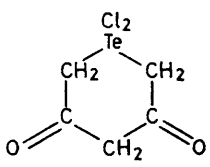
'Tellurium Acetylacetonates': Crystal Structures of 1,1-Dichloro-1-telluracyclohexane-3,5-dione and 1-Telluracyclohexane-3,5-dione

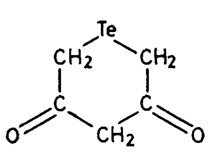
By **Colin L. Raston, Rodney J. Secomb,** and **Allan H. White,*** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands 6009, Western Australia

The crystal structures of the title compounds $Cl_2TeC_5H_6O_2$ (I) and $TeC_5H_6O_2$ (II) have been determined by the heavy-atom method and refined byl east squares to *R* 0.060 (I) (1 642 reflections) and 0.058 (II) (1 182 reflections). Crystals of (I) are monoclinic, *a* = 10.565(7), *b* = 22.03(1), *c* = 7.185(3) Å, β = 130.74(6)°, *Z* = 6, space group *Cm*; crystals of (II) are orthorhombic, *a* = 5.2765(9), *b* = 10.744(2), *c* = 22.296(6) Å, *Z* = 8, space group *I2cb*. The structures comprise monomeric units. In (I) the tellurium environment is pseudo-trigonal-bipyramidal with axial chlorines [means: Te–Cl 2.49 Å; Cl–Te–Cl 171.8° (opposite to the 'lone pair')]; C–Te–C is 95.5°. In (II) C–Te–C is reduced to 89.5°. Te–C in both compounds is 2.16 Å.

REACTION of $TeCl_4$ with acetylacetone in chloroform yields a compound formulated as $TeCl_2{\cdot}C_5H_6O_2$ (I); reduction of (I) with aqueous sodium bisulphite yields $TeC_5H_6O_2$ (II). [If the chloroform in the initial reaction is dry and alcohol-free a further derivative $TeCl_2{\cdot}2C_5H_7O_2$ (III) may be isolated.[1,2]] Spectroscopic studies [2] have suggested that the acetylacetone is not bonded to the tellurium through the oxygen or central carbon, as is usual, but instead yields derivatives of 1-telluracyclohexane-3,5-dione.



(I)



(II)

In order to confirm the structures of these unusual reaction products, crystallographic studies were initiated. All the derivatives were prepared, purified, and recrystallized as described in the literature, suitable crystals of (I) and (II) being obtained directly by slow evaporation. Although (III) was also crystalline, it was obtained as microscopic hairs of insufficient thickness, and only the structures of (I) and (II) were determined; a previous determination of the structure of (II) has been carried out by film methods.[3]

EXPERIMENTAL

A crystal section of (I), initially *ca.* 0.36 × 0.16 × 0.36 mm, and a crystal of (II), 0.18 × 0.07 × 0.07 mm, were used for the crystallographic work. Unit-cell dimensions were obtained in each case by a least-squares fit of 15 reflections with 2θ *ca.* 25° centred in the counter aperture

---

[1] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1919, **117**, 1456; 1922, **121**, 922.

[2] D. H. Dewar, J. E. Fergusson, P. R. Hentschel, C. J. Wilkins, and P. P. Williams, *J. Chem. Soc.*, 1964, 688.

[3] G. L. Parks, *Diss. Abs.*, 1969, **B29**, 3450.

of a Syntex $P\bar{1}$ four-circle diffractometer. Data were then gathered from each specimen by a conventional 2θ—θ scan. For (I) the range was $2\theta < 60°$; although the data extended beyond this range, consideration was taken of the fact that the crystal decomposed badly in the *X*-ray beam and data were collected rapidly in consequence. 1 654 Independent reflections were gathered, of which 1 642 with $I > \sigma(I)$ were considered observed and used in the structure solution and refinement after suitable scaling; the erosion of the crystal was considerable so that an absorption correction was considered of little use. For (II), the data although rather weak were also extensive and an independent set in the range $2\theta < 70°$ was gathered yielding 1 496 reflections of which 1 182 had $I < \sigma(I)$; an absorption correction was applied. Mo-K_α radiation (monochromatic, λ = 0.710 69 Å) was used for both structure determinations.

TABLE 1

Atomic fractional cell parameters, with least-squares estimated standard deviations in parentheses; the decimal preceding (*x*,*y*,*z*) is omitted

Atom	*x*	*y*	*z*
Compound (I)			
Molecule α			
Te	0	11 618(3)	0
Cl(1)	2 914(4)	1 520(2)	2 253(7)
Cl(2)	−3 052(6)	0 930(2)	−2 532(10)
C(1)	−041(2)	2 011(8)	098(3)
C(2)	019(2)	2 535(6)	042(2)
O	119(2)	2 909(6)	205(2)
C(3)	−056(2)	2 612(8)	−224(3)
C(1′)	−051(2)	1 502(6)	−326(2)
C(2′)	008(2)	2 136(6)	−294(2)
O′	094(2)	2 261(6)	−342(2)
Molecule β			
Te	4 979(2)	0(−)	1 991(2)
Cl(1)	7 923(7)	0(−)	3 877(15)
Cl(2)	1 846(6)	0(−)	−0 595(9)
C(1)	452(2)	0 733(6)	−042(3)
C(2)	323(2)	0 571(6)	−301(3)
O	197(2)	0 897(7)	−445(2)
C(3)	347(3)	0(−)	−396(4)
Compound (II)			
Te	0(−)	13 642(4)	06 635(2)
C(1)	−085(2)	3 323(9)	0 638(4)
H(1a) *	09(3)	38(1)	059(5)
H(1e)	−15(3)	32(1)	031(5)
C(2)	−264(2)	3 583(8)	1 113(4)
O	−485(3)	3 840(7)	1 030(4)
C(3)	−163(3)	3 458(9)	1 764(4)
H(3a)	07(3)	38(1)	172(5)
H(3e)	−25(3)	37(1)	198(6)
C(1′)	119(2)	1 560(9)	1 596(4)
H(1a′)	12(2)	04(5)	177(5)
H(1e′)	27(2)	22(1)	161(5)
C(2′)	−101(2)	2 108(8)	1 909(3)
O′	−235(2)	1 521(7)	2 248(3)

* a = Axial, e = equatorial.

Crystal Data.—(I). $C_5H_6Cl_2O_2Te$, *M* = 296, Monoclinic, *a* = 10.565(7), *b* = 22.03(1), *c* = 7.185(3) Å, β = 130.74(6)°, *U* = 1 267(1) Å^3, D_m = 2.33(1), *Z* = 6, D_c = 2.32 g cm^{-3}, *F*(000) = 828, μ(Mo-K_α) = 41 cm^{-1}. Space group *Cm* (C_s^3, no. 8).

(II). $C_5H_6O_2Te$, *M* = 225, Orthorhombic, *a* = 5.2765(9), *b* = 10.744(2), *c* = 22.296(6) Å, *U* = 1 264(1) Å^3, D_m = 2.35(1), *Z* = 8, D_c = 2.37 g cm^{-3}, *F*(000) = 832, μ(Mo-K_α) = 47 cm^{-1}. Space group *I2cb* (C_{2v}^{21}, no. 45).

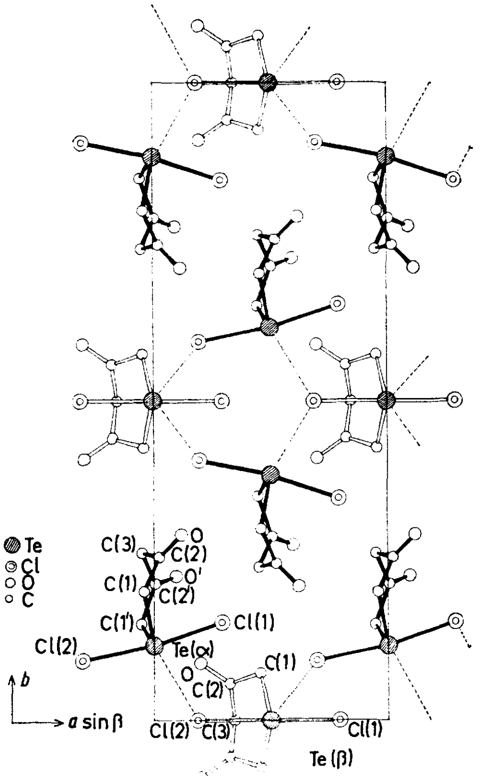


FIGURE 1 Unit-cell contents of (I) projected down *c*; dotted lines show intermolecular Te · · · Cl contacts

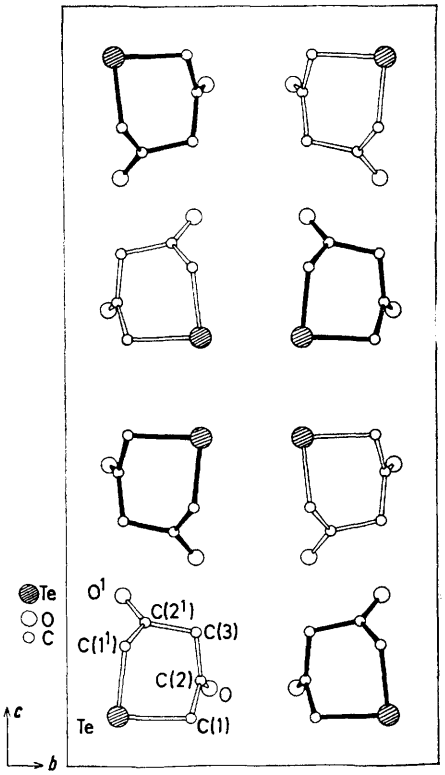


FIGURE 2 Unit-cell contents of (II) projected down *a*

Both structures were solved by the heavy-atom method and refined by full-matrix least squares with anisotropic thermal parameters in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{23}klb^*c^*)]$ for all atoms except hydrogens which were refined positionally in (II). Scattering factors used were for the neutral atoms,[4,5] those for Te and Cl being corrected for anomalous dispersion effects ($\Delta f'$, $\Delta f''$).[6] Refinement converged with no parameter shift $>0.2\sigma$, and R 0.060 (I) and 0.058 (II); $R' \{= [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ was 0.077 (I) and 0.060 (II); the weighting scheme was of the form $w = [\sigma^2(F_o) + 10^{-4}n(F_o)^2]^{-1}$ with $n = 6$ for (I) and $n = 5$ for (II).

TABLE 2

(*a*) Non-hydrogen inetratomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses

	(Iα)				(II)		
	Unprimed	Primed	(Iβ)	Mean	Unprimed	Primed	Mean
Te–C(1)	2.14(2)	2.16(2)	2.18(2)	2.16	2.15(1)	2.18(1)	2.17
C(1)–C(2)	1.50(3)	1.49(2)	1.46(2)	1.48	1.45(1)	1.48(1)	1.47
C(2)–C(3)	1.53(2)	1.50(3)	1.53(3)	1.52	1.55(1)	1.52(1)	1.54
C(2)–O	1.23(2)	1.20(3)	1.25(2)	1.23	1.21(2)	1.21(1)	1.21
C(1)–Te–C(1′)	95.2(7)		95.7(7)	95.5	89.5(4)		89.5
Te–C(1)–C(2)	112(1)	112(1)	112(1)	112	107.9(6)	105.2(6)	106.5
C(1)–C(2)–C(3)	117(1)	118(2)	119(1)	118	116.4(9)	116.7(8)	116.6
C(1)–C(2)–O	120(2)	120(2)	121(2)	120	124.0(9)	123.2(9)	123.6
O–C(2)–C(3)	123(2)	122(2)	122(2)	122	119.5(10)	120.1(9)	119.8
C(2)–C(3)–C(2′)	111(1)		110(3)	111	110.9(7)		110.9
Te · · · C(2)	3.05(2)	3.05(2)	3.04(2)	3.04	2.938(9)	2.937(8)	2.94
Te · · · C(3)	3.45(2)		3.46(3)	3.46	3.437(10)		3.44
Te–Cl(1)	2.493(5)		2.453(8)	2.49			
Te–Cl(2)	2.512(6)		2.521(6)				
Cl(1)–Te–Cl(2)	172.7(2)		170.9(3)	171.8			
Cl(1)–Te–C(1)	86.4(5)	85.6(4)	89.0(5)	87.3			
Cl(2)–Te–C(1)	88.7(5)	89.4(4)	84.9(5)				

Intermolecular contacts < van der Waals contacts in (I): Te(α) · · · Cl(β2) 3.409(6); Te(β) · · · Cl(α2) (at $1 + x, y, 1 + z$) 3.650(7).

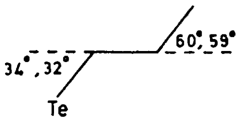
(*b*) Torsion angles (°) associated with the heterocyclic ring, In molecules (Iα) and (II) the two values correspond to the unprimed and primed ring sections respectively

	(Iα)	(Iβ)	(II)
C(1′)–Te–C(1)–C(2)	−37, 36	−34	−57, 57
Te–C(1)–C(2)–C(3)	59, −57	57	68, −71
Te–C(1)–C(2)–O	−126, 129	125	−108, 107
C(1)–C(2)–C(3)–C(2′)	−72, 72	72	−66, 69
O–C(2)–C(3)–C(2′)	112, −114	−109	111, −109

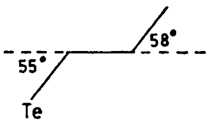
Data processing was carried out with a local adaptation of the '*X*-Ray' system [7] on a CDC 6200 computer. Structure amplitudes, least-squares planes, and thermal parameters are given in Supplementary Publication No. SUP 21778 (17 pp., 1 microfiche).* Results are given in the Tables 1 and 2, and atom labelling is shown in Figures 1 and 2. Primes denote the transformation ($x, \bar{y}, z$). Atoms in the upper half of each cell are shown with solid bonds.

DISCUSSION

The two structure determinations confirm the previously suggested formulations as 1-telluracyclohexane-3,5-dione and its dichloride, both with six-membered rings adopting the chair conformation and with no abnormally short intermolecular contacts except for some rather long Te · · · Cl interactions in (I) (Figure 1). Molecule (Iβ) has a crystallographic symmetry plane. Within the two molecules, the ring geometries at the atoms other than tellurium are reasonably close to those expected for trigonal-planar and tetrahedral carbon atoms, but subtle and significant differences are found both within the ring and about the tellurium itself between (I) and (II) as a consequence of the change in valence and co-ordination number of the tellurium atoms. These may be broadly justified or described in terms of conventional electron-pair repulsion theory. In (I), the tellurium geometry is best considered as that expected for tellurium(IV), being a distorted trigonal-bipyramidal configuration consistent with the presence of a stereochemically active lone pair in the equatorial plane. The two long Te–Cl bonds are axial but with the angle between them diminished from 180° by interaction with the lone pair; the C–Te–C angle is likewise considerably diminished from the tetrahedral value. In (II), the tellurium geometry is typical of that found for tellurium(II), the C–Te–C angle being further reduced to 90°. In consequence, changes are observed in the interplanar angles within the ring and significant differences are also observed in the angles involving C(1) and C(1′) and the dependent Te · · · C(2) distance as well as in the associated torsion angles (Table 2).



(I; α, β)



(II) C(1) and C(1′)

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[7] 'The *X*-Ray System,' Technical Report TR 172, June 1972, Computer Science Center, University of Maryland, U.S.A.

Te^{IV}–Cl bonded distances previously reported vary between 2.31 Å in solid $TeCl_4$ (ref. 8) and $[TeCl_3][AlCl_4]$ (ref. 9), in each of which the tellurium has three short and three long Te–Cl distances, and $[TeCl_6]^{2-}$ (2.54 Å)[10] with a regular octahedral co-ordination. The present mean value of 2.48 lies as expected in this range and is similarly comparable to those found in $TeMe_2Cl_2$ (2.48 and 2.54 Å)[11] which has similar stereochemistry. The tellurium–carbon distances are similar in (I) and (II) (a fact probably best ascribed to the change in C–Te–C angle), and comparable with previously reported values.

[5/2305 *Received, 25th November*, 1975]

---

[8] B. Buss and B. Krebs, *Inorg. Chem.*, 1971, **10**, 2795.

[9] B. Krebs, B. Buss, and D. Altena, *Z. anorg. Chem.*, 1971, **386**, 257.

[10] A. C. Hazell, *Acta Chem. Scand.*, 1966, **20**, 165; E. E. Aynsley and A. C. Hazell, *Chem. and Ind.*, 1963, 611.

[11] G. D. Christofferson, R. A. Sparks, and J. D. McCullough, *Acta Cryst.*, 1958, **11**, 782.