Secondary Bonding. Part 13.[1] Aryl-tellurium(IV) and -iodine(III) Acetates and Trifluoroacetates. The Crystal and Molecular Structures of Bis(*p*-methoxyphenyl)tellurium Diacetate, μ-Oxo-bis[diphenyltrifluoroacetoxytellurium] Hydrate, and [Bis(trifluoroacetoxy)iodo]benzene †

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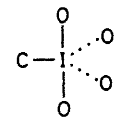
The crystal and molecular structures of the title compounds have been determined from diffractometer data by the heavy-atom method, and their preparations are described. Crystals of $(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{O}_2\text{CMe})_2$ (1) are monoclinic, space group $P2_1/c$, with unit-cell dimensions $a = 9.529(2)$, $b = 11.984(2)$, $c = 17.035(2)$ Å, $\beta = 101.70(2)°$, $Z = 4$, and for 3 033 observed reflections $[I/\sigma(I) > 3.0]$, $R = 0.022$. Crystals of $\{[\text{Ph}_2\text{Te}(\text{O}_2\text{CCF}_3)]_2\text{O}\}_2\cdot\text{H}_2\text{O}$ (2) are triclinic, space group $P\bar{1}$, with unit-cell dimensions $a = 13.988(3)$, $b = 14.287(3)$, $c = 15.689(3)$ Å, $\alpha = 80.40(2)$, $\beta = 81.89(2)$, $\gamma = 86.65(2)°$, $Z = 2$, and for 5 290 observed reflections, $R = 0.042$. Crystals of $\text{PhI}(\text{O}_2\text{CCF}_3)_2$ (3) are triclinic, space group $P\bar{1}$, with unit-cell dimensions $a = 9.787(4)$, $b = 9.055(3)$, $c = 7.674(3)$ Å, $\alpha = 91.45(3)$, $\beta = 99.78(3)$, $\gamma = 89.21(3)°$, $Z = 2$, and for 2 104 observed reflections, $R = 0.037$. All three compounds have pseudo-trigonal-bipyramidal primary geometry [Te–C 2.098(3) and 2.103(4), I–C 2.074(4); Te–O(μ-oxo) 1.981(7), Te–O and I–O (oxy-anion) 2.138—2.352 Å], and form secondary bonds to give pentagonal planar systems around Te and I, also with linear C–Te ··· O systems. In the light of these results, previously published tellurium nitrate structures are re-interpreted.

We have previously examined the intra- and inter-molecular bonding in phenyliodine acetate, dichloroacetate, and nitrate,[2] and in several phenyltellurium nitrates.[3] These have revealed a diversity of bonding patterns, markedly more complex than those found in the corresponding halides.[1,4] Both series of oxy-salts include an alternation between 'neutral' salts, *e.g.* $\text{PhI}(\text{O}_2\text{CMe})_2$ and $\text{Ph}_2\text{Te}(\text{ONO}_2)_2$, and μ-oxo-salts, *e.g.* $\text{PhI}(\text{ONO}_2)\text{–O–I}(\text{ONO}_2)\text{Ph}$. For the iodine compounds, a pattern has also been recognised of 'pentagonal planar' co-ordination, combining the T-shaped geometry expected for iodine(III) with two secondary I ··· O bonds, *e.g.* structure (A). Nothing similar has yet been recognised in the tellurium compounds. In this paper, additional evidence is brought to bear, from the structures of an aryltellurium acetate and trifluoroacetates of both tellurium and iodine.



(A)

Experimental

Preparations.—$(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{O}_2\text{CMe})_2$, *Compound* (1). Tellurium tetrachloride (27 g, 0.1 mol) was dissolved in a slight excess of anisole (25 cm³, 0.23 mol).[5] The yellow solution

$$2\text{MeOC}_6\text{H}_5 + \text{TeCl}_4 \longrightarrow (p\text{-MeOC}_6\text{H}_4)_2\text{TeCl}_2 + 2\text{HCl} \quad \text{(i)}$$

soon became orange and HCl was evolved [reaction (i)]. The solution was then gradually warmed (3 h) to about 100 °C until HCl evolution ceased and a solid red-brown mass of the crude product remained. This was recrystallised several times from methanol in the presence of charcoal, until colourless crystals of $(p\text{-MeOC}_6\text{H}_4)_2\text{TeCl}_2$ were obtained. This compound (0.41 g, 1 mmol) was then dissolved in benzene and AgO_2CMe added (0.35 g, 2.1 mmol). The mixture was stirred under reflux for 3 h, filtered, and evaporated slowly to give large crystals of $(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{O}_2\text{CMe})_2$ which were used directly for *X*-ray analysis.

$\text{Ph}_2\text{Te}(\text{O}_2\text{CMe})_2$. Diphenyltellurium dichloride was treated with a slight excess of AgO_2CMe in a variety of solvents including benzene, chloroform, and methanol. Most solvents gave sticky residues on slow evaporation but benzene gave short needle-like crystals of $\text{Ph}_2\text{Te}(\text{O}_2\text{CMe})_2$; however, these rapidly turned opaque in air and eventually crumbled, probably through loss of solvent. No useful *X*-ray data could be obtained.

$\{[\text{Ph}_2\text{Te}(\text{O}_2\text{CCF}_3)]_2\text{O}\}_2\cdot\text{H}_2\text{O}$, *Compound* (2). Diphenyltellurium oxide (0.759 g, 2.5 mmol) was dissolved in methanol (20 cm³) containing $\text{CF}_3\text{CO}_2\text{H}$ (0.6 g, 5 mmol). The solution was filtered and allowed to evaporate slowly to give colourless crystals of $\{[\text{Ph}_2\text{Te}(\text{O}_2\text{CCF}_3)]_2\text{O}\}_2\cdot\text{H}_2\text{O}$.

$\text{PhI}(\text{O}_2\text{CCF}_3)_2$, *Compound* (3). Peracetic acid (40%; 31 cm³, 0.24 mmol) (containing also 39% acetic acid, 15% water, 5% H_2O_2, and 1% H_2SO_4) was added dropwise to stirred iodobenzene (20.4 g, 0.1 mol) at 29—31 °C during 45 min. The solution was stirred for a further 20 min and then kept at 0 °C for 75 min; the precipitate was filtered off, washed with ice-water, and dried (P_4O_{10}; *in vacuo*) to give [di(acetoxy)-iodo]benzene (28.6 g, 88.8%), m.p. 160—161 °C (lit.,[6] 159—160 °C); ^{1}H n.m.r. (CDCl_3) δ 2.00 (s, 6 H, CH_3), 7.50 (m, 3 H, *m*- and *p*-H), and 8.10 (d, 2 H, *o*-H). This was then dissolved in 100% trifluoroacetic acid (50 cm³) at 50—55 °C, and the solution allowed to cool. The product was filtered off, washed with trifluoroacetic acid, and then dried to give [bis(trifluoroacetoxy)iodo]benzene (30.0 g, 78.5%), m.p. 119—122 °C (lit.,[7] 124—126 °C); ^{1}H n.m.r. (CDCl_3) δ 7.65 (m, 3 H, *m*- and *p*-H) and 8.22 (d, 2 H, *o*-H).

M.p.s are uncorrected. Proton n.m.r. spectra were recorded

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† *Supplementary data available* (No. SUP 23937, 65 pp.): structure factors, thermal parameters, and, for compound (1), H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Crystal data

	(1)	(2)	(3)
Compound	$(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{O}_2\text{CMe})_2$	$\{[\text{Ph}_2\text{Te}(\text{O}_2\text{CCF}_3)]_2\text{O}\}_2\cdot\text{H}_2\text{O}$	$\text{PhI}(\text{O}_2\text{CCF}_3)_2$
M	459.9	1 629.3	430.1
Formula	$C_{18}H_{20}O_6Te$	$C_{56}H_{42}F_{12}O_{11}Te_4$	$C_{10}H_5F_6IO_4$
System	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Absences	$h0l, l \neq 2n; 0k0, k \neq 2n$	—	—
a/Å	9.529(2)	13.988(3)	9.787(4)
b/Å	11.984(2)	14.287(3)	9.055(3)
c/Å	17.035(2)	15.689(3)	7.674(3)
α/°	90	80.40(2)	91.45(3)
β/°	101.70(2)	81.89(2)	99.78(3)
γ/°	90	86.65(2)	89.21(3)
U/Å^3	1 904.9(6)	3 058(1)	670.0(5)
D_c/g cm^{-3}	1.60	1.77	2.13
D_m/g cm^{-3}	—	1.62	2.11
Z	4	2	2
μ(Mo-K_α)/cm^{-1}	15.9	19.8	24.4
F(000)	912	1 564	408
Total reflections	3 772	6 408	2 406
Reflections with $I/\sigma(I) \geq 3.0$	3 033	5 290	2 104
$2\theta_{max.}$/°	50	50	50
Range (2θ) about α_1–α_2/°	±1.0	±1.0	±1.0
Minimum speed (2θ)/° min^{-1}	2.0	2.0	3.0
Temperature/°C	16	16	−100
Crystal dimensions/mm	0.5 × 0.5 × 0.3	0.4 × 0.2 × 0.2	0.5 × 0.2 × 0.1
Transmission factor range	0.60—0.74	0.74—0.82	0.67—0.86
Final R	0.022	0.042	0.037

at 220 MHz on a Perkin-Elmer R34 spectrometer with tetramethylsilane as the internal standard.

Crystal Structure Analysis.—Crystal data for compounds (1)—(3) are in Table 1. The data were collected with a Syntex $P2_1$ four-circle diffractometer, using variable scan speeds depending on the intensity of a 2-s pre-scan; for compound (2) reflections in the 30—50° range of 2θ were only measured if they exceeded a minimum count on an 8-s pre-scan. Backgrounds were measured at each end of the scan for a quarter of the time scan. In an initial study of compound (3) the crystal decomposed, and data collection was repeated with the crystal held at −100 °C with a Syntex LT-1 attachment. Three standard reflections were monitored every 200 reflections, and showed no significant changes during the data collections. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. Observed reflections only [$I/\sigma(I) \geq 3.0$] were used in refinement, and corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR.[8] Densities were measured by flotation; for compound (2), the discrepancy between observed and calculated density is probably due to partial hydrolysis as the crystals showed signs of decomposition during the measurement.

For compounds (1) and (3), the heavy atom was located by Patterson techniques and the light atoms were then found on successive Fourier syntheses. Compound (2) was initially supposed to be $\text{Ph}_2\text{Te}(\text{O}_2\text{CCF}_3)_2$, with six molecules per cell. The NORMAL link of MULTAN 80[9] suggested non-centrosymmetric statistics, and application of MULTAN 80 produced a number of peaks which were interpreted as six Te atoms in space group $P1$. Refinement from this starting point gradually revealed the structure, showing that it correctly had eight Te atoms in the unit cell, present as μ-oxo-dimers, and it was eventually found to be centrosymmetric. A careful search for a cell of higher symmetry[10] revealed an apparently monoclinic triple cell (19.398, 23.078, and 22.907 Å; 89.94, 116.56, and 90.26°), but a photographic survey showed the absence of m symmetry about the possible b axis.

Refinement was by least-squares methods, in large blocks. It was found necessary to include alternative fluorine atoms in both compounds (2) and (3), although the second positions in (3) had a population of only 0.2 (estimated from peak height on a Fourier difference synthesis and not refined). A water molecule was found in compound (2), which also had one phenyl ring with rotational disorder. Phenyl hydrogen atoms were inserted at calculated positions with fixed thermal parameters, and the methyl hydrogen atoms of compound (1) were refined satisfactorily as rigid groups with their carbon atoms. This compound showed signs of extinction, and therefore an extinction parameter was included in the refinement. This improved the agreement for a few strong reflections, but otherwise had little effect. For compounds (2) and (3), empirical weighting schemes were used, giving slightly reduced weight to reflections of low F and $\sin\theta$; for (1), a weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.000\,1$ was used. These schemes were shown to be satisfactory by weight analyses. For compounds (2) and (3) computing was with the X-RAY 76 system,[11] on a Burroughs B6700 computer; for (1), computing was with the SHELXTL system[12] on a Data General NOVA3, following initial processing on the Burroughs B6700. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 13. Final atomic co-ordinates are given in Table 2, bond lengths and angles in Table 3, and details of molecular planes in Table 4.

Discussion

Both I^{III} and Te^{IV} are expected to show pseudo-trigonal-bipyramidal geometry, with respectively two and one vacant position, and this is borne out in the present structures. Oxygen atoms occupy the axial positions, with O–X–O angles of 165—170°. These fairly large distortions from linearity are

Table 2. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $(p\text{-MeOC}_6\text{H}_4)_2\text{Te(O}_2\text{CMe)}_2$							
Te	4 913(1)	3 914(1)	1 184(1)	C(17)	8 629(4)	2 159(3)	5 006(2)
O(1)	9 130(2)	2 710(2)	4 364(1)	C(21)	3 222(3)	4 533(2)	1 676(2)
O(2)	−231(2)	5 930(2)	2 434(2)	C(22)	1 863(3)	4 547(3)	1 190(2)
O(11)	3 768(2)	2 376(2)	1 179(1)	C(23)	739(3)	5 012(3)	1 464(2)
O(12)	5 493(3)	1 654(2)	637(2)	C(24)	961(3)	5 463(2)	2 231(2)
O(21)	5 776(2)	5 590(2)	1 434(1)	C(25)	2 298(3)	5 438(3)	2 728(2)
O(22)	7 174(2)	5 232(2)	571(1)	C(26)	3 429(3)	4 977(3)	2 440(2)
C(11)	6 309(3)	3 431(2)	2 247(2)	C(27)	−94(4)	6 426(3)	3 199(2)
C(12)	7 741(3)	3 760(2)	2 380(2)	C(101)	4 338(3)	1 571(3)	820(2)
C(13)	8 648(3)	3 489(3)	3 087(2)	C(102)	3 405(5)	543(3)	665(3)
C(14)	8 150(3)	2 907(2)	3 676(2)	C(201)	6 700(3)	5 878(3)	1 009(2)
C(15)	6 745(3)	2 563(3)	3 542(2)	C(202)	7 164(4)	7 072(3)	1 089(2)
C(16)	5 823(3)	2 823(2)	2 826(2)				
(*b*) $\{[\text{Ph}_2\text{Te(O}_2\text{CCF}_3)]_2\text{O}\}_2\cdot\text{H}_2\text{O}$							
Te(1)	6 627.5(5)	6 788.5(6)	895.2(5)	C(302)	4 810(9)	8 928(10)	2 501(10)
Te(2)	8 829.4(5)	7 473.6(6)	1 266.1(5)	C(303)	3 835(12)	8 874(12)	2 735(14)
Te(3)	6 892.8(5)	9 056.6(6)	2 824.7(5)	C(304)	3 424(10)	9 022(14)	3 544(15)
Te(4)	7 572.4(5)	7 160.8(6)	4 368.9(5)	C(305)	3 986(10)	9 237(15)	4 139(12)
O(001)	3 084(8)	3 668(8)	7 177(6)	C(306)	4 965(9)	9 316(12)	3 910(9)
O(102)	8 068(5)	6 815(5)	597(5)	C(307)	7 158(9)	10 337(9)	3 235(7)
O(304)	6 924(5)	8 415(5)	4 030(5)	C(308)	7 891(9)	10 337(11)	3 728(9)
O(11)	4 966(6)	6 611(7)	1 047(6)	C(309)	8 094(12)	11 174(16)	4 012(11)
O(12)	4 991(8)	6 315(8)	2 479(6)	C(310)	7 569(18)	11 974(16)	3 769(13)
O(21)	10 030(6)	8 115(7)	1 898(6)	C(311)	6 842(20)	11 953(14)	3 287(14)
O(22)	9 023(6)	8 436(8)	3 014(6)	C(312)	6 624(14)	11 160(11)	2 994(11)
O(31)	6 648(7)	10 100(6)	1 516(6)	C(41)	8 113(9)	5 019(10)	4 700(10)
O(32)	7 043(8)	8 932(6)	757(6)	C(42)	8 508(13)	4 123(13)	5 195(11)
O(41)	8 202(7)	5 729(6)	5 059(6)	C(401)	8 098(9)	7 693(8)	5 369(8)
O(42)	7 778(8)	4 979(8)	4 041(6)	C(402)	8 964(11)	7 342(12)	5 643(12)
C(11)	4 570(8)	6 447(10)	1 839(9)	C(403)	9 349(16)	7 709(18)	6 259(14)
C(12)	3 445(14)	6 450(13)	1 871(10)	C(404)	8 882(20)	8 428(16)	6 594(15)
C(101)	6 725(9)	5 291(8)	973(8)	C(405)	7 984(22)	8 775(16)	6 369(14)
C(102)	6 033(11)	4 808(10)	716(10)	C(406)	7 627(14)	8 395(13)	5 742(11)
C(103)	6 144(17)	3 832(13)	765(15)	C(407)	6 263(9)	6 657(8)	5 039(8)
C(104)	6 927(18)	3 385(13)	1 052(15)	C(408)	5 446(8)	6 765(10)	4 606(10)
C(105)	7 608(15)	3 840(11)	1 336(14)	C(409)	4 555(12)	6 428(12)	5 020(16)
C(106)	7 521(11)	4 824(9)	1 286(11)	C(410)	4 497(12)	5 978(13)	5 841(17)
C(107)	6 407(8)	7 148(9)	−428(7)	C(411)	5 273(16)	5 856(13)	6 288(13)
C(108)	5 853(11)	7 934(9)	−657(10)	C(412)	6 181(12)	6 210(12)	5 893(10)
C(109)	5 670(16)	8 207(13)	−1 499(13)	F(11)	3 057(12)	7 115(12)	1 456(12)
C(110)	6 083(17)	7 667(17)	−2 093(12)	F(12)	3 285(17)	5 568(19)	1 751(27)
C(111)	6 615(17)	6 845(18)	−1 875(11)	F(13)	3 118(20)	6 316(31)	2 783(20)
C(112)	6 807(13)	6 608(14)	−1 033(10)	F(14)	3 199(21)	5 657(26)	2 434(29)
C(21)	9 811(8)	8 389(9)	2 606(8)	F(15)	3 158(22)	6 073(24)	1 184(25)
C(22)	10 664(11)	8 634(12)	3 040(9)	F(16)	3 015(23)	6 963(30)	2 345(27)
C(201)	9 614(9)	8 126(9)	88(8)	F(21)	10 425(14)	9 454(14)	3 349(13)
C(2021)	10 576(16)	8 197(17)	−19(16)	F(22)	10 788(16)	8 047(16)	3 703(14)
C(2031)	11 023(18)	8 635(20)	−817(18)	F(23)	11 425(14)	8 864(14)	2 466(13)
C(204)	10 548(15)	9 012(14)	−1 449(14)	F(24)	11 356(17)	7 993(16)	3 042(15)
C(2051)	9 552(23)	8 979(20)	−1 308(17)	F(25)	11 057(17)	9 422(17)	2 575(15)
C(2061)	9 088(17)	8 520(19)	−536(16)	F(26)	10 436(18)	8 847(17)	3 798(16)
C(2022)	9 591(26)	7 793(26)	−715(24)	F(31)	6 485(25)	11 324(26)	112(24)
C(2032)	10 182(35)	8 196(29)	−1 519(20)	F(32)	7 577(30)	10 325(28)	−654(25)
C(2052)	10 507(48)	9 403(45)	−739(38)	F(33)	5 973(49)	10 204(41)	−392(38)
C(2062)	10 124(38)	8 969(33)	−25(35)	F(34)	6 771(24)	10 118(21)	−644(19)
C(207)	9 709(8)	6 246(9)	1 511(8)	F(35)	5 707(47)	10 644(38)	11(36)
C(208)	9 746(14)	5 816(13)	2 334(11)	F(36)	7 127(24)	11 160(25)	−28(22)
C(209)	10 263(17)	4 997(14)	2 534(14)	F(41)	8 863(27)	3 510(22)	4 609(21)
C(210)	10 775(16)	4 603(15)	1 882(16)	F(42)	9 251(14)	4 168(12)	5 598(12)
C(211)	10 719(17)	4 977(16)	1 060(16)	F(43)	7 761(17)	3 569(16)	5 628(17)
C(212)	10 213(15)	5 814(14)	871(11)	F(44)	8 414(23)	4 091(20)	6 041(18)
C(31)	6 832(10)	9 721(9)	841(8)	F(45)	8 245(31)	3 349(23)	5 075(29)
C(32)	6 727(14)	10 456(10)	−47(10)	F(46)	9 282(29)	3 910(29)	4 721(24)
C(301)	5 376(8)	9 136(9)	3 092(8)				

Table 2 (*continued*)

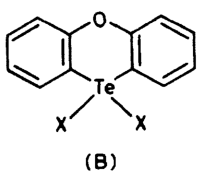
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*c*) $PhI(O_2CCF_3)_2$							
I	3 021.2(3)	−3 801.7(3)	1 032.4(3)	O(21)	2 316(5)	−5 238(5)	2 857(5)
F(11)	3 621(6)	−681(6)	−3 721(7)	C(11)	4 463(4)	−2 404(4)	−1 472(5)
F(12)	5 562(7)	−1 681(7)	−3 820(8)	C(12)	4 739(5)	−1 190(5)	−2 752(6)
F(13)	5 342(9)	−68(7)	−1 835(8)	C(21)	2 691(10)	−4 965(9)	4 492(9)
F(21)	1 262(9)	−5 448(9)	6 550(10)	C(22)	2 154(10)	−6 083(9)	5 687(10)
F(22)	3 173(8)	−6 568(9)	6 891(9)	C(1)	1 246(4)	−2 549(4)	1 144(5)
F(23)	1 584(9)	−7 235(7)	4 829(8)	C(2)	1 273(5)	−1 443(5)	2 417(6)
F(111)	4 185(35)	67(50)	−2 538(57)	C(3)	57(7)	−634(5)	2 468(7)
F(121)	5 975(47)	−854(51)	−2 647(58)	C(4)	−1 128(6)	−967(6)	1 284(8)
F(131)	4 282(51)	−1 506(51)	−4 364(62)	C(5)	−1 119(5)	−2073(5)	43(7)
F(211)	2 623(47)	−7 146(52)	5 725(58)	C(6)	62(4)	−2 872(4)	−38(6)
F(221)	791(50)	−6 183(51)	5 152(65)	H(2)	2 144	−1 218	3 243
F(231)	2 327(47)	−5 705(55)	7 187(67)	H(3)	20	126	3 353
O(22)	3 315(15)	−3 961(11)	5 153(9)	H(4)	−1 950	−382	1 300
O(11)	3 309(3)	−2 182(3)	−936(4)	H(5)	−1 972	−2 303	−790
O(12)	5 310(3)	−3 343(4)	−1 043(4)	H(6)	95	−3 634	−909

also found in the nitrates and acetates previously examined. They may result from the secondary bonds in these compounds causing deviations towards geometries in which they have a full stereochemical role, rather than being stereochemically inert; such distortions are prominent in tin(IV) compounds with secondary bonds.[14] The X–C distances have typical values, with I–C being slightly shorter, as expected [I–C 2.074(4) Å; Te–C 2.098(3) and 2.103(4) Å (av.)]. The X–O distances in the simple oxy-salts are almost identical (averaging 2.160—2.161 Å), although the individual values deviate both for I–O and Te–O by ±0.2 Å. Surprisingly, the increasing electron-attracting power for phenyliodine acetate (I–O 2.156 Å), dichloroacetate (2.150 Å), and trifluoroacetate has no effect on this distance. In contrast, there is a striking difference between the simple compounds and the μ-oxo-dimers. Te–O(μ-oxo) is 1.981(7) Å (av.) while Te–O(trifluoroacetate) is 2.352(10) Å (av.). Similarly short and long bonds are found in the μ-oxo-tellurium and iodine nitrates,[2,3] and presumably in all these compounds the oxy-anion is much nearer to being a free ion.

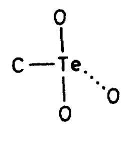
This agrees very satisfactorily with the chemical evidence. The simple and μ-oxo-species are related by reactions of the type (ii) and the ease of formation of the μ-oxo-species is

$$2Ph_2Te(O_2CCF_3)_2 + H_2O \rightleftharpoons [Ph_2Te(O_2CCF_3)]_2O + 2CF_3CO_2H \quad \text{(ii)}$$

clearly related to the acid strength of the oxy-ion. Thus, for both I and Te, the nitrates are predominantly μ-oxo-species, the trifluoroacetates occur in both forms, and the acetates are only known as simple salts.[2,3,15] Clearly, the closer approach to a free oxy-anion in the μ-oxo-species favours the stronger acids. However, other factors must also be involved, and these are not yet fully understood. The further hydrolysis to give PhIO or Ph_2TeO only occurs in the presence of base, less readily than would be expected. The phenoxatellurin derivatives (B)[16] have been prepared for X = NO_3^- and $CF_3CO_2^-$; only the former gives a μ-oxo-species, which is less stable than the $R_2Te(NO_3)_2$ compound. Thus their stability order does not entirely correspond to that of the phenyl compounds. Solution studies of the hydrolysis equilibrium and its dependence on R and X might well clarify this problem.



(B)



(C)

Secondary Bonding.—The Te and I atoms in all three compounds form secondary M···O bonds. The simplest pattern is found for $PhI(O_2CCF_3)_2$ (3) (Figure 1). Two secondary bonds with I···O 3.00—3.04 Å complete a pentagonal plane (Table 4) around iodine with the primary T-shaped ClO_2 unit, and the secondary bonds link the molecules into centrosymmetric dimers. The geometry around iodine, and this linkage, are identical to those found[2] in $PhI(O_2CCHCl_2)_2$, and in both molecules one anion is linked to both iodines of the dimer, while the other anion is twisted out of the pentagonal plane and has a longer I···O interaction (here 3.13 Å).

Confirmation of the importance of the pentagonal plane comes from $(p\text{-}MeOC_6H_4)_2Te(O_2CMe)_2$ (1). This shows exactly the same geometry, with Te···O distances of 2.95—3.02 Å, although here both acetates link to the same Te, giving monomers [as in $PhI(O_2CMe)_2$],[2] rather than dimers. In this compound, of course, the two phenyl groups offer alternatives for the pentagonal plane, and if the planes merely arose because the acetate groups favoured an asymmetrically bidentate co-ordination, the $Te(O_2)_2$ might not show any particular relationship to the phenyl groups. In reality, one carbon atom only is involved in the pentagonal plane. The second phenyl group forms part of a *linear* secondary bond system C–Te···O, to an oxygen atom in a second molecule. The Te···O is bond relatively long (3.40 Å), but the angle at Te is very close to 180° (176.6°). This linear secondary bond links the molecules into centrosymmetric dimers (Figure 3).

It is significant that in the pentagonal plane in compound (1) one of the oxygen atoms forming secondary bonds is relatively far from the plane (0.48 Å), and this compound is therefore intermediate between $PhI(O_2CCF_3)_2$ and the tellurium trifluoroacetate (2) (Figures 4—6). The latter solves the steric problem of forming secondary bonds from a pseudo-trigonal bipyramid containing two Te–C bonds by forming two *half*-pentagonal planes, structure (C). One such plane is formed with one carbon atom, and another with the second atom. Two of the phenyl groups are also involved in linear C—Te···O bonds with the water molecule [O(001)]. In comparison to compound (1), the secondary bonds to the $CF_3CO_2^-$ groups are longer [3.20(8) Å av.], while the bond to O(001) is shorter (3.101 Å av.). The water molecule is shared

Table 3. Bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses

(*a*) $(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{O}_2\text{CMe})_2$

Te–O(11)	2.142(2)	C(24)–O(2)	1.372(4)	O(11)–Te–O(12)	48.5(1)	Te–O(21)–C(201)	114.1(2)
Te–O(21)	2.179(2)	O(1)–C(17)	1.440(5)	O(11)–Te–O(21)	165.0(1)	C(14)–O(1)–C(17)	117.2(3)
Te–C(11)	2.099(3)	O(1)–C(27)	1.415(5)	O(11)–Te–C(11)	90.0(1)	C(24)–O(2)–C(27)	118.5(2)
Te–C(21)	2.097(3)	O(11)–C(101)	1.318(4)	O(11)–Te–C(21)	82.7(1)	O(11)–C(101)–O(12)	122.9(3)
Te ··· O(12)	2.953(3)	O(12)–C(101)	1.208(4)	O(21)–Te–O(22)	47.1(1)	O(11)–C(101)–C(102)	113.2(3)
Te ··· O(22)	3.023(2)	C(101)–C(102)	1.510(5)	O(21)–Te–C(11)	86.4(1)	O(12)–C(101)–C(102)	123.9(3)
Te ··· O(22′) [a]	3.395(2)	O(21)–C(201)	1.295(4)	O(21)–Te–C(21)	83.4(1)	O(21)–C(201)–O(22)	123.3(3)
C–C(phenyl)	1.382(av.)	O(22)–C(201)	1.224(4)	C(11)–Te–C(21)	99.0(1)	O(21)–C(201)–C(202)	115.2(3)
C(14)–O(1)	1.363(3)	C(201)–C(202)	1.496(4)	C(11)–Te–O(22′) [a]	176.6(1)	O(22)–C(201)–C(202)	121.5(3)
				Te–O(11)–C(101)	112.0(2)		

(*b*) $\{[\text{Ph}_2\text{Te}(\text{O}_2\text{CCF}_3)]_2\text{O}\}_2\cdot\text{H}_2\text{O}$ [b]

	Molecule 1		Molecule 2		Mean
	Te(1)	Te(2)	Te(3)	Te(4)	
Primary bonds					
Te(1)–C(101)	2.12(1)	2.11(1)	2.10(1)	2.09(1)	
Te(1)–C(107)	2.12(1)	2.10(1)	2.11(1)	2.08(1)	2.103(4)
Te(1)–O(11)	2.328(8)	2.365(10)	2.381(8)	2.335(9)	2.352(10)
Te(1)–O(102)	2.004(7)	1.971(8)	1.964(7)	1.986(8)	1.981(7)
O(11)–C(11)	1.27(2)	1.23(2)	1.26(2)	1.26(2)	
O(12)–C(11)	1.22(2)	1.20(1)	1.17(2)	1.21(2)	
C(11)–C(12)	1.57(2)	1.54(2)	1.62(2)	1.50(2)	
C(aryl)–C(aryl)	1.365(3) (av. over all ordered groups)				
C–F	1.310(16) (av. over all groups)				
Te(1)–O(102)–Te(2)	119.9(4)		124.9(4)		
C(101)–Te(1)–C(107)	98.3(5)	99.1(5)	97.2(5)	99.4(5)	
C(101)–Te(1)–O(11)	85.2(4)	83.1(4)	84.2(4)	82.3(4)	
C(101)–Te(1)–O(102)	88.9(4)	89.8(4)	88.4(4)	89.4(4)	
C(107)–Te(1)–O(11)	80.6(4)	81.1(4)	82.3(4)	83.6(4)	
C(107)–Te(1)–O(102)	92.6(4)	90.2(4)	88.3(4)	89.4(4)	
O(11)–Te(1)–O(102)	170.2(4)	167.7(3)	167.2(3)	168.1(3)	
Te–O(11)–C(11)	113.7(8)	119.3(7)	113.9(7)	114.9(9)	
O(11)–C(11)–O(12)	125(1)	128(1)	131(1)	129(1)	
O(11)–C(11)–C(12)	110(1)	116(1)	113(1)	112(1)	
O(12)–C(11)–C(12)	124(1)	117(1)	116(1)	119(1)	
Secondary bonds					
Te(1) ··· O(12)	3.144(9)	3.315(12)	3.256(10)	3.233(12)	
Te(1) ··· O(*nn*)	3.116(10)	3.259(11)	3.100(9)	3.143(9)	
bonded atom	O(32)	O(32)	O(22)	O(22)	
Te(1) ··· O(001$^{\text{I}}$)	3.064(9)	—	—	3.138(11)	
O(11)–Te(1) ··· O(12)	44.9(3)	41.0(3)	42.7(3)	43.6(3)	
O(12) ··· Te(1) ··· O(32)	106.6(3)	92.1(3)	96.3(3)	110.9(3)	
O(32) ··· Te(1)–O(102)	77.0(3)	73.7(3)	72.7(3)	71.4(3)	
C(*nn*)–Te(1) ··· O(001$^{\text{I}}$)	178.1(4)	—	—	176.4(4)	
bonded atom	C(107)			C(401)	

(*c*) $\text{PhI}(\text{O}_2\text{CCF}_3)_2$

I–O(11)	2.186(3)	C(6)–C(1)	1.375(5)	O(11)–C(11)	1.277(5)
I–O(21)	2.138(5)	C(1)–C(2)	1.379(6)	O(12)–C(11)	1.192(5)
I–C(1)	2.074(4)	C(2)–C(3)	1.395(8)	C(11)–C(12)	1.549(6)
I ··· O(12)	3.000(4)	C(3)–C(4)	1.378(8)	O(21)–C(21)	1.265(8)
I ··· O(22)	3.133(7)	C(4)–C(5)	1.366(8)	O(22)–C(21)	1.159(13)
I ··· O(12′) [c]	3.038(3)	C(5)–C(6)	1.364(6)	C(21)–C(22)	1.538(12)
C–F	1.306(4) Å. (av. for higher occupancy positions)				

O(11)–I–O(21)	168.5(1)	C(1)–I ··· O(12)	129.8(1)	I–O(11)–C(11)	110.6(2)
O(11)–I–C(1)	82.3(1)	C(1)–I ··· O(12′) [c]	154.7(1)	I–O(21)–C(21)	117.9(5)
O(21)–I–C(1)	86.7(2)	C(1)–I–O(22)	86.0(1)		
		O(21)–I ··· O(12)	143.4(1)	O(11)–C(11)–O(12)	128.3(4)
O(11)–I ··· O(12)	47.6(1)	O(12) ··· I ··· O(22)	126.7(3)	O(11)–C(11)–C(12)	111.3(3)
O(21)–I ··· O(22)	43.9(2)	O(12′) ··· I–O(11) [c]	116.8(1)	O(12)–C(11)–C(12)	120.3(4)
		O(12′) ··· I–O(21) [c]	72.6(1)	O(21)–C(21)–O(22)	127.7(8)
		O(12′) ··· I–O(12) [c]	71.8(1)	O(21)–C(21)–C(22)	118.4(7)
		O(12′) ··· I–O(22) [c]	88.9(2)	O(22)–C(21)–C(22)	113.7(7)

[a] O(22′): 1 − *x*, 1 − *y*, −*z* from O(22). [b] The numbering for bonds involving Te(2), Te(3), and Te(4) corresponds to that for Te(1), with the replacement of the initial digit in the atom number. [c] O(12′): 1 − *x*, −1 − *y*, −*z* from O(12).

Table 4. Deviations (Å) from planes (defining atoms asterisked)

Compound	Deviations
(1) $(p\text{-MeOC}_6\text{H}_4)_2\text{Te(O}_2\text{CMe)}_2$	Te*, −0.05; O(11)*, 0.03; O(21)*, 0.03; C(21)*, −0.01; O(12), −0.04; O(22), −0.48; C(11)*, 1.34
(2) $\{[\text{Ph}_2\text{Te(O}_2\text{CCF}_3)]_2\text{O}\}_2\cdot\text{H}_2\text{O}$	Te(1)*, 0.10; O(102)*, −0.06; O(11)*, −0.05; C(101)*, 0.01; O(32), 0.30 Te(1)*, 0.10; O(102)*, 0.05; O(11)*, −0.04; C(107)*, 0.01; O(12), 0.18 Te(2)*, 0.11; O(102)*, −0.06; O(21)*, −0.05; C(207)*, 0.01; O(32), 0.47 Te(3)*, −0.13; O(304)*, 0.08; O(31)*, 0.06; C(301)*, −0.01; O(22), −0.48 Te(4)*, 0.11; O(304)*, −0.06; O(41)*, −0.05; C(401)*, 0.01; O(42), 0.12
(3) $\text{PhI(O}_2\text{CCF}_3)_2$	I*, 0.00; O(11)*, −0.07; O(21)*, −0.05; C(1)*, 0.06; O(12), 0.00; O(12′), 0.00
$\text{Ph}_2\text{Te(NO}_3)_2$ [a]	Te*, 0.15; O(1)*, −0.08; O(1′)*, −0.08; C(1)*, 0.01; O(3′), −0.05
$[\{\text{Ph}_2\text{Te(NO}_3)\}_2\text{O}]\text{–Ph}_2\text{Te(NO}_3)\text{OH}$ [a]	Te(1)*, −0.06; O(8)*, 0.03; O(11)*, 0.04; C(25)*, −0.01; O(9), −0.25 Te(2)*, 0.07; O(1)*, −0.04; O(7)*, −0.05; C(1)*, 0.01; O(2), 0.33 O(2′), 0.33 Te(3)*, 0.12; O(4)*, −0.06; O(7)*, −0.07; C(13)*, 0.01; O(10), 0.38 Te(3)*, 0.16; O(4)*, −0.08; O(7)*, −0.10; C(19)*, 0.01; O(3′), 0.18
$[\text{PhTeO(NO}_3)]_n$ [a]	Te(1)*, 0.08; O(11)*, −0.04; O(14)*, −0.05; O(24)*, 0.01; O(11′), 0.09 Te(2)*, −0.09; O(21)*, 0.05; O(24′)*, 0.06; O(14)*, −0.02; O(23), −0.05
Phenoxatellurin dinitrate [b]	Te*, −0.11; O(1)*, 0.06; O(1′), 0.06; C(11)*, −0.01; O(2), −0.01
μ-Oxo-bis(phenoxatellurin nitrate) [b]	Te(1)*, 0.02; O(B)*, −0.01; O(N1)*, −0.01; C(14)*, 0.00; O(N3), −0.12 Te(1)*, −0.14; O(B)*, 0.08; O(N1)*, 0.06; C(11)*, 0.00; O(N5′), 0.04 Te(2)*, −0.08; O(B)*, 0.05; O(N4)*, 0.04; C(25)*, 0.00; O(N2′), 0.22 Te(2)*, −0.07; O(B)*, 0.04; O(N4)*, 0.03; C(28)*, 0.00; O(N5), 0.14
Phenoxatellurin bis(trifluoroacetate) [b]	Te*, −0.12; O(1)*, 0.06; O(3)*, 0.06; C(14)*, −0.01; O(2), 0.17 Te*, −0.11, O(1)*, 0.06; O(3)*, 0.06; C(11)*, −0.01; O(4), −0.11

[a] Ref. 3; numbering as in original paper. [b] Ref. 16; numbering as in original paper.

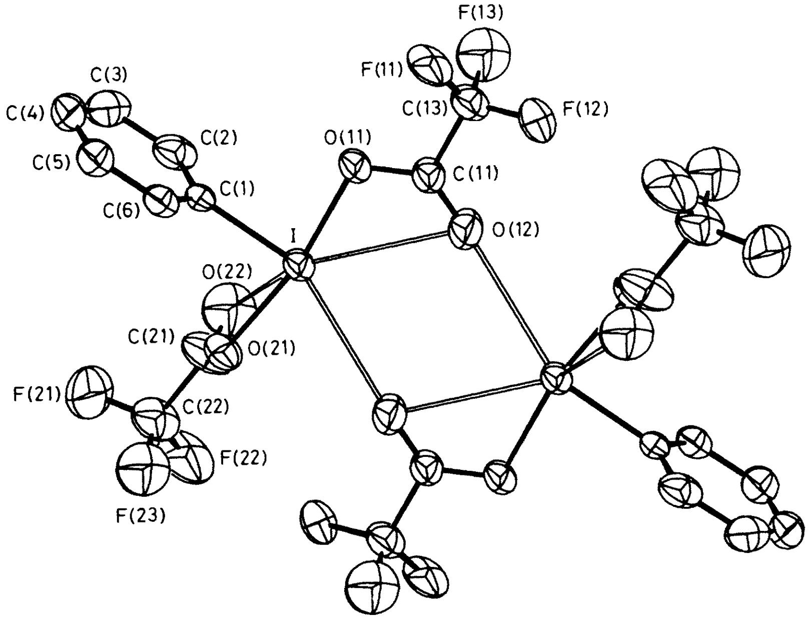


Figure 1. Centrosymmetric dimer of $\text{PhI(O}_2\text{CCF}_3)_2$ (3), showing the atomic numbering. Only the main fluorine positions are included. Primary bonds are solid, secondary bonds open

between the two oxo-bridged molecules, and with the trifluroroacetate groups links them into dimers (Figure 5). In the unit cell, the main interactions between these dimers involve the phenyl rings (Figure 6), which are aligned face-to-face.

The identification for the first time of the pentagonal plane primary and secondary bond geometry in tellurium compounds prompts a reconsideration of the phenyltellurium nitrate structures[3] previously reported, for which no clear pattern could at the time be recognised (see also Table 4). The

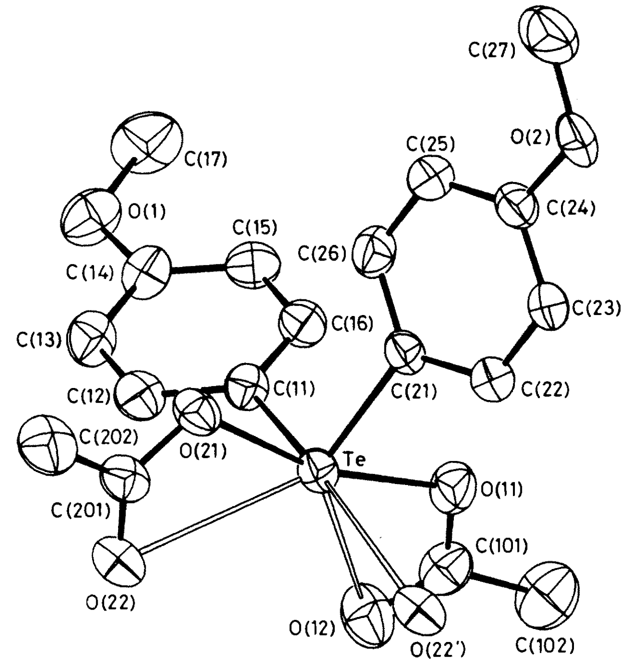


Figure 2. The molecule of ($(p\text{-MeOC}_6H_4)_2Te(O_2CMe)_2$) (1), showing the atomic numbering. Primary bonds are solid, secondary bonds open

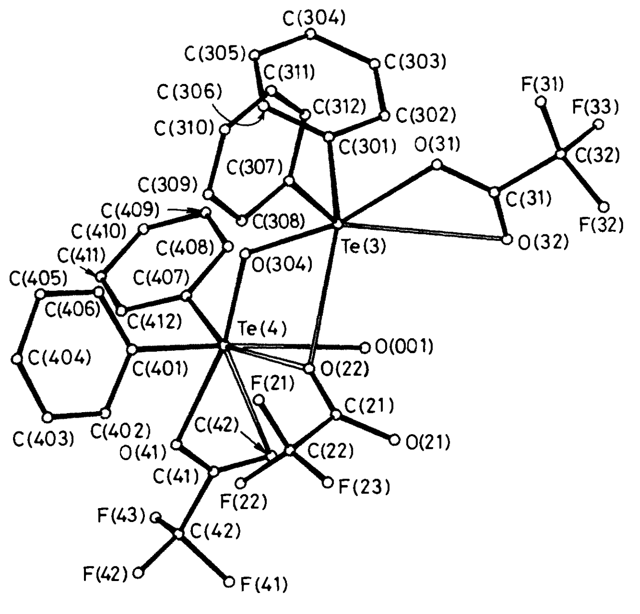


Figure 4. One molecule, and the shared water molecule [O(001)], of $\{[Ph_2Te(O_2CCF_3)]_2O\}_2{\cdot}H_2O$ (2) with one trifluoroacetate group of the other molecule, showing the atomic numbering. Only one set of fluorine atoms in included

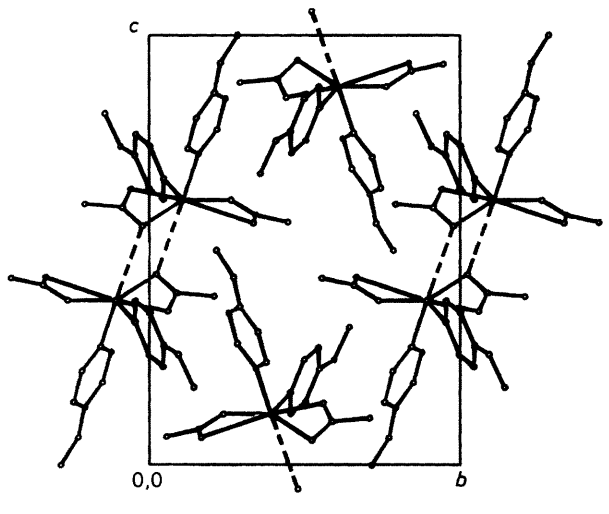


Figure 3. The unit cell of compound (1) projected down *a*, showing the intermolecular secondary bonds (broken)

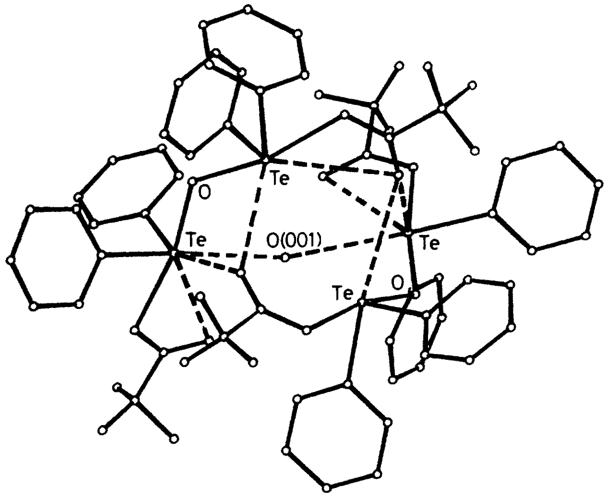


Figure 5. Double unit of compound (2), showing the secondary bonds that hold the two molecules together (dashed)

most symmetrical is $Ph_2Te(NO_3)_2$ and this also has half-pentagonal planes involving each carbon atom. As the molecule lies on a two-fold axis, both ($TeO_2C + O$) planes are identical. Exactly the same half-pentagonal planes are found for two of the three Te atoms in the very complex structure of $[\{Ph_2Te(NO_3)\}_2O]$–$Ph_2Te(NO_3)OH$, while the third forms a full pentagonal plane. In the monoaryl derivative $[PhTeO(NO_3)]_n$ the equatorial planes of both Te atoms are each occupied by an O and a C atom, and the TeO_3 units are considerably closer to planarity than the TeO_2C units. Both examples include one extra O atom, in one case this coming from a bidentate nitrate, and in the other case from another anion. Finally, phenoxatellurin bis(trifluoroacetate),[16] the tellurin dinitrate, and the μ-oxo-tellurin nitrate [structure (B)] [16] all share this geometry.

This work has therefore confirmed the importance of the pentagonal plane primary- and secondary-bond geometry which seems to be typical for the carboxylates, in preference to the linear C–M ··· O system (M = Te or I), although two examples of this are also present. A new structure related to this has appeared, particularly in the nitrates (although also in the tellurin trifluoroacetate), in which one secondary bond of the pentagonal plane is missing, the ideal geometry being the double version, exemplified by $Ph_2Te(NO_3)_2$, in which both $CTeO_2$ planes include one extra secondary bond.

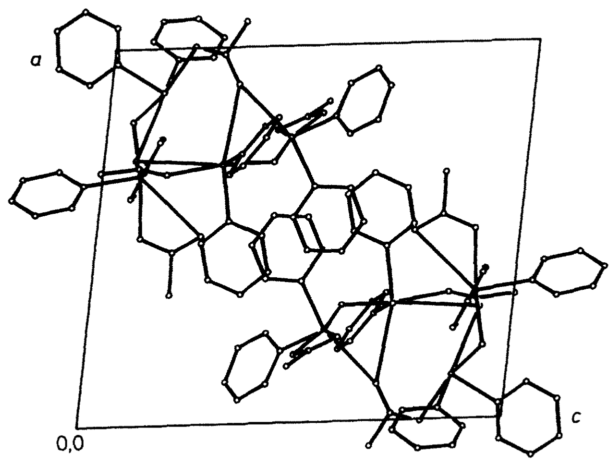


Figure 6. Packing diagram for compound (2), viewed down *b*

Acknowledgements

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