical shifts cited relative to Me_2Te), and external aqueous $HgCl_2$ for ^{199}Hg. The IR spectrum (KBr disc) was recorded with a Perkin Elmer FTIR model 1710 instrument.

Structure determination

Crystals of the material were very small, and yielded data of limited scope and intensity; a unique data set was measured to $2\theta_{max} = 50°$ at 295 K with an Enraf-Nonius CAD-4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo-K_α radiation, $\lambda = 0.71069$ Å), yielding 3577 independent reflections, of which 1156 with $I > 3\sigma(I)$ were considered 'observed' and used in the full matrix refinement after absorption correction and the solution of the structure by vector/Fourier methods. The limited data, combined with dominance of the scattering by the mercury, meant that anisotropic thermal parameter refinement was only realistic for Hg, Te, Cl; U_{iso} were refined for O, N, C. (x, y, z, U_{iso})H were included at estimated values. Residuals on $|F|$ at convergence were conventional R, $R' = 0.062$, 0.060; statistical reflection weights were derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$. Neutral atom complex scattering factors were employed [3]; computation involved the XTAL 2.6 program system [4] implemented by Hall. Pertinent results are given in the figures, tables and text. *

Crystal data

$[C_{19}H_{17}ClNOTe]^+$ $(HgCl_3)^-$, $M = 745.4$. Orthorhombic, space group *Pbca* (D_{2h}^{15}, No. 61), a 28.098(8), b 20.694(4), c 7.598(5) Å, U 4418 Å^3. D_c ($Z = 8$) 2.24 g cm^{-3}. $F(000) = 2768$. μ(Mo) 84 cm^{-1}, specimen: $0.02 \times 0.06 \times 0.44$ mm, $A^{*}_{min,max} =$ 1.18, 1.64.

Abnormal features

Identification of the pyridine nitrogen was based on the thermal parameter behaviour in refinement and its effect on residuals and associated geometry. In view of the imprecision in the positions of the light atoms this assignment is less definitive than we would wish.

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* Tables of anisotropic thermal displacement parameters, hydrogen atom coordinates and isotropic thermal parameters, non hydrogen interatomic distances and structure factors are available from the authors.

Table 1

Non-hydrogen coordinates and isotropic thermal parameters

Atom	x	y	z	U_{eq} (Å^2)
Hg(1)	−0.00113(8)	−0.21803(6)	0.9152(2)	0.059(1) [a]
Te(1)	0.10958(9)	0.10371(9)	0.7569(5)	0.046(1) [a]
Cl(1)	0.0642(3)	−0.2587(4)	0.743(2)	0.058(6) [a]
Cl(2)	−0.0156(3)	−0.1059(4)	0.976(1)	0.052(6) [a]
Cl(3)	−0.0530(3)	−0.2920(4)	1.074(1)	0.061(7) [a]
Cl(4)	0.1547(4)	0.1680(4)	0.965(2)	0.087(9) [a]
C(1)	0.167(1)	0.107(1)	0.590(5)	0.040(9)
C(2)	0.178(1)	0.165(2)	0.496(6)	0.08(1)
C(3)	0.214(1)	0.167(2)	0.386(5)	0.06(1)
C(4)	0.241(1)	0.113(1)	0.344(5)	0.04(1)
O(41)	0.2740(9)	0.116(1)	0.219(4)	0.075(8)
C(42)	0.283(2)	0.177(2)	0.139(6)	0.11(2)
C(43)	0.316(2)	0.165(2)	−0.020(7)	0.11(2)
C(5)	0.232(1)	0.056(2)	0.425(5)	0.05(1)
C(6)	0.196(1)	0.054(1)	0.548(5)	0.06(1)
C(7)	0.124(1)	0.018(1)	0.899(4)	0.025(8)
C(8)	0.147(1)	0.017(1)	1.050(5)	0.06(1)
C(9)	0.156(1)	−0.043(2)	1.140(5)	0.07(1)
C(10)	0.138(1)	−0.099(1)	1.066(5)	0.05(1)
C(11)	0.113(1)	−0.096(1)	0.906(5)	0.06(1)
C(12)	0.105(1)	−0.037(1)	0.814(4)	0.04(1)
C(13)	0.081(1)	−0.035(1)	0.647(4)	0.05(1)
C(14)	0.063(1)	−0.087(1)	0.561(5)	0.05(1)
C(15)	0.045(1)	−0.080(1)	0.399(5)	0.05(1)
C(16)	0.042(1)	−0.018(1)	0.322(4)	0.036(9)
C(17)	0.061(1)	0.034(1)	0.413(5)	0.037(9)
N(18)	0.0811(9)	0.025(1)	0.567(3)	0.031(7)

[a] U_{eq} anisotropic form refined (see deposition).

Non-hydrogen coordinates and iotropic thermal parameters are given in Table 1 and the metal atom environments are given in Table 2. Figure 1 shows the cation and anion with atom labelling.

Table 2

Metal atom environments

Distances (Å)		Angles (degrees)	
The cation			
Te–Cl(4)	2.43(1)	Cl(4)–Te–C(1)	88.7(9)
Te–C(1)	2.05(3)	Cl(4)–Te–C(7)	91.5(8)
Te–C(7)	2.11(3)	Cl(4)–Te–N(18)	166.6(6)
Te–N(18)	2.31(2)	C(1)–Te–C(7)	101(2)
		C(1)–Te–N(18)	85(2)
		C(7)–Te–N(18)	78(1)
The anion			
Hg–Cl(1)	2.406(10)	Cl(1)–Hg–Cl(2)	124.9(3)
Hg–C192)	2.400(8)	Cl(1)–Hg–Cl(3)	120.5(3)
Hg–Cl(3)	2.434(10)	Cl(2)–Hg–Cl(3)	114.2(3)

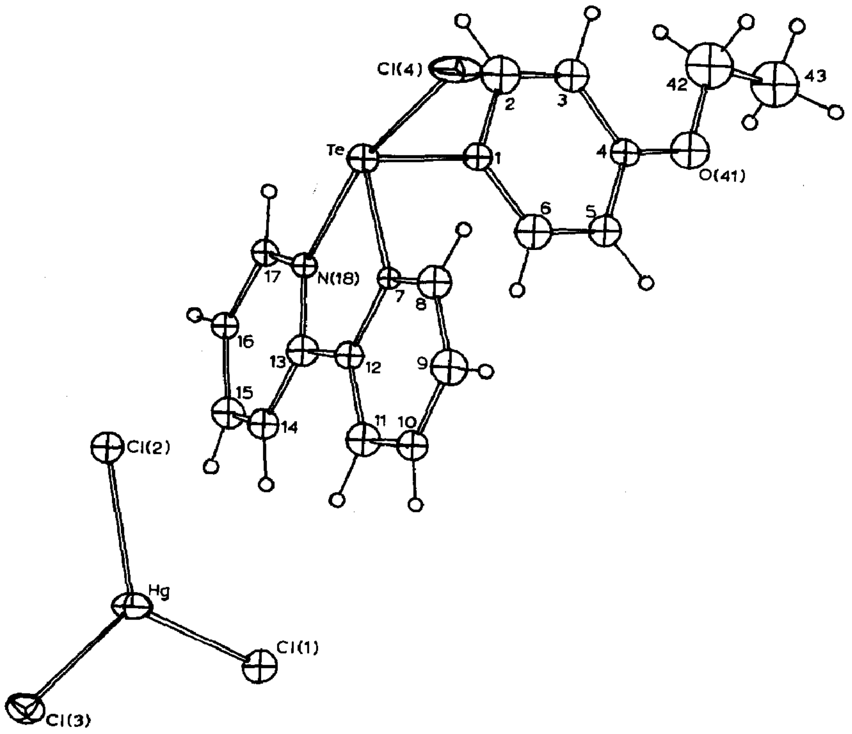
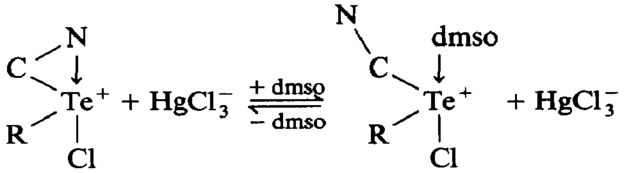


Fig. 1. Structures of the cation and anion, showing atom labelling; hydrogen atoms have arbitrary radii of 0.1 Å.

Discussion

Elemental analysis, IR spectroscopy, and m.p. confirmed that the material was identical to that prepared previously [1,5]. The compound was shown previously to be a 1/1 electrolyte in dimethyl sulphoxide (dmso) [1] and the opportunity was taken to examine the ^{1}H, ^{13}C, ^{125}Te, and ^{199}Hg NMR spectra of the compound in this solvent.

The proton NMR spectrum shows very clearly that there were two environments for the 2-pyridyl-group; the major species shows the α-proton at $\delta = 9.133$, the minor at 8.968 ppm (ratio major/minor = 7.25/1). No doubling of resonances is noted for the aromatic groups directly C-bonded to tellurium. Similarly in the ^{13}C NMR spectrum those resonances assignable to the 2-pyridyl-group [1] appear as weak signals a few ppm to higher field of the main resonance. The fact that the proton α to the 2-pyridyl-nitrogen is more deshielded in the major solution species suggests this is the ion with a coordinate Te ← N bond. A single resonance ($\delta = 371$ ppm relative of aqueous $HgCl_2$) is seen in the ^{199}Hg NMR spectrum implying the presence of a single chloromercurate(II) species. The ^{125}Te spectrum shows two peaks, the major one at $\delta = 1056.4$ ppm and the minor at 1059.1 ppm (both vs. Me_2Te). The tellurium chemical shifts of R_2TeXY species are sensitive to the electronegativity of X and Y [6], and the close similarity of the values for the major and minor species implies that the coordinated nitrogen atom of the major species must be replaced by a ligand atom of similar electronegativity. The NMR data, together with the earlier [1] conductivity data, are thus consistent with the following equilibrium in dmso solution:



Structural studies

The structure consists of discrete cations and chloromercurate anions, Interest centres on the structure of the cation. The geometry about tellurium can be described as ψ-trigonal bipyramidal, with N, Cl axial, and two Te–C bonds, together with the lone pair of electrons, constituting the equatorial plane. The C(1)–Te–C(7) angle (Table 2) falls within the range observed for R_2TeX_2 compounds e.g. bis-*cis*-2-chlorocyclohexyl dichloride [7], 103° and α-dimethyl-tellurium dichloride [8], 96.8°. The Cl(4)–Te–N(18) angle of 166.6(6)° probably departs from the ideal 180° owing to the geometric constraints imposed by the five membered ring created by coordination of the 2-pyridyl-group. The Te–C(7) bond length is in exact agreement with the sum of the Pauling [9] covalent radii for Te(1.37 Å) and sp^2C(0.74 Å), but Te–C(1) is some 0.06 Å shorter than the sum of the relevant covalent radii, although comparably short Te–C bonds have been noted for example for the *p*-tolyl-linkage in *p*-tolyl-2-chlorohexyltellurium dichloride [10] (2.08 Å) and in phenoxatellurium-10,10-bis(trifluoro acetate) [11] (2.07 Å). For R_2TeCl_2 compounds there is often one Te–Cl bond slightly shorter than the other, typical ranges being 2.42–2.49 Å for the shorter and 2.50–2.57 Å for the longer bond; the situation is often complicated by the presence of secondary Te ··· Cl interactions, which in the case of phenoxatellurium-10,10-dichloride [12] actually lead to the formation of discrete stepped tetrameric clusters. However no such interactions appear to be present in the present structure. Thus the Te–Cl(4) bond length of 2.43 Å is at the lower end of the above ranges. We have argued previously [13] that for ψ-trigonal bipyramidal R_2TeXY, it is sensible to view the central tellurium atom as ellipsoidal rather than spherical, and have suggested use of the Pauling radius [9] for $r_{\text{equatorial}}$ (1.37 Å). The axial radius is estimated to be 1.53 Å for Te^{IV}, so that, taken with the Pauling radii for Cl (0.99 Å) and N (0.70 Å), the prediction for Te–Cl (axial) is 2.52 Å and Te–N (axial) 2.23 Å; the observed values (Table 2) are, respectively, shorter and longer than those estimates, lending credibility to a model in which a telluronium cation $R(R')TeCl^+$ is stabilised by weak intramolecular coordination.

A significant amount of data has now been gathered for Te–N interactions in 2-(2-pyridyl)phenyltellurium compounds. If the length of the Te–N coordinate bond can be taken as a measure of the Lewis acidity of the central tellurium atom, then the following order of Lewis acidity is observed (Te–N in parentheses):

$$RTeBr_3(2.244\ \text{Å})\ [1] > R(R')TeCl^+(2.31\ \text{Å}) > RTe(dmdtc)(2.35\ \text{Å})\ [1]$$

$$> R_2Te_3(2.554\ \text{Å})\ [14] > R(R')Te(2.695\ \text{Å})\ [1]$$

(R = 2-pyridyl)phenyl; R′ = *p*-ethoxyphenyl; dmdtc = dimethyldithiocarbamate)

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