

X-RAY STUDY OF BONDING IN CRYSTALLINE BIS(4-HYDROXY-3-METHYLPHENYL)TELLURIUM(IV) DICHLORIDE (β -ISOMER) *

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Summary

The crystal structure of the compound $(C_7H_7O)_2TeCl_2$, has been determined from X-ray counter data. The coordination about Te is trigonal-bipyramidal with a vacant equatorial position, Cl atoms apical, aryl ligands equatorial. An intermolecular $OH \cdots Cl$ hydrogen bond occurs in the crystal, but unlike other $R_2Te^{IV}Cl_2$ structures there is no significant secondary bonding between Te and Cl in neighbouring molecules. Crystals are monoclinic, space group $C2/c$, with a 14.651(3), b 12.787(3), c 8.279(2) Å, β 92.64(2)° and $Z = 4$. $R = 0.0298$ for 1907 observed reflections.

Introduction

Reaction of $TeCl_4$ with an excess of 2-methylphenol (*o*-cresol) results in the formation of three isomers R_2TeCl_2 , $R = 2$ -methylphenol [1]. The 1H NMR spectra can best be explained by assuming substitution of the aromatic ring by the chlorotellurium group at the *para* position with respect to the OH group in all three cases and the isomerism is considered to be steric. Cryoscopic and conductivity measurements indicate that these compounds are essentially monomeric and molecular in nature [2].

We now report the crystal structure analysis of the isomer (designated β) obtained by chloroform extraction of the reaction product. It has not been possible to obtain suitable crystals of the other two isomers designated α and γ which were obtained by benzene and acetonitrile extraction, respectively.

Experimental

Cell parameters and reflection intensities were measured from a needle-like crystal $0.4 \times 0.1 \times 0.1$ mm using an Enraf-Nonius CAD-4 diffractometer as de-

* Contribution from the Crystallography Unit, Universities of Aston and Birmingham.

TABLE 1
FRACTIONAL ATOMIC COORDINATES

	<i>x</i>	<i>y</i>	<i>z</i>
Te(1)	0.5	0.36807(2)	-0.25
Cl(1)	0.4715(1)	0.3592(1)	0.0473(1)
C(1)	0.6081(2)	0.2615(2)	-0.2100(3)
C(2)	0.5952(2)	0.1710(3)	-0.1232(4)
C(3)	0.6678(2)	0.1027(3)	-0.0918(4)
C(4)	0.7530(2)	0.1293(3)	-0.1478(4)
C(5)	0.7655(2)	0.2202(3)	-0.2331(5)
C(6)	0.6928(2)	0.2881(3)	-0.2659(4)
C(7)	0.6546(4)	0.0037(4)	0.0001(8)
O(1)	0.8221(2)	0.0598(2)	-0.1160(4)
H(1)	0.5397(28)	0.1594(31)	-0.0762(47)
H(2)	0.7067(29)	0.3555(29)	-0.3266(52)
H(3)	0.8275(29)	0.2387(35)	-0.2692(53)
H(4)	0.6012(32)	0.0024(49)	0.0723(68)
H(5)	0.7105(30)	-0.0138(54)	0.0741(60)
H(6)	0.6598(44)	-0.0623(40)	-0.0681(72)
H(7)	0.8712(42)	0.0923(51)	-0.1290(81)

scribed previously [3]. The scan range (ω°) was calculated from $(1.0 + 0.35 \tan \theta)$ and the scan speed varied from 1.0 to $3.3^\circ \text{ min}^{-1}$ depending on the intensity. 2994 reflections were scanned in the range $2 < \theta < 30^\circ$. Two standard reflections remeasured every 2 h showed no significant variation. Lorentz and polarisation factors were applied; 1907 unique reflections [$F > 5\sigma(F)$] were considered observed and were used in the structure analysis.

Crystal data. $\text{C}_{14}\text{H}_{14}\text{O}_2\text{TeCl}_2$, $M = 412.8$, monoclinic, a 14.651(3), b 12.787(3), c 8.279(2) Å, β 92.64(2) $^\circ$, U 1549 Å³, $Z = 4$, D_c 1.77 g cm⁻³, $F(000) = 800$, $\mu(\text{Mo-K}\alpha, \lambda$ 0.71069 Å) 2.1 mm⁻¹, space group Cc or $C2/c$ from systematic absences; $C2/c$ established as a result of the analysis.

The structure was solved by Patterson and Fourier methods. Following least squares refinement, first with isotropic temperature factors and then anisotropically, hydrogen atoms were located from a difference map; those attached to phenyl C were refined isotropically; methyl H atoms were refined with constraints and one common isotropic temperature factor. The calculations were terminated when all shifts were less than 0.1σ and R and R_w 0.030 and 0.038, respectively with $w = 1/[\sigma^2(F) + 0.0008F^2]$.

Computations were carried out largely with SHELX [4]. Atomic coordinates are given in Table 1. Structure factors and thermal parameters are available from the authors.

Results and discussion

The molecule possesses exact 2-fold rotation (C_2) symmetry, atoms numbered 21–27 being related by the symmetry to those numbered 1–7, respectively, and Cl(2) is symmetry related to Cl(1) (see Fig. 1). The coordination about tellurium can be considered as trigonal bipyramidal with a lone pair of electrons occupying the third

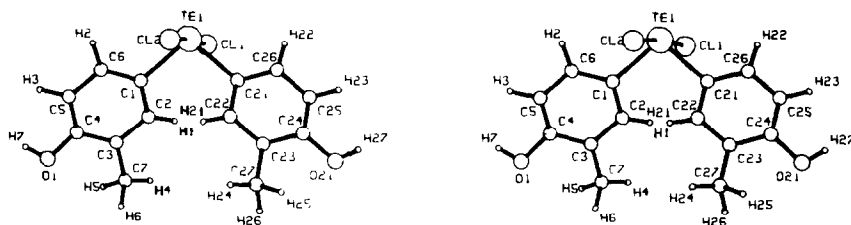


Fig. 1. Stereoscopic view of $(C_7H_7O)_2TeCl_2$ showing the atom numbering.

equatorial site, similar to that in a number of other R_2TeX_2 compounds ($X = F, Cl$ or Br) [5–10]. The Cl atoms occupy the apical sites. The equatorial $C-Te-C$ angle (99.2°) (Table 2) is compressed by the lone pair in accord with VSEPR theory [11]. The $Te-C$ bond length, 2.104 \AA , is, as might be expected, slightly shorter than is generally found [3] in crystal structures containing tellurium bonded to sp^3 -hybridised carbon atoms, but is in good agreement with the sum of the Pauling [12] single bond covalent radii of Te (1.37 \AA) and sp^2 -hybridised carbon (0.74 \AA), and with the values in the crystal structures of the analogous compounds Ph_2TeCl_2 [6], Ph_2TeF_2 [7], and phenoxatellurin-10,10-dichloride [8], range 2.087 – 2.111 \AA . In Ph_2TeCl_2 and Ph_2TeF_2 the $C-Te-C$ angles are $99.0(3)$ and $96.9(1)^\circ$, respectively, very close to the value in the title compound.

The $Te-Cl$ distance, 2.518 \AA is much larger than the sum of the covalent radii, 2.36 \AA [12] or the $Te-Cl$ distance in $TeCl_4$, mean 2.311 \AA [13], but is close to the values found in the crystal structures of four other R_2TeCl_2 compounds, range 2.45 – 2.58 \AA , mean 2.51 \AA [5,6,8,9]; these lengths are, however, very much shorter than the sum of the Van der Waals radii of Te and Cl , 4.00 \AA according to Pauling [12], or 3.81 \AA according to Bondi [14], and the $Te-Cl$ bonds can be considered to be

TABLE 2
BOND DISTANCES (\AA) AND ANGLES ($^\circ$)^a

$Te-Cl(1)$	2.518(1)	$C(3)-C(7)$	1.494(5)
$Te-C(1)$	2.104(3)	$C(4)-C(5)$	1.377(5)
$C(1)-C(2)$	1.380(4)	$C(4)-O(1)$	1.364(4)
$C(2)-C(3)$	1.391(4)	$C(5)-C(6)$	1.391(5)
$C(3)-C(4)$	1.393(5)	$C(6)-C(1)$	1.386(4)
$Te \cdots Cl(1')$	3.884(1)	$H(7) \cdots Cl''$	2.45(5)
$O(1) \cdots Cl(1'')$	3.222(3)		
$Cl(1)-Te-Cl(2)$	174.8(1)	$C(2)-C(3)-C(4)$	118.3(3)
$Cl(1)-Te-C(1)$	88.5(1)	$C(7)-C(3)-C(4)$	121.0(3)
$Cl(1)-Te-C(21)$	88.1(1)	$C(7)-C(3)-C(2)$	120.8(3)
$C(1)-Te-C(21)$	99.2(2)	$C(3)-C(4)-C(5)$	121.3(3)
$C(2)-C(1)-Te$	120.3(2)	$O(1)-C(4)-C(3)$	116.5(3)
$C(6)-C(1)-Te$	117.9(2)	$O(1)-C(4)-C(5)$	122.3(3)
$C(2)-C(1)-C(6)$	121.7(3)	$C(4)-C(5)-C(6)$	120.6(3)
$C(1)-C(2)-C(3)$	120.1(3)	$C(5)-C(6)-C(1)$	118.1(3)

^a Atoms labelled $Cl(2)$ and $C(21)$ are related by the molecular two-fold rotation axis to $Cl(1)$ and $C(1)$ respectively (coordinate transformation $1-x, y, -\frac{1}{2}-z$). Prime and double prime refer to equivalent positions $1-x, 1-y, -z$ and $1\frac{1}{2}-x, \frac{1}{2}-y, -z$ respectively.

essentially covalent in nature. The Cl–Te–C angles are slightly less than 90° so that the Te–Cl bonds are bent slightly away from the lone pair, as might be expected from VSEPR theory, resulting in a Cl–Te–Cl angle of 174.8° .

The geometry of the organic residue is unexceptional. The phenyl ring is planar to within ± 0.005 Å and the tellurium, hydroxyl oxygen and methyl carbon atoms are displaced by 0.09, -0.02 and -0.02 Å respectively.

The coordination of the tellurium in the title compound is thus very similar to that in other R_2TeX_2 structures and in particular it is virtually identical to that in Ph_2TeCl_2 [6]. There is, however, a difference when next-nearest $Te \cdots Cl$ interactions are considered. In the crystal structure of Ph_2TeCl_2 there is a $Te \cdots Cl$ contact of $3.677(2)$ Å, corresponding to a secondary [15] interaction, approximately *trans* to one of the Te–C bonds giving a coordination geometry described [6] as octahedral with one site vacant; secondary interactions of 3.37 – 3.65 Å occur also in 1,1-dichloro-1-telluracyclohexane-3,5-dione [5], phenoxatellurin-10,10-dichloride [8] and Me_2TeCl_2 [9]. These are all considerably less than the accepted [12,14] Van der Waals contact distance. In the title compound, the next-nearest $Te \cdots Cl$ distance is $3.884(1)$ Å, to two symmetry-related chlorine atoms. This distance is greater than the Van der Waals contact distance of Bondi [14] and only slightly less than that proposed by Pauling [12]. These contacts occur on the vacant face of the tellurium coordination polyhedron, but they are not sterically significant [15] in the sense that they are not *trans* to any of the covalent bonds at tellurium. A stronger intermolecular interaction appears to be a hydrogen bond between the hydroxyl group and another neighbouring chlorine atom with $O(1) \cdots Cl(1'')$ $3.222(3)$, $H[O(1)] \cdots Cl(1'')$ $2.45(5)$ Å and the angle $H-O \cdots Cl''$ $20(4)^\circ$. This is, however, only a fairly weak hydrogen bond [16].

The reason for the absence of a significant $Te \cdots Cl$ secondary interaction in this structure, unlike the situation in the crystal structure of Ph_2TeCl_2 and other R_2TeCl_2 compounds, is not entirely clear. ^{13}C NMR studies [17] of a series of organotellurium(IV) dihalides in solution indicate some weakening of the Te–C(aryl) bond in going from phenyl to *p*-methoxyphenyl derivatives. A similar effect would probably be operative in the title compound due to the 4-hydroxy substituent. The observed Te–C bond lengths, however, show no such distinction ($2.111(7)$ and $2.102(7)$ Å [6] in Ph_2TeCl_2 compared with $2.104(3)$ Å in our compound). There are also no major conformational changes due to the substituents in the phenyl ring which were suggested [17] to be the cause of the bond weakening by reducing *5p*–*2p* conjugation between tellurium and the ring. Thus in Ph_2TeCl_2 the angles between the two phenyl rings and the equatorial plane of the trigonal bipyramid are 29.6 and 43.8° and the Ph–Ph inter-ring angle is 55.9° . In our compound the corresponding dihedral angles are 37.1 , 37.1 (equal by symmetry) and 58.2° . The molar conductivities (in acetonitrile solution) are also very similar, 3.5 and 3.9 $\text{ohm}^{-1} \text{cm}^2$, respectively [18,1].

A more likely rationale for the difference in solid state structure of these two compounds is the occurrence of intermolecular hydrogen bonding in the title structure. In none of the R_2TeCl_2 compounds, whose crystal structures have been reported [5,6,8,9,19], is hydrogen bonding possible and the structure involves, in every case, short $Te \cdots Cl$ secondary interactions. This suggests that such $Te \cdots Cl$ interactions can only be quite weak, probably energetically less favourable than the rather weak hydrogen bond present in the title structure. In further support of this

argument, the crystal structure of the closely related bis(4-methoxyphenyl)-tellurium(IV) dichloride, where hydrogen bonding is not possible, exhibits secondary Te-Cl interactions with lengths in the range 3.44–3.65 Å (A.J. Edwards personal communication).

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