Secondary Bonding. Part 15.[1] Influence of Lone Pairs on Co-ordination: Comparison of Diphenyl-Tin(IV) and -Tellurium(IV) Carboxylates and Dithiocarbamates†

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Seven complexes of general type Ph_2MX_2 with X = carboxylate or dithiocarbamate have been prepared and their molecular structures determined (M = Sn, X = O_2CMe, O_2CCH_2Cl, or S_2CNEt_2; M = Te, X = O_2CCCl_3, S_2CNEt_2, $S_2CNEtPh$, or S_2CNPh_2). All but one show unsymmetrical bidentate co-ordination by the carboxylate or dithiocarbamate ligands; the tellurium complexes show substantially greater differences between the longer and shorter M–O or M–S distances. The presence of the lone pair transforms the co-ordination geometry from approximately tetrahedral (M = Sn) to pseudo-trigonal bipyramidal (M = Te). Replacing carboxylate by dithiocarbamate has a modest effect when M = Te, but in the tin compound the sulfur ligand co-ordination is almost symmetrical. This contrasts with the unsymmetrical bonding in $Me_2Sn(S_2CNEt_2)_2$.

The effect of lone pairs on the co-ordination geometry of main-group elements is well explained by the valence shell electron pair repulsion (VSEPR) model for compounds in which all the bond pairs are of similar character and the attached groups are independent, so that bonded pair–bonded pair repulsions have their full effect. The interpretation is much less clear for compounds containing short-bite ligands, especially when their bonding is unsymmetrical. Comparison of compounds of Sn^{IV} with those of Te^{IV} allows the effect of the lone pair to be observed directly. It is important in making such comparisons to retain similar 'innocent' groups on the central atoms, because of the well known steric effects found with Sn on changing the bulk of its organosubstituents.

As an extension of our work on the inter- and intra-molecular interactions of main-group elements,[1] we here report and compare structures in two series, Ph_2M (M = Sn or Te) complexes with carboxylates and with dithiocarbamates. The notable variety of co-ordination modes for carboxylates can be expected to lead to their bonding being sensitive to fairly small changes in the steric and electronic character of their bonded element. The differing basicities of the ligands in the two series add another dimension to the comparisons. The secondary bonding that tin and tellurium complexes have already been shown to adopt is also of interest.

Predictions of the carboxylate bonding mode have frequently been based on IR data, with the differences between the C–O ν_{asym} and ν_{sym} frequencies being considered particularly informative; values of $\delta\nu$ greater than 200–260 cm^{-1} have been taken to indicate unidentate co-ordination.[2] It was therefore a subsidiary aim to examine the validity of this correlation.

Results

The compounds studied are listed in Table 1, and a summary of their dimensions is given in Table 2; data for the previously published $(MeOC_6H_4)_2Te(O_2CMe)_2$ and $Ph_2Te(S_2CNMe_2)_2$ are also included.[3] It is clear that Sn and Te are of virtually the same size, from their closely similar M–C and M–O (short) distances. The three carboxylates (Figs. 1–3) are broadly similar, with unsymmetrically bidentate co-ordination. The infrared spectra (Table 3, including those for three carboxylates not structurally characterised) all show $\delta\nu$ > 260 cm^{-1}, indicating that this test for unidentate carboxylates from IR data is not unambiguous, but may indicate anisobidentate as

Table 1 Compounds studied

	Carboxylates		Dithiocarbamates	
Tin(IV)	**1**	$Ph_2Sn(O_2CMe)_2$	**3**	$Ph_2Sn(S_2CNEt_2)_2$
	2	$Ph_2Sn(O_2CCH_2Cl)_2$		
Tellurium(IV)	**4**	$Ph_2Te(O_2CCCl_3)_2$	**5**	$Ph_2Te(S_2CNEt_2)_2$
			6	$Ph_2Te(S_2CNEtPh)_2$
			7	$Ph_2Te(S_2CNPh_2)_2$

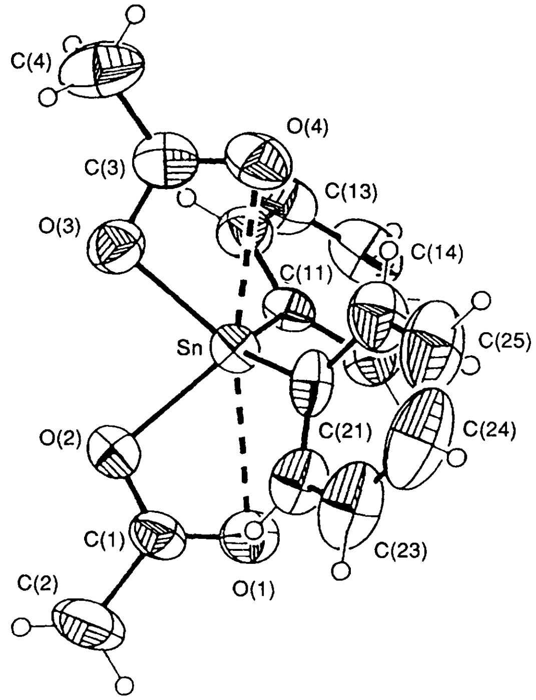

Fig. 1 View of $Ph_2Sn(O_2CMe)_2$ **1**, showing the atomic numbering. Weaker Sn ··· O interactions are dashed

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 2 Summary of dimensions (Å and °) in $Ph_2M(O_2CR)_2$ and $Ph_2M(S_2CNR_2)_2$ compounds (M = Sn or Te)

Compound	M	X	R	M–X	M–X′	M–C	C–M–C	X–M–X	X′–M–X′
1	Sn	O	Me	2.078	2.555	2.115	131.4	82.0	167.8
2	Sn	O	CH_2Cl	2.095	2.541	2.112	147.2	82.3	167.5
4	Te	O	CCl_3	2.156	3.142	2.110	100.0	166.6	105.8
a	Te	O	Me	2.160	2.988	2.098	99.0	165.0	100.3
3	Sn	S	$(Et)_2$	2.582	2.704	2.160	101.8	155.3	81.0
5	Te	S	$(Et)_2$	2.615	3.130	2.143	93.9	179.0	109.2
6	Te	S	(EtPh)	2.618	3.184	2.134	95.0	171.2	111.1
7	Te	S	$(Ph)_2$	2.608	3.204	2.152	96.7	172.5	114.0

[a] $(MeOC_6H_4)_2Te(O_2CMe)_2$, ref. 3*a*.

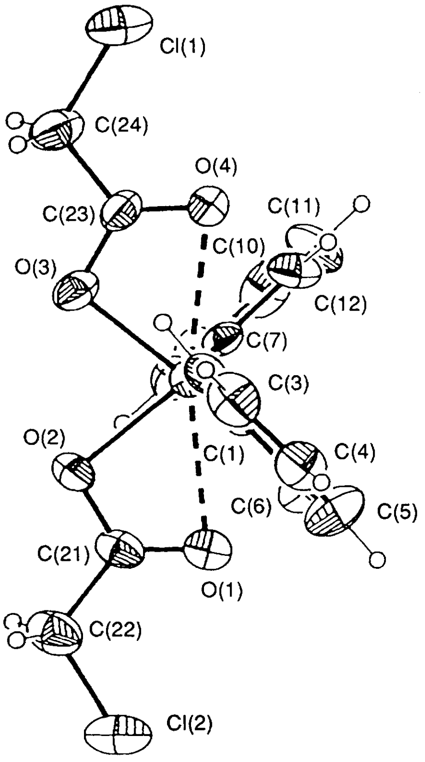

Fig. 2 View of $Ph_2Sn(O_2CCH_2Cl)_2$ **2**, showing the atomic numbering

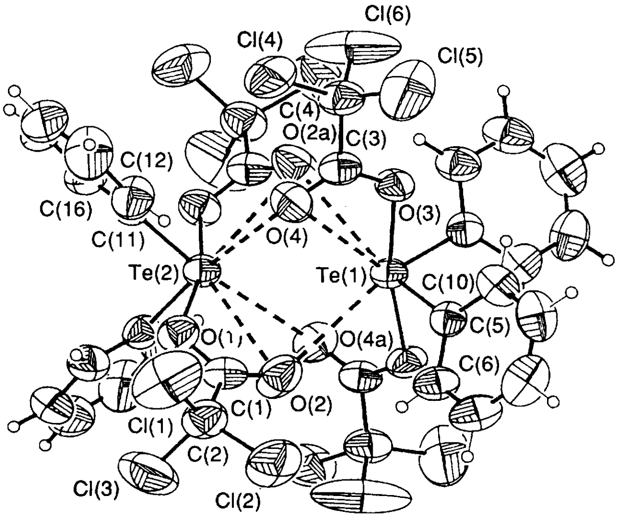

Fig. 3 View of $Ph_2Te(O_2CCCl_3)_2$ **4**, showing the atomic numbering. The Te(1) • • • O(4a) interaction is concealed

Table 3 Infrared spectra (cm^{-1})

	Compound	ν_{asym}	ν_{sym}	$\delta\nu$
1	$Ph_2Sn(O_2CMe)_2$	1610	1335	265
2	$Ph_2Sn(O_2CCH_2Cl)_2$	1620	1240	380
	$Ph_2Sn(O_2CCHCl_2)_2$	1670	1330	340
	$Ph_2Te(O_2CMe)_2$	1640	1290	350*
	$Ph_2Te(O_2CCHCl_2)_2$	1660	1310	350*
4	$Ph_2Te(O_2CCCl_3)_2$	1705	1270	435

* Average value.

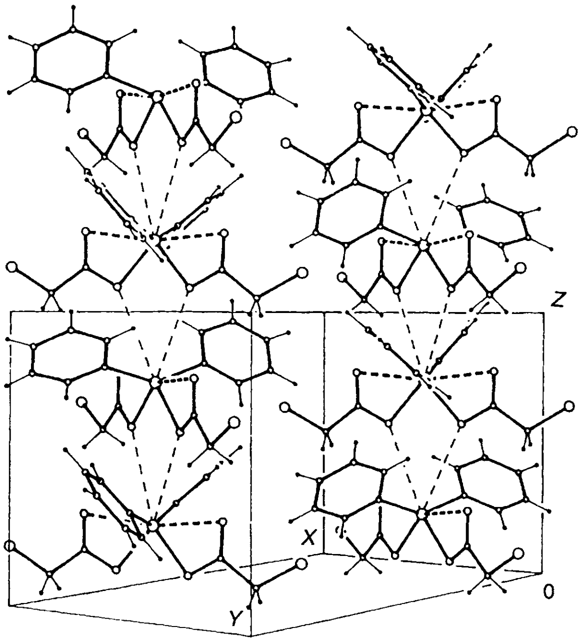

Fig. 4 Packing diagram for complex **2**, showing the weak intermolecular Sn • • • O interactions

well as unidentate complexes. The value of $\delta\nu$ increases broadly in line with the basicity of the acid, but is poorly correlated with the M–O distances. A marked lengthening of the weaker Te–O bond *and* an increase in $\delta\nu$ are seen only when comparing $(MeOC_6H_4)_2Te(O_2CMe)_2$ and $Ph_2Te(O_2CCCl_3)_2$. However, the latter complex has a distinctive pattern of M • • • O interactions, making direct comparison suspect. The C–O distances in the carboxylates are consistent with the variation in IR stretching frequencies, being inversely correlated with the M–O distances, typically with short and long C–O distances of 1.21 and 1.30 Å. The dithiocarbamates show similar variations in their C–S distances.

Comparison of the C–Sn–C and C–Te–C angles shows the marked effect of the tellurium lone pair. The tellurium carboxylates can be described as pseudo-trigonal bipyramidal, with axial Te–O primary bonds and the lone pair in an

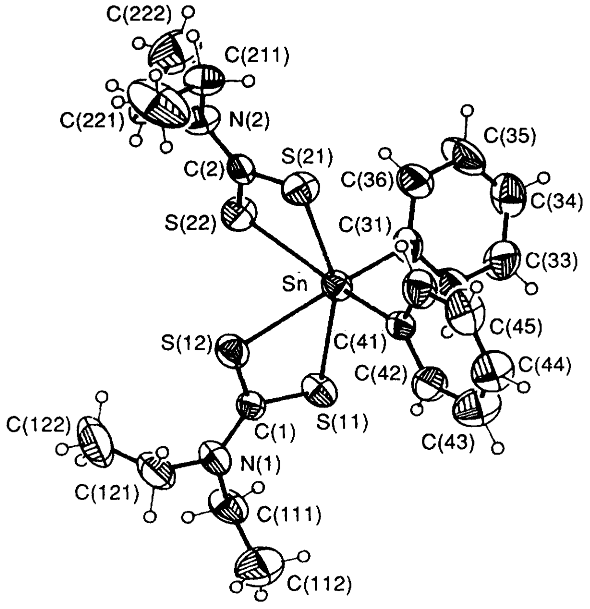

Fig. 5 View of $Ph_2Sn(S_2CNEt_2)_2$ **3**, showing the atomic numbering

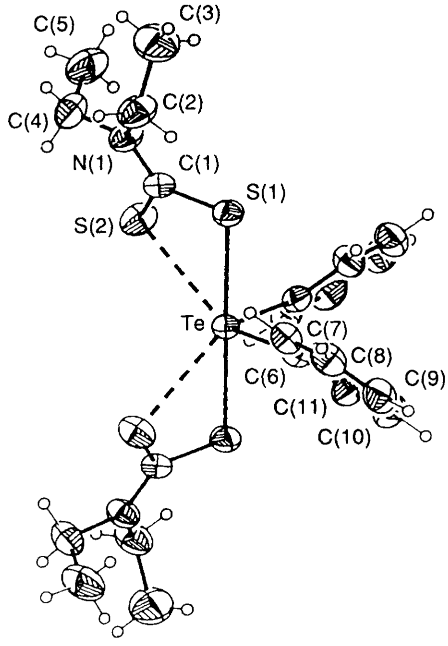

Fig. 6 View of $Ph_2Te(S_2CNEt_2)_2$ **5**, showing the atomic numbering

equatorial position. The weak Te • • • O interactions add to the steric effect of the lone pair in closing the C–Te–C angle, and the short Te–O bonds are also bent back from this side of the molecule. The distinctive geometry of $Ph_2Te(O_2CCCl_3)_2$ involves carbonyl oxygens bonded to both tellurium atoms by long-range interactions (3.032–3.250 Å), substantially shorter than the sum of the van der Waals radii (3.60 Å).[4]

The tin carboxylates are close to tetrahedral in geometry. The weak M • • • O interactions form on the opposite side of the short M–O bonds for the tellurium complex; the O–Sn–O angles are reduced from tetrahedral by about 25°, and the C–Sn–C angles are increased by a similar amount. The considerably larger C–Sn–C angles in the $[O_2CCH_2Cl]^-$ complex is explicable when the crystal packing is examined (Fig. 4). The molecules are stacked along the *c* axis, making two additional Sn • • • O links [3.416(6) and 3.552(6) Å]. Despite their length, approaching the sum of the van der Waals radii (3.6 Å),[4] these interactions are clearly responsible for the wide C–Sn–C angle. A similar sensitivity to long interactions was found in Et_2SnX_2 (X = halogen), which have C–Sn–C angles enlarged by the formation of Sn • • • X links.[5] Complex **1** has no such contacts, the shortest additional Sn • • • O distance being 5.4 Å. We can compare these structures with that of $Me_2Sn(O_2CMe)_2$ (lacking long contacts);[6] it has C–Sn–C of 135.9°, slightly larger than in **1**; its Sn–O and Sn • • • O distances (2.106 and 2.539 Å) are similar to those in **1**. Generally the weak Sn • • • O interactions are shorter than those for Te, possibly due to the repulsive effect of the lone pair for the latter.

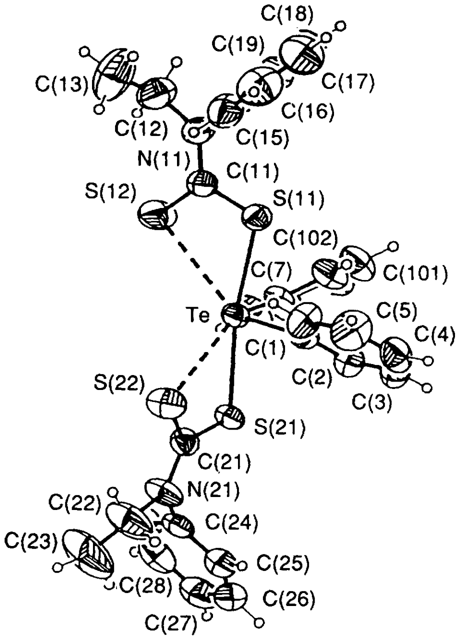

Fig. 7 View of $Ph_2Te(S_2CNEtPh)_2$ **6**, showing the atomic numbering

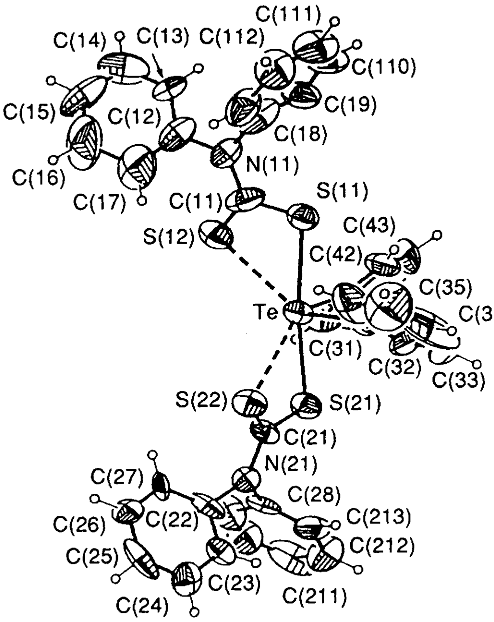

Fig. 8 View of $Ph_2Te(S_2CNPh_2)_2$ **7**, showing the atomic numbering

In overall geometry the dithiocarbamates (Figs. 5–8) are similar to the caboxylates. Changing the organosubstituents in these ligands has less effect on the ligand basicity than for the carboxylates, and thus the shorter Te–S distances are only slightly and irregularly affected by the nature of the **R** groups. The longer Te • • • S distances increase systematically as Ph is

Table 4 Unit cells and crystal structure analysis data

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{16}H_{16}O_4Sn$	$C_{16}H_{14}Cl_2O_4Sn$	$C_{22}H_{30}N_2S_4Sn$	$C_{16}H_{10}Cl_6O_4Te$	$C_{22}H_{30}ClN_2S_4Te$	$C_{30}H_{30}N_2S_4Te\cdot0.5C_7H_8$	$C_{38}H_{30}N_2S_4Te\cdot2C_7H_8$
M	390.99	459.88	569.0	606.85	578.34	720.49	954.79
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Absences	$h00\ h = 2n + 1$ $0k0\ k = 2n + 1$ $00l\ l = 2n + 1$	$h0l\ l = 2n + 1$ $0kl\ k = 2n + 1$	$h0l\ l = 2n + 1$ $0k0\ k = 2n + 1$	$hkl\ h + k = 2n + 1$ $h0l\ l = 2n + 1$	$hkl\ h + k = 2n + 1$ $h0l\ l = 2n + 1$	None	$h0l\ l = 2n + 1$ $0k0\ k = 2n + 1$
Space group	$P2_12_12_1$	$Pbcm$	$P2_1/c$	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$
a/Å	8.512(2)	9.909(6)	14.954(5)	25.047(9)	16.538(5)	9.804(2)	9.613(2)
b/Å	9.038(2)	17.782(11)	9.415(6)	11.242(8)	14.380(4)	11.156(3)	22.453(7)
c/Å	21.309(6)	9.599(7)	18.252(11)	19.208(6)	12.169(3)	16.274(5)	21.552(7)
α/°	—	—	—	—	—	79.33(2)	—
β/°	—	—	90.47(4)	124.58(3)	121.57(2)	74.46(2)	93.92(2)
γ/°	—	—	—	—	—	84.48(2)	—
U/Å^3	1639.2(7)	1692(2)	2570(2)	4453.2 (4.3)	2466(1)	1683.2(7)	4637(2)
D_c/g cm^{-3}	1.58	1.81	1.47	1.81	1.56	1.42	1.37
Z	4	4	4	8	4	2	4
μ(Mo-Kα)/cm^{-1}	15.7	18.5	13.2	21.3	15.8	11.7	8.7
F(000)	776	904	1160	2336	1168	716	1952
Reflections for cell (2θ/°)	20–22	20–22	16–20	18–22	20–22	20–22	20–22
hkl ranges	0–10, 0–10, 0–24	0–12, 0–21, 0–11	0–16, 0–10, −19 to 19	0–24, 0–13, −22 to 22	0–16, 0–16, −14 to 14	0–10, −12 to 13, −18 to 18	0–10, 0–24, −23 to 23
Crystal size/mm	0.5 × 0.3 × 0.1	0.6 × 0.4 × 0.4	0.07 × 0.15 × 0.26	0.2 × 0.4 × 0.2	0.2 × 0.2 × 0.6	0.4 × 0.2 × 0.2	0.4 × 0.2 × 0.2
Transmission factor range	0.69–0.87	0.55–0.63	0.83–0.91	0.52–0.69	0.76–0.82	0.86–0.93	0.88–0.94
Scan range (2θ)	±1.0	+1.2, −1.0	±1.2	+1.2, −1.0	±1.0	±1.1	±1.1
Max. scan rate (°min^{-1})	2.0	2.0	5.0	3.0	4.0	3.0	3.0
Max. 2θ/°	50	50	50	50	50	50	50
Total unique reflections	1704	1596	3369	3937	2350	5972	6179
Reflections with $I/\sigma(I) \geqslant 2.0$	1575	1409	2382	2916	1854	4014	2863
R_{int}	—	—	0.031	0.011	0.011	0.043	0.022
δF max., min./e Å^{-3}	+0.3, −0.8	+0.6, −2.3	+0.9, −2.1	+0.5, −0.6	±0.35	±0.5	±1.5
Shift/σ (last cycle)	0.013	0.011	0.01	0.019	0.001	0.006	0.006
Parameters refined	196	207	275	100	138	352	421
g (weighting parameter)	0.000 74	0.036	0.000 25	0.000 44	0.000 39	0.000 83	0.002 84
Final R	0.028	0.046	0.050	0.042	0.025 5	0.045 4	0.090 8
Final R'	0.031	0.049	0.050	0.048	0.027 7	0.045 9	0.093 9

substituted for Et, but the effect is not marked and the values for the dimethyl compound do not fit the sequence. For the tellurium complexes the C–Te–C angles are rather smaller than in the carboxylates, though the S–Te–S groups are closer to linear. We can therefore deduce that the increased steric repulsion from S compared to O dominates over the repulsion from the lone pair.

The geometry of $Ph_2Sn(S_2CNEt_2)_2$ resembles that of the tin carboxylates rather more than that of the tellurium compounds. Its four Sn–S are nearly equal, though they show a surprising variation between the two dithiocarbamate groups; the differences are 0.025 and 0.219 Å between the longer and shorter bonds, compared to 0.4–0.5 Å for the carboxylates. It is now the longer pair of bonds which define the smallest S–Sn–S angle (close to the O–Sn–O angles between the shorter Sn–O bonds in the carboxylates). Several $Me_2Sn(S_2CNR_2)_2$ compounds have been characterised. They have broadly similar geometries though they are rather variable in detail.[7] In contrast to the correspondence between Ph_2Sn and Me_2Sn carboxylates, these methyltin dithiocarbamates differ markedly from the phenyl derivatives. The methyl complexes have C–Sn–C of 136–142° (phenyl 102°), with short (2.50 Å) and long (3.00 Å) Sn–S bonds, a difference of 0.5 Å, compared to the mean of 0.1 Å for the diphenyl complex. Like the carboxylates, the short S–Sn bonds form the smaller S–Sn–S angles. It is difficult to identify a simple cause for this remarkable variation. Steric differences between the Me and Ph groups can hardly be responsible, because of the similarity in the carboxylates, while the effect seems disproportionately large to have an electronic origin. Equally there are no obvious packing interactions. We can only conclude that the dithiocarbamate coordinate is exceptionally sensitive to small variations in environment. This suggestion does find some support from the variation noted between the two dithiocarbamate groups in **4**, from the polymorphism observed in $Me_2Sn(S_2CNEt_2)_2$, which exists in three crystal forms with significant geometrical variation,[7] and also from the variation between the dimethyl- and diethyl-tellurium compounds. The methyl complexes have been described as distorted *trans*-octahedral, a description which is clearly inappropriate to **3**. It could however be considered as *cis*-octahedral, with the departure of the S(11)–Sn–S(21) angle (155°) from 180° as the largest distortion.

Table 5 Atom coordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Compound **1**							
Sn	8 567.0(4)	4 836.9(4)	6 040.1(2)	C(13)	10 366(8)	5 659(8)	4 166(3)
O(1)	8 681(5)	7 517(5)	6 458(2)	C(14)	9 537(8)	6 850(8)	3 957(3)
O(2)	10 163(5)	5 624(4)	6 697(2)	C(15)	8 452(9)	7 525(8)	4 346(3)
O(3)	9 975(5)	2 963(4)	6 100(2)	C(16)	8 196(8)	6 976(6)	4 940(3)
O(4)	8 062(6)	2 444(5)	5 460(2)	C(21)	6 438(7)	4 512(7)	6 528(3)
C(1)	9 797(7)	7 033(7)	6 750(3)	C(22)	6 183(7)	5 256(8)	7 104(3)
C(2)	10 782(10)	7 933(10)	7 181(3)	C(23)	4 796(9)	5 098(12)	7 407(4)
C(3)	9 270(9)	2 049(7)	5 717(3)	C(24)	3 618(10)	4 266(11)	7 156(5)
C(4)	10 043(13)	611(8)	5 617(4)	C(25)	2 831(9)	3 581(11)	6 611(5)
C(11)	9 039(6)	5 746(5)	5 143(2)	C(26)	5 257(9)	3 685(8)	6 283(4)
C(12)	10 115(7)	5 084(7)	4 760(3)				
Compound **2**							
Sn	2 423.8(4)	2 526.8(2)	2 500.0	C(2)	704(5)	1 118(3)	2 562(7)
Cl(1)	−2 550(2)	3 510(2)	1 597(5)	C(3)	318(7)	390(4)	2 883(7)
Cl(2)	7 310(2)	1 494(2)	1 376(5)	C(4)	1 043(7)	−10(3)	3 817(7)
O(1)	4 825(5)	2 054(3)	2 731(5)	C(5)	2 190(7)	283(4)	4 374(8)
O(2)	3 760(6)	2 370(3)	825(7)	C(6)	2 611(7)	1 002(4)	4 019(9)
O(3)	1 049(5)	2 718(4)	887(6)	C(7)	3 028(5)	3 614(3)	3 151(7)
O(4)	12(4)	2 991(3)	2 844(5)	C(8)	4 083(5)	3 967(3)	2 467(7)
C(21)	4 787(6)	2 084(4)	1 468(6)	C(9)	4 482(6)	4 668(4)	2 895(6)
C(22)	5 883(7)	1 816(5)	489(8)	C(10)	3 834(7)	5 024(3)	3 975(7)
C(23)	24(6)	2 986(4)	1 573(6)	C(11)	2 803(7)	4 691(5)	4 644(9)
C(24)	−1 102(7)	3 256(5)	660(8)	C(12)	2 351(6)	3 994(4)	4 251(8)
C(1)	1 842(5)	1 434(3)	3 092(7)				
Compound **3**							
Sn	7 544.5(4)	465.7(7)	8 628.4(3)	C(221)	8 692(7)	−1 824(12)	6 095(5)
S(11)	5 968.9(15)	1 647.8(25)	8 574.0(13)	C(222)	8 511(8)	−3 416(13)	6 110(7)
S(12)	7 536.7(16)	2 752.9(27)	7 799.1(13)	C(31)	7 056(6)	−1 472(10)	9 110(5)
N(1)	5 940(5)	3 986(8)	7 761(4)	C(32)	6 365(7)	−1 433(10)	9 604(5)
C(1)	6 436(6)	2 930(9)	8 011(4)	C(33)	6 105(7)	−2 635(12)	9 977(6)
C(111)	4 984(6)	4 164(10)	7 921(5)	C(34)	6 520(8)	−3 925(12)	9 845(6)
C(112)	4 814(8)	5 299(13)	8 470(6)	C(35)	7 190(8)	−3 966(11)	9 336(7)
C(121)	6 321(7)	5 055(11)	7 270(6)	C(36)	7 460(7)	−2 764(10)	8 988(5)
C(122)	6 235(9)	4 643(16)	6 492(6)	C(41)	8 080(6)	1 567(9)	9 577(5)
S(21)	9 068.9(15)	−261.7(28)	8 125.5(13)	C(42)	7 550(7)	2 326(10)	10 026(5)
S(22)	7 431.3(15)	−828.8(27)	7 263.5(13)	C(43)	7 861(8)	2 918(12)	10 685(6)
N(2)	9 086(5)	−1 336(8)	6 787(4)	C(44)	8 728(8)	2 757(11)	10 869(6)
C(2)	8 573(6)	−863(9)	7 322(5)	C(45)	9 299(7)	2 009(12)	10 438(6)
C(211)	10 071(6)	−1 380(11)	6 845(5)	C(46)	8 967(7)	1 410(11)	9 796(5)
C(212)	10 512(8)	−77(13)	6 553(9)				
Compound **4**							
Te(1)	0.0	1 724.4(5)	7 500.0	C(3)	−1 247(3)	1 028(5)	7 167(3)
Te(2)	0.0	−1 649.7(5)	7 500.0	C(4)	−1 997(3)	1 109(6)	6 661(4)
Cl(1)	413(2)	−1 787(3)	10 363(2)	C(5)	242(3)	2 942(5)	8 471(4)
Cl(2)	1 352.0(14)	44.8(20)	10 823.8(13)	C(6)	805(3)	2 774(6)	9 262(4)
Cl(3)	1 607.0(13)	−2 322.3(27)	10 563.8(15)	C(7)	966(4)	3 576(7)	9 897(4)
Cl(4)	−2 336.2(11)	−72.6(20)	6 844.9(17)	C(8)	576(5)	4 521(8)	9 743(5)
Cl(5)	−2 209.9(13)	2 388.9(25)	6 929.0(26)	C(9)	8(4)	4 676(6)	8 956(5)
Cl(6)	−2 293.3(11)	1 153.6 (45)	5 596.2(14)	C(10)	−157(3)	3 888(6)	8 323(4)
O(1)	361(2)	−1 886(4)	8 815(2)	C(11)	−735(3)	−2 844(5)	7 272(4)
O(2)	816(3)	−108(4)	9 057(3)	C(12)	−1 028(3)	−2 653(6)	7 696(4)
O(3)	−999(2)	1 936(4)	7 052(3)	C(13)	−1 534(4)	−3 389(7)	7 500(6)
O(4)	−959(2)	177(4)	7 601(3)	C(14)	−1 739(4)	−4 264(8)	6 916(6)
C(1)	703(3)	−1 020(6)	9 277(3)	C(15)	−1 448(4)	−4 458(7)	6 512(5)
C(2)	986(3)	−1 250(7)	10 214(4)	C(16)	−937(3)	−3 730(6)	6 686(4)
Compound **5**							
Te	0.0	5 529.4(2)	7 500.0	C(5)	−3 895(3)	3 487(3)	4 314(4)
S(1)	−1 589.0(6)	5 545.0(6)	7 480.2(8)	C(6)	515(2)	6 547(2)	9 006(3)
S(2)	−1 667.6(7)	4 268.9(7)	5 493.1(9)	C(7)	379(2)	6 396(2)	10 021(3)
N(1)	−2 727(2)	4 075(2)	6 525(3)	C(8)	767(3)	7 015(3)	11 047(3)
C(1)	−2 061(2)	4 565(2)	6 470(3)	C(9)	1 288(3)	7 764(3)	11 061(4)
C(2)	−2 998(3)	4 234(3)	7 491(4)	C(10)	1 418(3)	7 916(3)	10 049(4)
C(3)	−3 999(3)	4 505(3)	6 906(6)	C(11)	1 032(2)	7 301(2)	9 019(3)
C(4)	−3 156(3)	3 247(3)	5 699(4)				

Table 5 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Compound **6**							
Te	2 057.6(4)	2 062.3(3)	2 134.6(2)	C(14)	2 112(7)	1 337(6)	5 445(4)
S(11)	2 530.9(20)	1 340.6(14)	3 643.9(10)	C(15)	1 404(9)	295(6)	5 725(4)
S(12)	778.7(24)	3 685.7(16)	3 618.1(12)	C(16)	1 984(11)	−728(7)	6 160(5)
S(21)	1 958.3(16)	2 634.2(14)	496.5(9)	C(17)	3 254(11)	−666(8)	6 325(5)
S(22)	−386.3(21)	1 030.6(17)	1 565.4(11)	C(18)	3 922(10)	382(9)	6 065(5)
N(11)	1 492(6)	2 398(4)	4 995(3)	C(19)	3 379(8)	1 441(7)	5 615(5)
N(21)	−159(5)	2 127(5)	−54(3)	C(21)	390(6)	1 920(5)	629(4)
C(1)	3 308(7)	439(5)	1 857(4)	C(22)	−1 402(9)	1 476(8)	−63(6)
C(2)	4 512(7)	445(5)	1 190(4)	C(23)	−2 352(11)	2 054(11)	−463(7)
C(3)	5 339(8)	−621(6)	1 074(5)	C(24)	472(7)	2 894(5)	−848(4)
C(4)	4 944(8)	−1 685(6)	1 614(5)	C(25)	1 351(7)	2 390(6)	−1 520(4)
C(5)	3 731(9)	−1 719(6)	2 266(5)	C(26)	1 883(8)	3 141(8)	−2 301(4)
C(6)	2 894(8)	−644(5)	2 397(4)	C(27)	1 538(9)	4 375(8)	−2 401(5)
C(7)	3 808(6)	3 214(5)	1 748(4)	C(28)	672(8)	4 857(7)	−1 728(5)
C(8)	3 614(7)	4 410(5)	1 354(4)	C(29)	129(7)	4 132(5)	−950(4)
C(9)	4 741(8)	5 179(6)	1 094(5)	C(001)	6 087(15)	4 231(15)	5 005(11)
C(10)	6 025(8)	4 784(6)	1 252(5)	C(002)	5 199(15)	5 099(15)	5 434(11)
C(101)	6 210(8)	3 608(6)	1 650(5)	C(003)	4 058(15)	5 662(15)	5 126(11)
C(102)	5 102(7)	2 814(5)	1 902(4)	C(004)	3 805(15)	5 357(15)	4 388(11)
C(11)	1 546(7)	2 504(5)	4 155(4)	C(005)	4 692(15)	4 489(15)	3 959(11)
C(12)	829(9)	3 355(6)	5 515(4)	C(006)	5 833(15)	3 926(15)	4 268(11)
C(13)	−436(10)	2 950(8)	6 170(7)				
Compound **7**							
Te	4 501.1(1.4)	6 938.5(6)	6 953.5(6)	C(210)	10 225(22)	5 961(16)	5 433(11)
S(11)	2 726(6)	7 575(3)	7 536(3)	C(211)	10 541(23)	5 449(17)	5 753(12)
S(12)	4 697(6)	8 356(3)	6 909(3)	C(212)	9 488(31)	5 103(12)	5 915(11)
S(21)	6 350(5)	6 236(2)	6 512(2)	C(213)	8 069(25)	5 256(11)	5 791(10)
S(22)	3 868(5)	6 326(3)	5 612(2)	C(31)	3 392(22)	6 184(9)	7 289(9)
N(11)	2 301(18)	8 708(8)	7 312(8)	C(32)	4 016(24)	5 758(10)	7 582(10)
N(21)	6 350(14)	5 968(6)	5 330(6)	C(33)	3 339(43)	5 284(16)	7 794(17)
C(11)	3 226(23)	8 259(9)	7 238(9)	C(34)	1 946(63)	5 252(16)	7 667(19)
C(12)	2 341(22)	9 272(12)	7 032(13)	C(35)	1 302(36)	5 714(19)	7 383(16)
C(13)	2 311(20)	9 787(11)	7 328(11)	C(36)	1 954(32)	6 187(15)	7 139(10)
C(14)	2 277(27)	10 322(13)	7 058(15)	C(41)	6 020(24)	7 003(9)	7 731(10)
C(15)	2 228(36)	10 338(13)	6 430(19)	C(42)	5 589(25)	6 904(10)	8 331(10)
C(16)	2 247(46)	9 857(17)	6 083(15)	C(43)	6 619(31)	6 963(11)	8 810(10)
C(17)	2 321(33)	9 292(13)	6 385(15)	C(44)	7 966(36)	7 061(11)	8 710(17)
C(18)	1 137(24)	8 653(10)	7 691(12)	C(45)	8 367(29)	7 145(12)	8 119(14)
C(19)	1 418(24)	8 590(11)	8 314(12)	C(46)	7 360(23)	7 111(9)	7 637(11)
C(110)	265(30)	8 568(11)	8 676(14)	C(61)	6 244(36)	1 933(24)	4 980(13)
C(111)	−1 073(32)	8 571(13)	8 466(18)	C(62)	7 162	2 274	5 363
C(112)	−1 287(26)	8 659(13)	7 819(18)	C(63)	7 952	2 005	5 853
C(113)	−198(26)	8 676(10)	7 445(14)	C(64)	7 824	1 395	5 960
C(21)	5 526(18)	6 176(8)	5 771(8)	C(65)	6 905	1 054	5 578
C(22)	5 908(17)	5 929(10)	4 686(8)	C(66)	6 115	1 323	5 087
C(23)	5 914(18)	5 382(9)	4 395(9)	C(71)	37(50)	2 168(25)	4 320(22)
C(24)	5 602(20)	5 319(11)	3 764(11)	C(72)	1 260	2 336	4 053
C(25)	5 296(21)	5 841(13)	3 454(9)	C(73)	2 403	1 951	4 081
C(26)	5 236(18)	6 392(10)	3 728(10)	C(74)	2 323	1 400	4 374
C(27)	5 583(19)	6 437(9)	4 350(9)	C(75)	1 100	1 232	4 641
C(28)	7 814(20)	5 806(10)	5 489(8)	C(76)	−43	1 616	4 613
C(29)	8 873(21)	6 143(11)	5 300(9)				

Secondary Bonding.—These compounds show less significant intermolecular secondary bonding than has been found in other main-group carboxylates.[8] One reason for this probably lies in the extensive intramolecular secondary bonding, from the second S or O atom of each ligand. Tellurium and iodine carboxylates previously examined have shown 'pentagonal-planar' co-ordination, in which the two short M–O, one M–O and two long M • • • O bonds are coplanar; for Te this involved one of the M–C bonds, ignoring the other. This bonding mode is absent from most of the present complexes. Instead, they have one of the M • • • O or M • • • S long bonds approximately coplanar with the two M–O and one of the M–C bonds, while the other M • • • O or M • • • S is coplanar with the other M–C bond. An approximation to the pentagonal plane is found only in **4**, through the formation of secondary Te • • • O bonds (Fig. 3), two of which are approximately coplanar with one and two with the other Te–C bond.

Experimental

Infrared data were recorded on a Perkin-Elmer 580B spectrophotometer in the range 4000–400 cm^{-1} using KBr discs or Nujol mulls.

Synthesis of Compounds.—The compound Ph_2SnCl_2 was purchased from Aldrich and used as received.

Silver carboxylates. Silver(I) oxide and the appropriate acid were stirred in distilled water. The water was reduced in volume using a rotary evaporator until crystallisation occurred. The flask was cooled in a refrigerator and the product filtered off. Repeated reduction of the solvent volume and filtration gave a good yield of white crystals. These were used immediately or stored wrapped in foil in a desiccator. Infrared spectra showed that these compounds are anhydrous.

Diphenyltin dicarboxylates. Typically, Ph_2SnCl_2 and AgO_2CMe (1:2) were refluxed in dry hexane for 3 h. The hot solution was filtered to remove AgCl and solvent removed on a rotary evaporator. The product was recrystallised from hot light petroleum (b.p. 30–40 °C). For the monochloroacetate, CH_2Cl_2 was used as the solvent and crystals obtained by liquid diffusion with light petroleum. Suitable crystals could not be isolated for the dichloroacetate complex, most solvents giving very thin platy crystals, and the spectroscopic data recorded are from the crude product. The bis(trichloroacetate) complex was not isolable by this method, and hydrolysis of the product is suspected, from a comparison with the behaviour of triphenyltin trichloroacetate.[9]

Diphenyltellurium dichloride. Tellurium tetrachloride (3.8 g, 0.014 mol) and Ph_2Hg (5.0 g, 0.014 mol) were refluxed in dry benzene (100 cm^3) for 24 h. The solution was then filtered while hot and solvent removed by rotary evaporation. The product was recrystallised from hot ethanol.

Diphenyltellurium dicarboxylates. The compound Ph_2TeCl_2 and the sodium salt of the respective acid (acetic, dichloro- or trichloro-acetic) (1:2) were stirred in dry benzene (30 cm^3) for 24 h. The solution was filtered through Celite to remove the NaCl and the solvent removed by rotary evaporation. The white products were recrystallised from CCl_4–hexane by liquid diffusion. X-Ray data were not obtained for the acetate, because those of the corresponding $MeOC_6H_4$ derivative were already known, while suitable crystals of the dichloroacetate could not be obtained.

Pottasium diethyldithiocarbamate. The salt $K[S_2CNEt_2]$ was prepared by the method of Graziani *et al.*[10] To a mixture of CS_2 (7.6 g, 0.1 mol) and water (25 cm^3) containing KOH (5.6 g, 0.1 mol) was added dropwise, with cooling and stirring, Et_2NH (7.3 g, 0.1 mol). The solution was stirred for 1.5 h during which time it turned yellow. The solvent was then removed and the product dried *in vacuo.*

Potassium ethylphenyldithiocarbamate. The first stages of the previous preparation were followed substituting EtPhNH for Et_2NH. The solution turned pale orange. Hydrogen peroxide was added dropwise until no further reaction was visible. A yellow precipitate formed. The solvent was removed under reduced pressure and the solid dried *in vacuo.*

Lithium diphenyldithiocarbamate. Diphenylamine (1.69 g, 0.01 mol) was stirred, under N_2, in dry hexane (25 cm^3) until dissolved. The solution was cooled in a solid CO_2–acetone bath and BuLi (6.25 cm^3, 0.01 mol, 1.6 mol dm^{-3}) was added dropwise *via* a syringe. The solution was allowed to warm to room temperature to react then cooled to −78 °C again. Carbon disulfide (0.6 cm^3, 0.01 mol) was added slowly and the solution allowed to warm again. It turned yellow. The solvent was removed and the product stored under N_2.

Diphenyltin diethyldithiocarbamate. The compound Ph_2SnCl_2 (3.53 g, 0.01 mol) in ethanol (100 cm^3) was added to a solution of potassium dithiocarbamate (5.90 g, 0.03 mol) in ethanol (100 cm^3) and stirred for 0.5 h. The white precipitate was filtered off and recrystallised from ethanol–dichloromethane, to give needle crystals.

Diphenyltellurium dithiocarbamates. The compound Ph_2TeCl_2 (3.52 g, 0.01 mol) and the respective dithiocarbamate (0.02 mol) were stirred in acetone for 3 h. The yellow precipitate was filtered off and recrystallised from hot toluene. The needle crystals were used directly for structure determination.

Table 6 Selected dimensions (lengths in Å, angles in °)

Compound 1			
Sn–C(11)	2.119(5)	Sn–O(4)	2.527(5)
Sn–C(21)	2.110(6)	O(2)–C(1)	1.315(8)
Sn–O(2)	2.076(4)	O(3)–C(3)	1.308(8)
Sn–O(3)	2.079(4)	O(1)–C(1)	1.216(8)
Sn–O(1)	2.583(4)	O(4)–C(3)	1.218(9)
C(11)–Sn–C(21)	131.4(2)	O(1)–Sn–O(4)	167.8(1)
O(2)–Sn–O(3)	82.0(3)		
Compound 2			
Sn–C(1)	2.105(6)	Sn–O(4)	2.549(6)
Sn–C(7)	2.118(6)	C(21)–O(2)	1.294(8)
Sn–O(2)	2.101(6)	C(23)–O(3)	1.301(8)
Sn–O(3)	2.090(6)	C(21)–O(1)	1.214(8)
Sn–O(1)	2.534(6)	C(23)–O(4)	1.220(7)
C(1)–Sn–C(7)	147.2(2)	O(1)–Sn–O(4)	167.5(2)
O(2)–Sn–O(3)	82.3(2)		
Compound 3			
Sn–C(31)	2.155(9)	C(1)–S(11)	1.735(9)
Sn–C(41)	2.165(8)	C(2)–S(21)	1.734(9)
Sn–S(11)	2.607(3)	C(1)–S(12)	1.702(9)
Sn–S(21)	2.558(3)	C(2)–S(22)	1.709(9)
Sn–S(12)	2.632(3)	N(1)–C(1)	1.320(11)
Sn–S(22)	2.777(3)	N(2)–C(2)	1.323(11)
C(31)–Sn(1)–C(41)	101.8(3)	S(12)–Sn(1)–S(22)	81.0(1)
S(11)–Sn(1)–S(21)	155.3(1)		
Compound 4[a]			
Te(1)–C(5)	2.106(6)	Te(2)–O(2)	3.032(4)
Te(2)–C(11)	2.114(7)	Te(2)–O(4)	3.250(4)
Te(1)–O(3)	2.149(4)	C(1)–O(1)	1.267(7)
Te(2)–O(1)	2.163(4)	C(3)–O(3)	1.278(8)
Te(1)–O(4)	3.060(4)	C(1)–O(2)	1.204(9)
Te(1)–O(2)	3.229(4)	C(3)–O(4)	1.202(7)
C(5)–Te(1)–C(5a)	98.9(3)	O(4)–Te(1)–O(4a)	110.7(3)
C(11)–Te(2)–C(11a)	101.2(3)	O(2)–Te(1)–O(2a)	100.7(3)
O(3)–Te(1)–O(3a)	167.3(3)	O(2)–Te(2)–O(2a)	110.2(3)
O(1)–Te(2)–O(1a)	165.9(3)	O(4)–Te(2)–O(4a)	101.6(3)
Compound 5[b]			
Te–C(6)	2.143(3)	C(1)–S(1)	1.761(3)
Te–S(1)	2.615(1)	C(1)–S(2)	1.682(4)
Te–S(2)	3.130(1)	C(1)–N(1)	1.338(5)
C(6)–Te–C(6a)	93.9(2)	S(2)–Te–S(2a)	109.2(1)
S(1)–Te–S(1a)	179.0(1)		
Compound 6			
Te–C(1)	2.137(6)	C(11)–S(11)	1.744(6)
Te–C(7)	2.130(6)	C(21)–S(21)	1.743(7)
Te–S(11)	2.588(2)	C(11)–S(12)	1.673(6)
Te–S(21)	2.649(2)	C(21)–S(22)	1.687(5)
Te–S(12)	3.200(2)	C(11)–N(11)	1.337(8)
Te–S(22)	3.168(2)	C(21)–N(21)	1.334(9)
C(1)–Te–C(7)	95.0(2)	S(12)–Te–S(22)	111.1(1)
S(11)–Te–S(21)	171.2(1)		
Compound 7			
Te–C(31)	2.152(2)	C(11)–S(11)	1.74(2)
Te–C(41)	2.151(2)	C(21)–S(21)	1.74(2)
Te–S(11)	2.612(6)	C(11)–S(12)	1.64(2)
Te–S(21)	2.603(5)	C(22)–S(22)	1.64(2)
Te–S(12)	3.188(6)	C(11)–N(11)	1.36(3)
Te–S(22)	3.221(6)	C(21)–N(21)	1.36(2)
C(31)–Te–C(41)	96.7(8)	S(12)–Te–S(22)	114.0(2)
S(11)–Te–S(21)	172.5(2)		

[a] Position a: −*x*, 1 + *y*, 1.5 − *z*. [b] Position a: −*x*, *y*, 1.5 − *z*.

Crystal Structure Analysis.—Data were collected with a Nicolet P2$_1$ four-circle diffractometer in ω–2θ mode with the parameters given in Table 4. Variable scan speed, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections; the data were rescaled if necessary to correct for any decay. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections. Reflections were processed using profile analysis. Those with $I/\sigma(I) \geqslant 2.0$ were considered observed and were corrected for Lorentz, polarisation and absorption effects (by the Gaussian method).

Anisotropic thermal parameters were generally used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.08$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid CH_3 units. Final refinements were on F by least-squares methods. Weighting schemes of the form $w = 1/[\sigma^2(F) + gF^2]$ were used and shown to be satisfactory by a weight analysis. Computing with SHELXTL[11] on a Data General DG30 or SHELXTL PLUS[12] on a DEC MicroVax-II (for **3**). Scattering factors in the analytical form and anomalous dispersion factors taken from ref. 13. Coordinates and selected bond lengths and angles are given in Tables 5 and 6.

Diphenyltin diacetate **1**. Systematic absences gave the space group as $P2_12_12_1$.

Diphenyltin bis(monochloroacetate) **2**. Systematic absences indicated space group *Pbcm* or $Pbc2_1$ (non-standard setting of $Pca2_1$). From density calculations the expected number of molecules per unit cell was 4, giving $D_c = 1.81$ g cm^{-3}. Space group $Pbc2_1$ was therefore initially chosen for the refinement but did not give encouraging results. It was changed to *Pbcm* with the condition that the heavy atom must lie on the mirror plane at $z = \frac{1}{4}$. Structure solution from the Patterson synthesis and refinement was then satisfactory.

Diphenyltin bis(diethyldithiocarbamate) **3**. The standards showed a 2% decrease during data collection. Systematic absences indicate space group $P2_1/c$. The structure was solved by direct methods using SHELXTL, locating the Sn and two S atoms; the light atoms were then found on successive Fourier syntheses. This structure has been previously determined, using a limited set of photographic data.[14] The results are qualitatively similar to those of the present study but less precise.

Diphenyltellurium bis(trichloroacetate) **4**. Systematic absences indicate space group *Cc* or *C*2/*c*. From density calculations eight molecules were expected, suggesting *C*2/*c* as the most likely choice. This was proved correct by satisfactory refinement. Two heavy atoms were found from the Patterson synthesis, lying on the two-fold axis at 0, y, $\frac{3}{4}$. These positions were used and gave good refinement. Residual electron density is located in the rotation circles of the CCl_3 groups.

Diphenyltellurium bis(diethyldithiocarbamate) **5**. Systematic absences indicate the space group as either *Cc* or *C*2/*c*. Analysis of the E statistics indicated a centrosymmetric space group, the density calculation gave four molecules per unit cell and the Patterson synthesis gave the heavy-atom position at 0, y, $\frac{1}{2}$ on the two-fold axis; *C*2/*c* was therefore chosen, and proved correct by satisfactory refinement.

Diphenyltellurium bis(ethylphenyldithiocarbamate) **6**. Space group $P\bar{1}$ was chosen on the basis of density calculations and proved correct. All the non-hydrogen atoms were refined anisotropically except for those in the solvent toluene. This was very disordered and was refined at half occupancy. It is centred around ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The residual electron density is all located around the solvent molecule.

Diphenyltellurium bis(diphenyldithiocarbamate) **7**. Systematic absences gave the space group as $P2_1/c$. All the non-hydrogen atoms except those of C(31) and solvent molecules were refined anisotropically. The solvent toluenes were disordered and were refined as rigid hexagons. The methyl group on the toluene was not located. Residual electron density is located close to the tellurium and the solvent. The high R factor is probably a consequence of the presence of disordered solvent.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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