Dichlorobis(4-methylpentan-2-onato-C^4,O)tin(IV) and bis(4-methylpentan-2-onato-C^4,O)(2-thioxo-1,3-dithiole-4,5-dithiolato-S,S′)tin(IV) at 150 K

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The structures of the ketotins determined here, $[SnCl_2(C_6H_{11}O)_2]$ and $[Sn(C_3S_5)(C_6H_{11}O)_2]$, respectively, along with that previously reported for $[MeC(O)CH_2CMe_2]_2SnI_2$, are compared with the structures of the analogous estertins $[MeOC(O)CH_2CH_2]_2SnX_2$. Pairwise comparison of the mean ketotin [estertin] Sn—X and Sn—O distances as Sn—X 2.4422 (4) [2.4054 (7) Å], 2.4970 (4) [2.471 (2) Å] and 2.8463 (4) [2.7788 (8) Å] and Sn—O 2.4926 (12) [2.528 (1) Å], 2.6110 (11) [2.629 (7) Å] and 2.435 (3) [2.525 (4) Å] (for X = Cl, S and I, respectively) clearly demonstrates the superior donor ability of the ketotin O atom in chelate formation.

Comment

γ-Oxoalkyltin compounds, such as $[RC(O)CH_2CR'_2]_2SnX_2$ [(I), X = Cl] and $[ROC(O)CH_2CR'_2]_2SnX_2$ [(II), X = Cl], are readily available from the reactions of Sn, HCl and $RC(O)CH{=}CR'_2$ or $ROC(O)CH{=}CR'_2$ (Hutton & Oakes, 1976). Of the two groups of compounds, it is the so-called estertins, (II), which have attracted the greater interest. Considerable attention has been paid to the coordination chemistry of estertin compounds, especially the ability of the organic ligand to act as a C,O-chelating group (Wang & Liu, 2000; Zhang et al., 2000; Balasubramanian et al., 1997, and references therein). While fewer studies have been reported on the ketotin compounds, (I), their coordination chemistry should be equally as diverse and worthy of investigation. Recently, the crystal structure of diiodobis(4-methylpentan-2-onato-C^4,O)tin(IV), $[MeC(O)CH_2CMe_2]_2SnI_2$, (III), was reported and compared with that of $[MeOC(O)CH_2CH_2]_2SnI_2$ (Howie & Wardell, 2000).

As shown by the crystal structures of two further ketotin compounds, namely dichlorobis(4-methylpentan-2-onato-C^4,O)-tin(IV), $[MeC(O)CH_2CMe_2]_2SnCl_2$, (IV), and [bis(4-methylpentan-2-onato-C^4,O)(2-thioxo-1,3-dithiole-4,5-dithiolato-S,S′)tin(IV), $[MeC(O)CH_2CMe_2]_2Sn(dmit)$ (dmit is

2-thioxo-1,3-dithiole-4,5-dithiolate, (V), subtle changes in the geometries about the six-coordinate tin centres in $[MeC(O)CH_2CMe_2]_2SnX_2$ result from changing the X_2 functional groups. Selected geometric parameters for (IV) and (V) are listed in Table 1.

(IV)   (V)
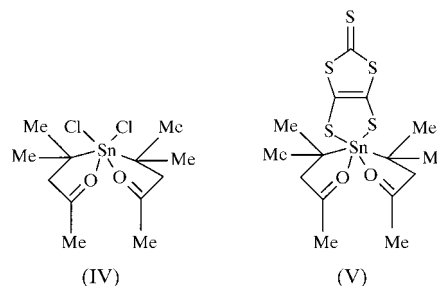
As in the structure of (III), both $MeC(O)CH_2CMe_2$ ligands act as C^4,O-chelating groups in both (IV) and (V). However, there are differing degrees of asymmetry in the Sn—O bond lengths of the chelating ligands within each of the three compounds: $\Delta d(Sn{-}O)$ is 0.165 (2) Å in (V), 0.098 (2) Å in (IV), and 0.010 (6) and 0.004 (6) Å in the two independent molecules of (III). The geometry at tin in (III) is best described as being distorted octahedral. This distortion is due, in the main, to the chelate bite angles being ca 75°, which have a consequential effect on the trans angles, between 160.4 (2) and 163.68 (11)°, in (III). There is even greater octahedral distortion in (IV); despite similar chelate bite angles [72.80 (8) and 75.17 (8)°], the trans angles in (IV) are quite different [172.28 (4), 165.21 (5) and 152.23 (10)°]. As in (III), the C atoms in (IV) are trans to each other, with each of the O atoms trans to a halide. The longer Sn—O bond is trans to the shorter Sn—X bond. The structure of (V), with three chelating ligands, is still further displaced from octahedral, with the three largest angles subtended at the Sn atom being 161.13 (4) (O1—Sn—S1), 155.25 (4) (O2—Sn—S2) and only 131.15 (9)° (C1—Sn—C7). The bite angle of the dmit ligand is 87.95 (2)°, near ideal for a cis-relationship in an octahedral array, and so on geometric grounds this cannot be the cause of the further displacement from octahedral geometry. A description of the geometry as a distorted trigonal prism also appears rather far-fetched, since for this structure, all trans angles would be
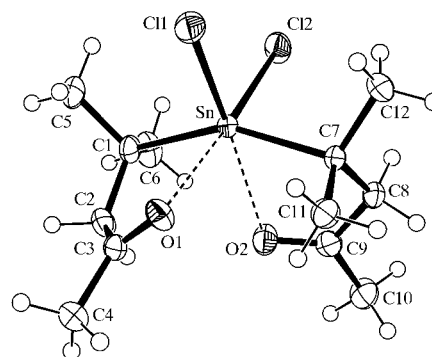

Figure 1
The molecular structure of (IV) showing the atom-labelling scheme. Non-H are shown as 50% ellipsoids and H as open circles. Dashed lines represent Sn—O bonds.

expected to be near 136° for the ideal arrangement. Another possible description for the structure of (V) is a bicapped tetrahedron, with the two C and two S atoms in tetrahedral sites and with the two O atoms capping this tetrahedron. However, the angles subtended by the C and S atoms at Sn range from 87.95 (2) to 131.15 (9)° and are thus far from ideal. Thus, a highly distorted six-coordinate complex seems to be the most appropriate description for the geometry. A similar situation is found for the estertin analogue, [MeOC(O)CH$_2$-CH$_2$]$_2$Sn(dmit), although it was not mentioned in the publication (Buchanan *et al.*, 1996). The five-membered chelate rings, Sn—O—C—C—C, have similar envelope conformations, and as expected from geometric considerations, the MeC(O)CH$_2$CMe$_2$ chelate bite angle generally increases with a decrease in the Sn—O bond length.
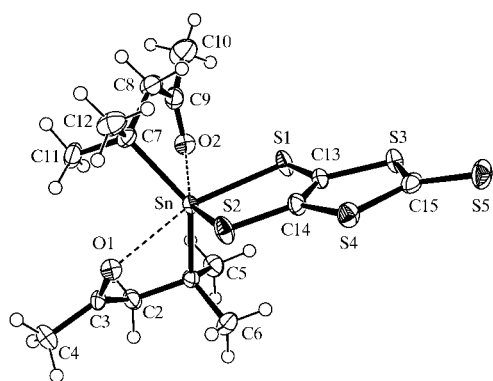

Figure 2
The molecular structure of (V) represented as for Fig. 1.

The mean Sn—O bond length is 2.435 (2) Å in (III), 2.4926 (12) Å in (IV) and 2.6110 (11) Å in (V), all of which were determined at 150 (2) K. Corresponding values for [MeOC(O)CH$_2$CH$_2$]$_2$SnX_2, (VI), determined at 300 (2) K, are 2.525 (4) Å [(VI), X = I; Balasubramanian *et al.*, 1997], 2.528 (7) Å [(VI), X = Cl; Ng, 1993] and 2.629 (2) Å [(VI), X_2 = dmit; Buchanan *et al.*, 1996]. If the mean Sn—O bond lengths can be taken as a guide and assuming little bond shortening on reducing the temperature, the MeC(O)-CH$_2$CMe$_2$ ligand appears to be the stronger chelating group. Selected comparisons of the geometric parameters for analogous ketotin and estertin compounds are given in Table 2.

Experimental

[MeC(O)CH$_2$CMe$_2$]$_2$SnCl$_2$, (IV), was prepared according to the procedure of Hutton & Oakes (1976) and was recrystallized from EtOH solution [m.p. 432–433 K; literature value 431 K (Hutton & Oakes, 1976)]. [MeC(O)CH$_2$CMe$_2$]$_2$Sn(dmit), (V), was obtained from (IV) (0.2 mmol) and [NEt$_4$]$_2$[Zn(dmit)$_2$] (0.1 mmol) in acetone (30 ml). The reaction mixture was refluxed for 30 min, left overnight and evaporated to leave a red–brown residue. The residue was crystallized by slow evaporation of a solution in acetone/EtOH. Dark orange–red crystals were collected, which darkened on heating and finally decomposed to give a black residue at 461–465 K. Analysis found: C 35.3, H 4.4%; calculated for C$_{15}$H$_{22}$O$_2$S$_5$Sn: C 35.1, H 4.3%. ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.43 [s, 6H, J(^{119,117}Sn-^{1}H) =111.7, 106.8 Hz, Me$_2$C)], 2.28 (s, 3H, MeCO), 2.96 [s, 2H, J(^{119,117}Sn-^{1}H) = 116.6, 112.3 Hz, CH$_2$].

Compound (IV)

Crystal data

[SnCl$_2$(C$_6$H$_{11}$O)$_2$]
M_r = 387.89
Monoclinic, $P2_1/c$
a = 9.6242 (2) Å
b = 11.9846 (3) Å
c = 14.5866 (3) Å
β = 106.1048 (17)°
V = 1616.42 (6) Å^3
Z = 4

D_x = 1.594 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 928 reflections
θ = 1.0–27.5°
μ = 1.90 mm^{-1}
T = 150 (2) K
Block, colourless
0.28 × 0.18 × 0.16 mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill the Ewald sphere
Absorption correction: multi-scan (*SORTAV*: Blessing, 1995, 1997)
T_{min} = 0.600, T_{max} = 0.744
20 493 measured reflections

3654 independent reflections
3167 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 27.5°
h = −12 → 12
k = −15 → 15
l = −18 → 18

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.074
S = 1.08
3654 reflections
160 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 1.0246P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.75 e Å^{-3}
$\Delta\rho_{min}$ = −1.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for compounds (IV) and (V).

	(IV)	(V)
Sn—C1	2.189 (2)	2.182 (2)
Sn—C7	2.189 (2)	2.185 (2)
Sn—O1	2.4439 (17)	2.5286 (16)
Sn—O2	2.5414 (18)	2.6933 (16)
Sn—XA	2.4216 (6)	2.4921 (6)
Sn—XB	2.4629 (6)	2.5018 (6)
C1—Sn—C7	152.53 (10)	131.15 (9)
C1—Sn—XA	103.53 (7)	109.25 (6)
C7—Sn—XA	99.57 (7)	106.33 (6)
C1—Sn—O1	75.17 (8)	73.07 (7)
C7—Sn—O1	91.94 (8)	84.38 (7)
XA—Sn—O1	86.07 (5)	76.14 (4)
C1—Sn—XB	97.21 (7)	103.49 (6)
C7—Sn—XB	94.46 (7)	110.20 (7)
XA—Sn—XB	97.11 (2)	87.95 (2)
O1—Sn—XB	172.28 (4)	161.13 (4)
C1—Sn—O2	81.27 (8)	89.78 (7)
C7—Sn—O2	72.80 (8)	69.20 (7)
XA—Sn—O2	165.21 (5)	155.25 (4)
O1—Sn—O2	81.63 (6)	125.95 (5)
XB—Sn—O2	96.13 (5)	71.88 (4)

Notes, for (IV): X = Cl, A = 1 and B = 2; for (V): X = S, A = 2 and B = 1.

Compound (V)

Crystal data

[Sn(C$_3$S$_5$)(C$_6$H$_{11}$O)$_2$]
M_r = 513.32
Monoclinic, $P2_1/c$
a = 11.0670 (2) Å
b = 15.4499 (4) Å
c = 12.2682 (2) Å
β = 94.7892 (16)°
V = 2090.34 (7) Å^3
Z = 4

D_x = 1.631 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 433 reflections
θ = 2.9–27.5°
μ = 1.73 mm^{-1}
T = 150 (2) K
Block, orange
0.24 × 0.20 × 0.12 mm

Table 2
Comparison of selected geometric parameters (Å, °) for ketotin [MeC(O)CH$_2$CMe$_2$]$_2$SnX$_2$ and estertin [MeOC(O)CH$_2$CH$_2$]$_2$SnX$_2$.

X_2	Ketotin at 150 (2) K				Estertin at 300 (2) K		
	dmit[a]	Cl$_2$[a]	I$_2$[b]		dmit[c]	Cl$_2$[d]	I$_2$[e]
			Molecule 1	Molecule 2			
Largest angles	161.13 (4)	172.28 (4)	163.68 (11)	163.49 (10)	162.3 (2)	175.54 (6)	173.7 (2)
at tin	155.25 (4)	165.21 (5)	163.11 (11)	162.56 (10)	162.3 (2)	175.18 (6)	173.5 (2)
	131.15 (9)	152.53 (10)	160.4 (2)	161.1 (2)	121.0 (4)	144.5 (2)	144.0 (5)
(Sn—X)$_{mean}$	2.4970 (4)	2.4422 (4)	2.8463 (4)	2.8464 (4)	2.471 (2)	2.4054 (7)	2.7788 (8)
Δ(Sn—X)	0.0097 (8)	0.0413 (8)	0.0218 (7)	0.0173 (7)	0[f]	0.0100 (13)	0.0026 (16)
(Sn—O)$_{mean}$	2.6110 (11)	2.4926 (12)	2.433 (3)	2.437 (3)	2.629 (7)	2.528 (1)	2.525 (4)
Δ(Sn—O)	0.165 (2)	0.098 (2)	0.010 (6)	0.004 (6)	0[f]	0.017 (3)	0.006 (8)

Notes: (a) this study; (b) Howie & Wardell (2000); (c) Buchanan et al. (1996); (d) Ng (1993); (e) Balasubramanian et al. (1997); (f) s.u.'s of bond-length differences calculated as the square root of the sum of the squares of the s.u.'s of the individual observations not applicable to ketotin with X = dmit due to the crystallographic twofold axial symmetry of this molecule; s.u.'s of the mean values one half those of the differences except in this case.

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill the Ewald sphere
Absorption correction: multi-scan (*SORTAV*: Blessing, 1995, 1997)
$T_{min} = 0.542$, $T_{max} = 0.823$
15 800 measured reflections
4730 independent reflections
4025 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -20 \rightarrow 20$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.068$
$S = 1.04$
4730 reflections
215 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 0.0744P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.91$ e Å^{-3}
$\Delta\rho_{min} = -1.22$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0050 (3)

In the final stages, in both cases, H atoms were introduced in calculated positions with C—H = 0.98 Å [0.99 Å] and refined with a riding model with $U_{iso} = 1.5[1.2]U_{eq}$ of the non-H atoms to which they were attached for methyl [methylene] H atoms.

For both compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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