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CRYSTAL STRUCTURE OF DIMERIC *p*-PHENOXYPHENYLTELLURIUM(IV) TRICHLORIDE

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Summary

p-$PhOC_6H_4TeCl_3$ crystallises with a dimeric molecular unit. The two approximately square pyramidal coordination polyhedra are linked *trans* to each other through two bridging chlorine atoms. The dimeric units are further connected through Te...Cl secondary interactions producing a distorted octahedral geometry about each tellurium atom. The crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions a 8.521(2), b 10.917(2), c 14.813(2) Å, α 81.84(1), β 83.38(1), γ 88.41(1)°, V 1353.4(4) Å^3 and $Z = 2$(dimers) from 3887 observed reflections [$I > 3\sigma(I)$], $R = 0.0359$.

Introduction

Crystal structures of a number of compounds of the general formula R_2TeCl_2 have been reported [1–6] with a view to studying secondary bond interactions. In contrast, only a few organotellurium trichlorides have been studied crystallographically [1,7–9]. Part of the reason is the difficulty encountered in recrystallization of these compounds, which are highly insoluble due to their polymeric structures. The compounds studied so far, namely, $PhTeCl_3$, *p*-$EtOC_6H_4TeCl_3$ and $ClC_2H_4TeCl_3$, all exhibit $CTeCl_4$ structural units, which have approximate square pyramidal geometry, and which extend into chains by chlorine bridges. We present herein the crystal structure of *p*-$PhOC_6H_4TeCl_3$ which has a dimeric molecular unit.

Experimental

p-$PhOC_6H_4TeCl_3$ was prepared by the method described by Drew [10] and recrystallized from glacial acetic acid. The density was measured by the flotation method in CCl_4/CH_3I. A single crystal was mounted along the largest dimension and the cell parameters were obtained from 28 strong reflections with $15 < 2\theta < 30°$. Data were collected on a Syntex $P2_1$ diffractometer following the procedure de-

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TABLE 1

CRYSTALLOGRAPHIC DATA

a (Å)	8.512(2)
b (Å)	10.917(2)
c (Å)	14.813(2)
α (°)	81.84(1)
β (°)	83.38(1)
γ (°)	88.41(1)
V (Å^3)	1353.4(4)
crystal system	triclinic
space group	$P\bar{1}$
mol. wt.	403.1
Z	2 (dimers)
ρ_c (g cm^{-3})	1.98
ρ_0 (g cm^{-3})	1.95
crystal dimensions (mm)	0.12×0.27×0.38
radiation	Mo-K_α, 0.71069 Å
monochromator	highly oriented graphite
temperature (°C)	21
abs. coeff, μ (cm^{-1})	25.71
min abs. corr.	1.324
max abs. corr.	1.976
2 θ angle (°)	4–50
scan type	coupled θ(crystal)/2θ(counter)
scan width	$K_{\alpha_1} - 1°$ to $K_{\alpha_2} + 1°$
scan speed (° min^{-1})	variable, 2.02–4.88
bkgd time/scan time	0.5
total reflcns measd	5000
unique data used	3887 [$I > 3\sigma(I)$]
no. of parameters (NP)	326 (163, 163)
R	0.0359
$R_{\omega F}$	0.0449

scribed previously [3]. The intensities of three monitored reflections did not change significantly during data collection. The data were corrected for absorption, Lorentz and polarization effects. Details of X-ray data are given in Table 1.

The positions of both the tellurium atoms were obtained from a sharpened Patterson synthesis. The positions of remaining non-hydrogen atoms were determined from a difference Fourier map. The structure was refined anisotropically by the blocked-matrix least squares methods using 163 parameters in each block. The parameters of both the tellurium atoms were common in the two blocks. One block contained all the chlorine and oxygen atoms and eight carbon atoms and a scale factor. The second block contained the remaining carbon atoms and a scale factor. The refinement converged to $R = (\Sigma||F_0| - |F_c||/\Sigma|F_0|) = 0.0390$. A difference map at this stage showed peaks at plausible hydrogen positions. Hydrogen atoms were included in subsequent refinements in ideal positions (C–H 0.95 Å and CCH 120°). Refinement gave final values of $R = 0.0359$ and $R_{\omega F} = [\Sigma_\omega \Delta^2/\Sigma_\omega F_0^2]^{1/2} = 0.0449$. In the final two cycles of refinement the largest shift/error ratio was 0.06 and the final difference map had no feature of chemical significance with the largest peak 0.9 eÅ^{-3} at (−0.079, 0.837, 0.571). The function $(|F_0| - |F_c|)^2$ was minimized during least squares refinement and in the final cycles, a weighting scheme of the

TABLE 2

FINAL FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS (Å^2 × 10^3) FOR NON-HYDROGEN ATOMS OF (p-PhOC$_6$H$_4$)TeCl$_3$ WITH STANDARD DEVIATIONS IN PARENTHESES.

Atom	x	y	z	U_{eq} [a]
Te(1)	0.37743(5)	0.38104(4)	0.43163(3)	31.8(2)
Te(2)	0.05227(5)	0.13521(3)	0.56958(3)	31.1(2)
Cl(1)	0.3712(3)	0.5654(2)	0.3269(2)	66(1)
Cl(2)	0.6581(2)	0.3765(2)	0.4165(1)	55(1)
Cl(3)	0.0520(2)	0.3557(2)	0.4533(1)	40(1)
Cl(4)	0.3710(2)	0.1734(2)	0.5665(1)	47(1)
Cl(5)	−0.2220(2)	0.1069(2)	0.5665(1)	52(1)
Cl(6)	0.0728(3)	−0.0529(2)	0.6720(1)	64(1)
O(1)	0.3567(7)	0.0456(4)	0.1261(3)	52(3)
O(2)	−0.0974(7)	0.4534(4)	0.8876(3)	51(3)
C(11)	0.3727(8)	0.2678(6)	0.3272(4)	31(3)
C(12)	0.4545(8)	0.1557(6)	0.3319(5)	36(4)
C(13)	0.4515(8)	0.0853(6)	0.2614(5)	39(4)
C(14)	0.3641(9)	0.1235(6)	0.1898(4)	39(4)
C(15)	0.2784(8)	0.2350(6)	0.1871(4)	36(4)
C(16)	0.2819(8)	0.3058(6)	0.2567(4)	38(4)
C(21)	0.3444(9)	0.0955(6)	0.0351(5)	44(4)
C(22)	0.2376(11)	0.0397(7)	−0.0091(6)	57(5)
C(23)	0.2298(12)	0.0798(9)	−0.1011(6)	72(6)
C(24)	0.3176(13)	0.1747(9)	−0.1469(6)	69(6)
C(25)	0.4235(11)	0.2314(8)	−0.1006(5)	60(5)
C(26)	0.4367(10)	0.1914(7)	−0.0088(5)	49(4)
C(31)	0.0079(7)	0.2392(5)	0.6793(4)	30(3)
C(32)	−0.1017(7)	0.1960(6)	0.7534(4)	33(3)
C(33)	−0.1375(8)	0.2636(6)	0.8244(4)	35(3)
C(34)	−0.0607(8)	0.3768(6)	0.8217(4)	37(4)
C(35)	0.0467(8)	0.4200(6)	0.7491(4)	37(4)
C(36)	0.0817(8)	0.3504(6)	0.6768(4)	37(4)
C(41)	−0.1504(8)	0.4036(6)	0.9768(4)	35(4)
C(42)	−0.0750(10)	0.3046(7)	1.0222(5)	50(4)
C(43)	−0.1267(11)	0.2620(8)	1.1134(5)	61(5)
C(44)	−0.2504(13)	0.3190(9)	1.1571(5)	69(6)
C(45)	−0.3227(12)	0.4172(9)	1.1133(7)	75(6)
C(46)	−0.2750(10)	0.4609(7)	1.0212(6)	57(5)

[a] U_{eq} for non-H atoms is calculated from the refined anisotropic thermal parameters. ($U_{eq} = \frac{1}{3}\Sigma_{i=1}^{3}(\mathrm{RMSD})_i^2$, RMSD values are taken from ORTEP output).

form $\omega = 1/[\sigma^2(F) + \rho F^2]$ was employed with a final ρ value of 0.0001. No evidence of secondary extinction was found.

Sources of scattering factors and computer programs have been given elsewhere [3]. The final atomic coordinates for non-hydrogen atoms are given in Table 2 and important distances and angles in Table 3. Lists of structure factors, anisotropic thermal parameters and fractional coordinates for hydrogen atoms may be obtained from the authors.

Discussion

Figure 1 shows the dimeric unit of p-PhOC$_6$H$_4$TeCl$_3$ and atom labeling. The geometry at each tellurium atom is that of a slightly distorted square pyramid with

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) IN p-PhOC$_6$H$_4$TeCl$_3$

Te(1)–Cl(1)	2.363(2)	Cl(1)–Te(1)–Cl(2)	92.3(1)
Te(1)–Cl(2)	2.372(2)	Cl(1)–Te(1)–Cl(3)	93.6(1)
Te(1)–Cl(3)	2.768(2)	Cl(2)–Te(1)–Cl(3)	173.1(1)
Te(1)–Cl(4)	2.798(2)	Cl(1)–Te(1)–Cl(4)	175.2(1)
Te(1)–C(11)	2.116(6)	Cl(2)–Te(1)–Cl(4)	90.0(1)
		Cl(3)–Te(1)–Cl(4)	84.3(1)
Te(2)–Cl(3)	2.754(2)	Cl(1)–Te(1)–C(11)	92.7(2)
Te(2)–Cl(4)	2.751(2)	Cl(2)–Te(1)–C(11)	91.6(2)
Te(2)–Cl(5)	2.370(2)	Cl(3)–Te(1)–C(11)	84.7(2)
Te(2)–Cl(6)	2.389(2)	Cl(4)–Te(1)–C(11)	91.3(2)
Te(2)–C(31)	2.105(6)	Cl(3)–Te(2)–Cl(4)	85.4(1)
O(2)–C(34)	1.376(8)	Cl(3)–Te(2)–Cl(5)	92.6(1)
O(2)–C(41)	1.386(7)	Cl(4)–Te(2)–Cl(5)	177.8(1)
		Cl(3)–Te(2)–Cl(6)	175.6(1)
O(1)–C(14)	1.366(9)	Cl(4)–Te(2)–Cl(6)	90.3(1)
O(1)–C(21)	1.395(8)	Cl(5)–Te(2)–Cl(6)	91.7(1)
		Cl(3)–Te(2)–C(31)	87.4(2)
mean C-C [a]		Cl(4)–Te(2)–C(31)	89.4(2)
C(11)–C(16)	1.385(9)	Cl(5)–Te(2)–C(31)	91.5(2)
C(21)–C(26)	1.378(14)	Cl(6)–Te(2)–C(31)	91.9(2)
C(31)–C(36)	1.387(9)		
C(41)–C(46)	1.372(14)	Te(1)–Cl(3)–Te(2)	95.0(1)
		Te(1)–Cl(4)–Te(2)	94.0(1)
mean C-C-C		C(14)–O(1)–C(21)	119.1(5)
C(11)–C(16)	120.0(6)	C(34)–O(2)–C(41)	120.0(5)
C(21)–C(26)	120.0(9)	Te(1)–C(11)–C(12)	120.4(5)
C(31)–C(36)	120.0(6)	Te(1)–C(11)–C(16)	118.4(5)
C(41)–C(46)	120.0(9)		
Te(1)...Cl(2′) [b]	3.695(2)	O(1)–C(14)–C(13)	117.6(6)
Te(2)...Cl(5″)	3.709(2)	O(1)–C(14)–C(15)	122.1(6)
Te(1)...Te(2)	4.073(2)	O(1)–C(21)–C(22)	116.0(6)
Te(1)...Te(1′)	4.239(2)	O(1)–C(21)–C(26)	122.0(7)
Te(2)...Te(2″)	4.007(2)	O(2)–C(34)–C(33)	122.2(5)
		O(2)–C(34)–C(35)	116.6(6)
		O(2)–C(41)–C(42)	121.6(6)
		O(2)–C(41)–C(46)	118.0(6)
		C(11)–Te(1)...Cl(2′)	168.5(2)
		C(31)–Te(2)...Cl(5″)	159.7(2)
		Te(1)–Cl(2)...Te(1)	85.7(2)
		Te(2)–Cl(5)...Te(2″)	79.1(2)

[a] E.s.d.'s on average values are calculated with the use of the 'scatter formula': $\sigma = [\Sigma(d_i - \bar{d})^2/(N-1)]^{1/2}$ [b] Symmetry equivalent positions are: ′ $1-x, 1-y, 1-z$; ″ $-x, -y, 1-z$.

the chlorine atoms in the basal positions and the organic group apical. The pyramids are fused in pairs by a shared basal edge, i.e., the two chlorine atoms are bridging. The two p-phenoxyphenyl groups are *trans* to each other, so that the dimer has a pseudo centre of inversion. The structure of p-PhOC$_6$H$_4$TeCl$_3$ is thus quite dissimilar from those of PhTeCl$_3$ [1], p-EtOC$_6$H$_4$TeCl$_3$ [7] and ClC$_2$H$_4$TeCl$_3$ [8], where the structural units, CTeCl$_4$, are linked into polymeric chains through *cis* basal chlorine atoms. The structure, instead, is similar to p-EtOC$_6$H$_4$TeX$_3$ (X = Br, I) [7] with the difference that the two aryl groups in the dimer of these compounds are *cis*

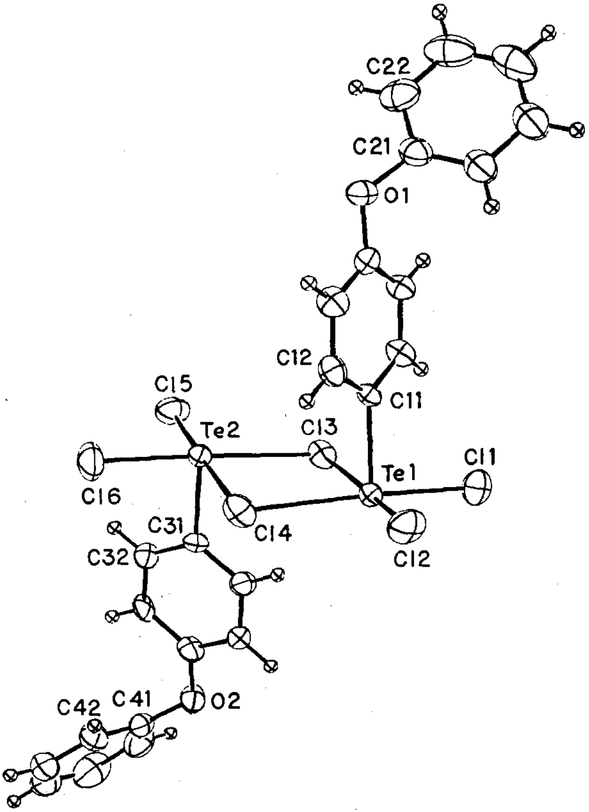

Fig. 1. Structure of p-$PhOC_6H_4TeCl_3$ showing the dimeric molecular unit and the atom numbering. The atoms are drawn with 50% probability ellipsoids.

to each other. The pair of pyramid bases are more tilted in p-$PhOC_6H_4TeCl_3$ than in p-$EtOC_6H_4TeBr_3$ and p-$EtOC_6H_4TeI_3$, which is clear from the dihedral angle of 9.6° between the pair of planes in the trichloride as compared to the angle of 1.2° and 5.2° [7] in the tribromide and triiodide, respectively. It was argued by Alcock and Harrison [1] that the dimeric structure is adopted by p-$EtOC_6H_4TeX_3$ (X = Br and I) and not by $RTeCl_3$ compounds, because the formation of a double bridge is less favorable with the smaller chlorine atoms. The present structure, however, indicates that the size of the chlorine atom does not prohibit the formation of the double-bridge, which was predicted on the basis of vibrational spectroscopic studies [11].

It is generally assumed that the square pyramidal geometry around tellurium is derived from an octahedron with the remaining position occupied by the non-bonding electron pair. This compound, like a few others, such as $SeOCl_2 \cdot 2py$ [12], $(C_9H_8NO)^+$ $(SeOCl_3)^-$ [13], $(Me_3Te)^+$ $(MeTeI_4)^-$ [14] and $(Et_2NH_2)^+$ (p-$PhOC_6H_4TeCl_4)^-$ [15] shows a secondary bond interaction towards the vacant site of the coordination octahedron. This interaction occurs between the tellurium atom of one dimer and the chlorine atom on the adjacent dimer at an average distance of 3.702(2) Å which is typical of Te...Cl secondary bonds [2–6,15]. This interaction not only completes the coordination octahedron of each of the tellurium atoms of

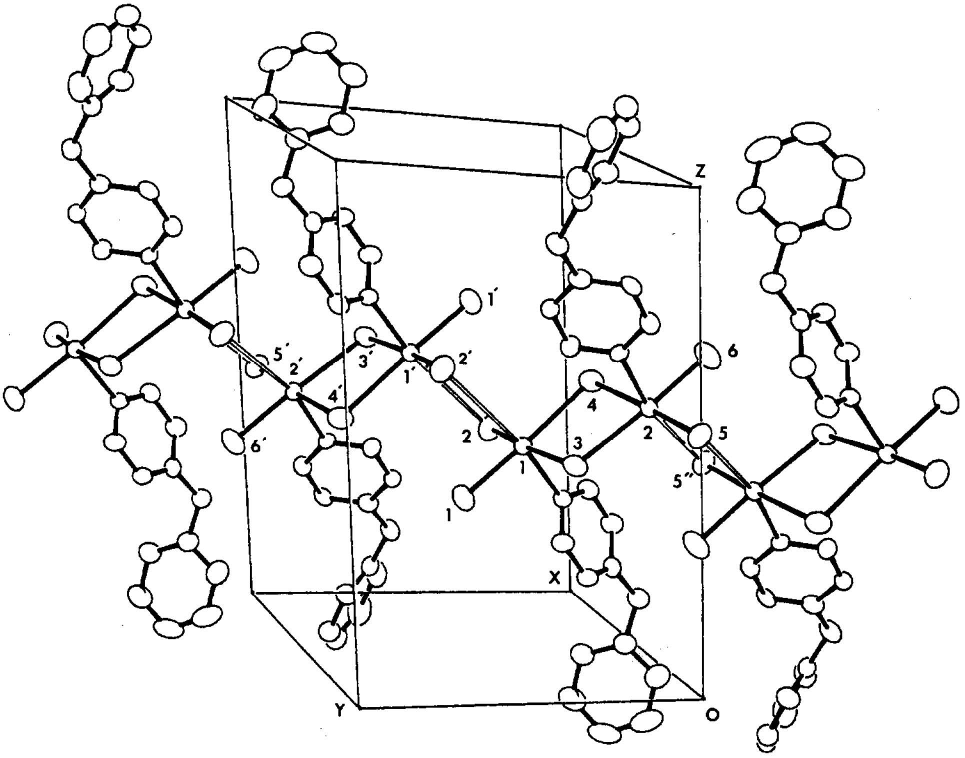

Fig. 2. Packing diagram illustrating continuous chains of p-PhOC$_6$H$_4$TeCl$_3$ dimers. Secondary bonds are shown as open bonds. Hydrogen atoms are omitted for clarity. Symmetry related possitions are same as in Table 3.

the dimer, but also links the dimers into continuous step-like chains perpendicular to the crystallographic z-axis as shown in Fig. 2. The bond angles, C(11)–Te(1)...Cl(2′) of 168.5(2)° and C(31)–Te(2)...Cl(5″) of 159.7(2)° are less than the ideal 180°, but are comparable to 166.2(2)° in p-PhOC$_6$H$_4$TeCl$_4^-$ [15] and 166° in MeTeI$_4^-$ [14]. Distortions along Te–Cl...Te′ are less in p-PhOC$_6$H$_4$TeCl$_3$ (85.7(2) and 79.1(2)°) than in p-PhOC$_6$H$_4$TeCl$_4^-$ (78.5(3)°) [15]. These distortions put tellurium atoms closer together so that Te(1)...Te(1′) and Te(2)...Te(2″) distances are 4.239(2) and 4.007(2) Å respectively, considerably shorter than the Te...Te Van der Waals distance of 4.4 Å [16].

It is interesting to compare the environment about tellurium in each p-PhOC$_6$H$_4$TeCl$_3$ unit with that in solid TeCl$_4$ [17]. In TeCl$_4$, there are three mutually *cis*-Te–Cl(terminal) bonds (2.377(3) Å) and another three mutually *cis*-Te–Cl(bridging) bonds 2.929(3) Å) to form a distorted octahedron around each tellurium atom within the tetrameric Te$_4$Cl$_{16}$ unit. The substitution of one Te–Cl(t) bond by a Te–C bond in p-PhOC$_6$H$_4$TeCl$_3$ leads to a slight lengthening of the remaining *cis*-Te–Cl(t) bonds (average 2.374(2) Å) and a shortening of the two remaining Te–Cl(br) bonds (average 2.768(2) Å). The bridging chlorine *trans* to the Te–C bond is replaced by a secondary Te...Cl interaction at a much greater distance (average 3.702(2) Å). The fact that the Te–Cl(br) distances are shorter in p-PhOC$_6$H$_4$TeCl$_3$ is not surprising because the chlorine atoms bridge only two tellurium atoms rather than three as in

Te_4Cl_{16}. However, it is notable that the average Cl(br)–Te–Cl(br) bond angle is 85.0(2)° in Te_4Cl_{16} and 84.9(2)° in $[p\text{-}PhOC_6H_4TeCl_3]_2$. The slight lengthening of the Te–Cl(t) bonds on substitution of one chlorine atom by a *p*-phenoxyphenyl group is consistent with the substitution by a less electronegative ligand. The average distance of 2.374(2) Å is the shortest of all similar distances reported for $RTeCl_3$ compounds. The Te–C distance (average 2.111(6) Å) is typical for Te–C bonds. The average CTeCl(br) angle is 87.8(2)°, whereas the average CTeCl(t) angle is 91.5(2)°.

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