Preparation, Properties, and Structures of Bis(*O*-ethyl dithiocarbonato)-dihalogenotin(IV) and Di-μ-thio-bis[bis(*O*-ethyl dithiocarbonato)tin(IV)] †

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The complexes $[Sn(S_2COEt)_2X_2]$, X = Cl, Br, or I, have been isolated as stable crystalline compounds. The corresponding complexes $[Sn(S_2COEt)_3X]$ and $[Sn(S_2COEt)X_3]$ could not be isolated, it being postulated that the former rearranges to yield the dimeric compound $[(EtOCS_2)_2SnS_2Sn(S_2COEt)_2]$. Structure determinations carried out by single-crystal *X*-ray diffraction methods of $[Sn(S_2COEt)_2Br_2]$ and $[Sn(S_2COEt)_2I_2]$ show that in both cases the tin atom is six-co-ordinate with the halide atoms *cis* (Sn–Br, I = 2.54, 2.75 Å). The mutually *trans* Sn–S distances in each complex are shorter (2.52 Å) than the Sn–S distances *trans* to the halide [2.59 (bromide), 2.64 Å (iodide)]. For $[Sn(S_2COEt)_2Br_2]$, the cell is monoclinic, space group $C2/c$, with a = 14.27(1), b = 16.894(8), c = 6.360(5) Å, β = 100.41(5)°, Z = 4; R was 0.037 for 1 342 ' observed ' reflections. For $[Sn(S_2COEt)_2I_2]$, the cell is monoclinic, space group $P2_1/n$, with a = 14.026(6), b = 11.210(4), c = 10.203(4) Å, β = 91.96(3)°; Z = 4, R being 0.030 for 2 512 ' observed ' reflections.

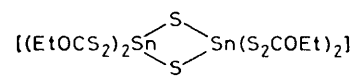
ONLY three examples of mixed halogenometal xanthates (*O*-alkyl dithiocarbonates) have so far been reported. Reaction of rhodium trichloride–phosphine adducts with xanthate ion yields the phosphine adducts of rhodium dichloro-xanthate and the corresponding monochlorocation.[1] Oxidative addition of bromine or iodine to dimolybdenum(II) tetraxanthate results in the formation of dihalogenodimolybdenum(III) tetraxanthate.[2] Copper(II) chloro- and bromo-xanthates have recently been reported[3] to result from reaction of copper(I) xanthate with copper(II) chloride or bromide and by addition of bromine to copper(I) xanthate. In continuing our study of the chemistry of tin xanthates[4] we have found that dihalogeno-xanthates of tin(IV) are stable complexes that may be prepared by a variety of methods whereas the corresponding mono- and tri-halides could not be isolated.

RESULTS

Preparation and Properties of the Complexes.—*Oxidative addition of halogens.* Reaction of chlorine, bromine, and iodine with tin(II) ethyl xanthate in chloroform proceeded smoothly to yield the corresponding tin(IV) dihalogeno-dixanthates as crystalline solids.

Oxidative addition of dixanthogen. The reaction of dixanthogen with tin(II) chloride and tin(II) bromide, in boiling chloroform, also gave the corresponding tin(IV) dihalogeno-dixanthates.

Reactions of potassium ethyl xanthate with tin(IV) *halides.* The reaction between potassium ethyl xanthate and tin(IV) halides yields the tin(IV) tetraxanthate if the ratio of the reagents is >4 : 1.[4] On reducing the ratios to 3 : 1, 2 : 1, and 1 : 1 tin(IV) dihalogeno-xanthates, $[Sn(S_2COEt)_2X_2]$, were obtained but the expected mono- and tri-halides could not be isolated. From the 3 : 1 reaction mixture an additional unexpected product was obtained in crystalline form whose analytical composition is consistent with that required by the tin(IV) thio-dixanthate, $[Sn(S_2COEt)_2S]$. Its molecular weight (825, 835) as determined by vapour-pressure osmometry in chloroform is about twice the formula weight (393) so that it might reasonably be formulated as compound I.§ A sulphur-bridged dimer, $[\{Mo(S_2COEt)(O)S\}_2]$, has previously been proposed for the reaction product of the oxomolybdenum(V) xanthate with hydrogen sulphide or ethanol.[5]



I

Reaction of tin(IV) *xanthate with tin*(IV) *halides.* The tin(IV) dihalogeno-dixanthate was the only product that could be isolated from the reactions of tin(IV) xanthate and tin(IV) chloride, bromide, and iodide when the ratios of reagents were 1 : 3 and 1 : 1. When the ratio was 3 : 1 no product could be isolated and the i.r. absorptions in the ' C–O ' and ' C–S ' region of the mixture after evaporation of the solvent were identical to those of tin(IV) xanthate.

Reaction of tin(IV) *xanthate with halogens.* From the reaction of tin(IV) xanthate with chlorine, bromine, and iodine in the ratios 1 : 1.5 and 1 : 1, again the corresponding tin(IV) dihalogeno-dixanthates were isolated, together with dixanthogen. When the ratio was 1 : 0.5, no product could be isolated from the reaction mixture.

Properties of tin(IV) *dihalogeno-dixanthates.* The dichloro-, dibromo-, and di-iodo-dixanthates were obtained as crystalline solids. Their characteristic i.r. absorptions show a progressive shift to higher frequency of the position of the band in the C–O region in the sequence iodide < bromide < chloride. Their u.v. absorptions in cyclohexane solution are attributed to internal transitions of the OCS_2 chromophore. For the di-iodo-xanthate a second modification was obtained when the solution was allowed to stand for several days prior to crystallisation. Analytically, the two pro-

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† Part 1 of the immediately preceding series contains general descriptive crystallographic detail.

§ An *X*-ray structure determination of this compound has been undertaken by B. F. Hoskins and P. Cosgrave, Department of Inorganic Chemistry, University of Melbourne, which confirms the proposed binuclear nature of the compound.

ducts are identical but their *X*-ray patterns differ [see Figure 1(*a*)]. There are also differences in the i.r. spectra, in particular, in the region around 200 cm^{-1} where the bands due to Sn–I bonds are expected a very marked difference is observed [see Figure 1(*b*)]. Unfortunately, the crystals of the second modification were too small to permit a single-crystal structure determination.

DISCUSSION

Tin(IV) dihalogeno-dixanthates were obtained by five different methods [see equations (1)—(5)] but attempts

$$[Sn(S_2COEt)_2] + X_2 \longrightarrow [Sn(S_2COEt)_2X_2] \quad (1)$$

$$SnX_2 + (EtOCS_2)_2 \longrightarrow [Sn(S_2COEt)_2X_2] \quad (2)$$

$$SnX_4 + 2\,K[S_2COEt] \longrightarrow [Sn(S_2COEt)X_2] + 2\,KX \quad (3)$$

$$[Sn(S_2COEt)_4] + SnX_4 \longrightarrow 2\,[Sn(S_2COEt)_2X_2] \quad (4)$$

$$[Sn(S_2COEt)_4] + X_2 \longrightarrow [Sn(S_2COEt)_2X_2] + (EtOCS_2)_2 \quad (5)$$

to prepare the monohalogeno- or the trihalogeno-xanthates were not successful; this appears to indicate a special stability of the dihalide and may be a manifestation of a tendency on the part of the central metal to achieve six-co-ordination. The importance of six-co-ordination in tin(IV) xanthates is illustrated by the structure of tin(IV) ethyl xanthate where two xanthate moieties are bidentate, the remaining two being unidentate;[4] in the dihalogeno-dixanthates these unidentate moieties are replaced by halogen. A maximum of five-co-ordination can be attained by the trihalogeno-monoxanthate unless halogen bridges are involved. The monohalogeno-tris(xanthate) can achieve six-co-ordination and its initial formation may be postulated by assuming a spontaneous rearrangement to the observed tin(IV) thio-dixanthate [equations (6)—(9)].

$$4\,SnX_4 + 10\,K[S_2COEt] \longrightarrow 2\,[Sn(S_2COEt)_3X] + 2\,[Sn(S_2COEt)_2X_2] + 10\,KX \quad (6)$$

$$2\,[Sn(S_2COEt)_3X] \longrightarrow [\{Sn(S_2COEt)_2S\}_2] + 2\,EtOCSX \quad (7)$$

$$2\,EtOCSX + 2\,K[S_2COEt] \longrightarrow 2\,(EtOCS)_2S + 2\,KX \quad (8)$$

i.e.

$$4\,SnX_4 + 12\,K[S_2COEt] \longrightarrow 2\,[Sn(S_2COEt)_2X_2] + [\{Sn(S_2COEt)_2S\}_2] + 2\,(EtOCS)_2S + 12\,KX \quad (9)$$

When two of the ligand moieties in tin(IV) ethyl xanthate are replaced by two units of another chelating ligand such as oxinate to yield $[Sn(S_2COEt)_2(C_9H_6ON)_2]$, the essential structural arrangement is maintained in so

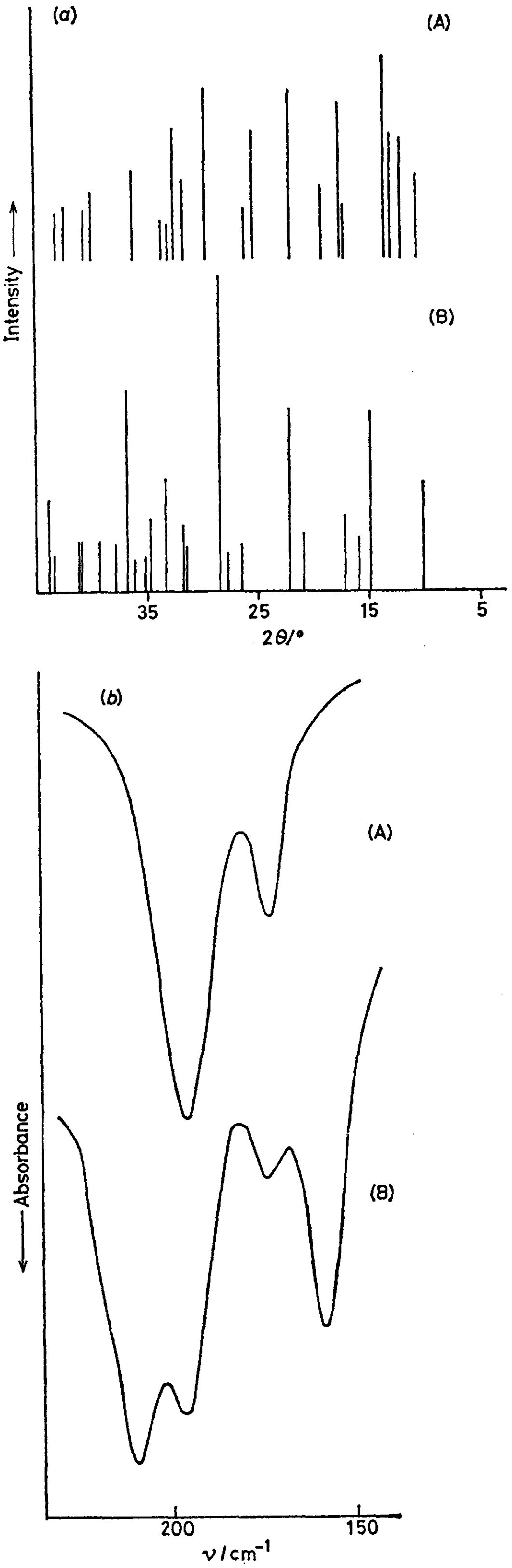

FIGURE 1 (*a*) *X*-Ray powder patterns for the two forms, (A) and (B), of $[Sn(S_2COEt)_2I_2]$, (2); (*b*) infrared absorption in the 200 cm^{-1} region for the two forms of (2)

TABLE 1

Metal atom core geometries in (1) and (2): r_{Sn-X} in Å; the other entries are the angles (°) subtended at the metal by the two ligand atoms at the head of the row/column. The two values in each entry are for compounds (1) and (2) respectively. For (1), the asymmetric unit ligand is defined as ligand a; and its symmetry image as ligand b

Atom	r_{Sn-X}	X(b)	S(a1)	S(a2)	S(b1)	S(b2)
X(a)	2.537(2), 2.761(1)	95.34(6), 98.64(3)	97.55(7), 99.88(6)	90.19(7), 91.36(5)	94.23(7), 92.33(5)	164.60(6), 161.18(6)
X(b)	2.537(2), 2.738(1)		94.23(7), 95.81(4)	164.60(5), 163.60(6)	97.55(7), 103.60(5)	90.19(7), 91.37(4)
S(a1)	2.520(3), 2.525(2)			70.76(8), 69.54(6)	162.48(8), 155.24(5)	96.36(8), 94.87(6)
S(a2)	2.588(3), 2.645(2)				96.36(8), 88.86(6)	88.17(9), 82.89(5)
S(b1)	2.520(3), 2.525(2)					70.76(8), 69.74(6)
S(b2)	2.588(3), 2.638(2)					

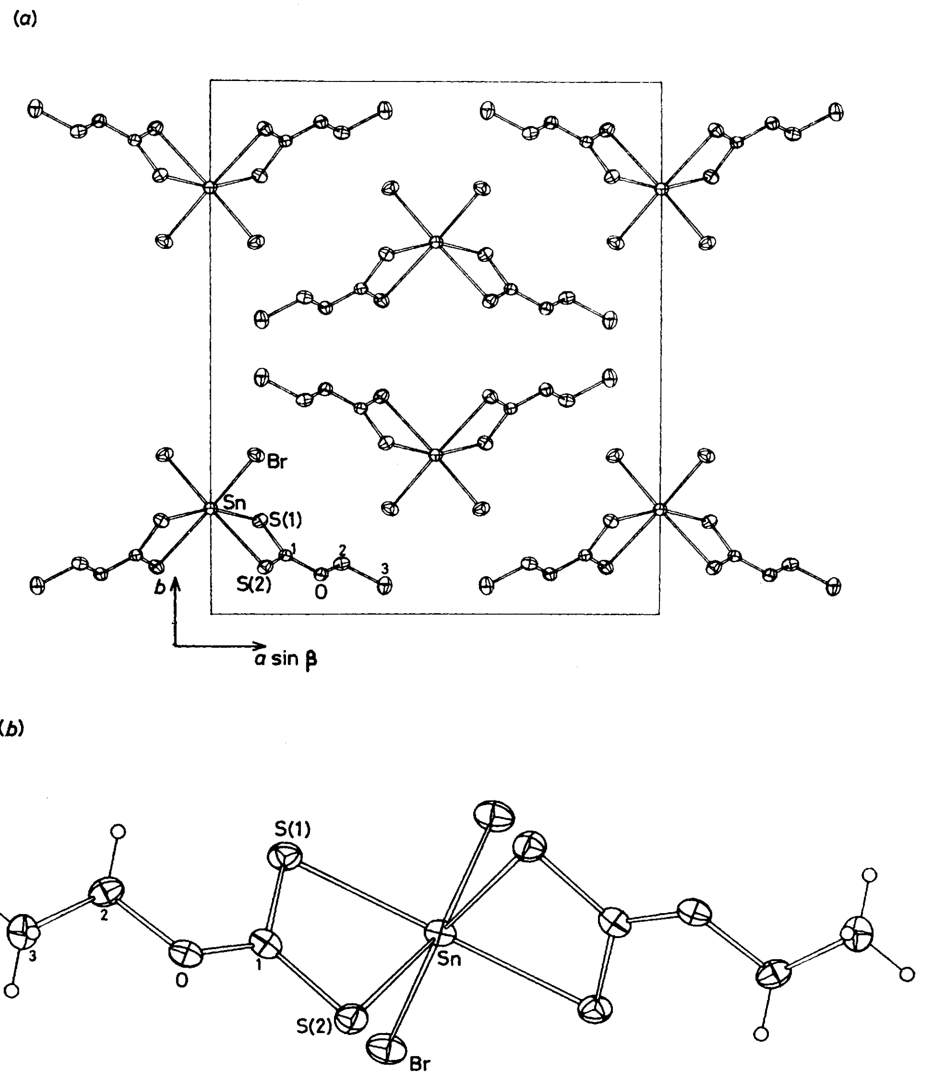

FIGURE 2 (a) Unit-cell contents of $[Sn(S_2COEt)_2Br_2]$, (1), projected down *c*. (*b*) A single molecule of (1) projected down the two-fold axis far as two bidentate oxinate and two unidentate xanthate ligands surround the tin atom.[6] Reaction of this latter compound with tin(IV) halide results in a ligand exchange in such a way that the arrangement of two chelating and two unidentate ligands around the tin atom is preserved.

$$[\mathrm{Sn(S_2COEt)_2(C_9H_6ON)_2}] + \mathrm{SnX_4} \longrightarrow [\mathrm{Sn(C_9H_6ON)_2X_2}] + [\mathrm{Sn(S_2COEt)_2X_2}]$$

Single-crystal *X*-ray structure determinations were carried out on $[\mathrm{Sn(S_2COEt)_2Br_2}]$, (1), and its iodo-analogue $[\mathrm{Sn(S_2COEt)_2I_2}]$, (2) [' first modification ' (see above)]. A cell determination on the chloro-analogue shows it to be isomorphous with the bromide. In both (1) and (2), the structure determinations are consistent with the formulations presented above on the basis of analytical and other data as monomeric $[\mathrm{Sn(S_2COEt)_2X_2}]$; the molecular configurations (Table 1) in both cases are consistent with six-co-ordinate tin(IV) with the unidentate ligands *cis*. In (1), the unit cell (Figure 2) comprises four molecules of the complex in space group $C2/c$, requiring the molecule, in keeping with the observed *cis* configuration, to lie disposed about a crystallographic two-fold axis with the tin atom on that axis. In (2), the whole of the molecule comprises the asymmetric unit (Figure 3) and all atoms are crystallographically independent; the conformation to point symmetry 2, nevertheless, is still very close. Each ethyl xanthate ligand is unsymmetrically chelated and this is reflected in corresponding asymmetry in the $\mathrm{CS_2}$ section of the ligand geometry (Table 2). Unlike many of the Group 5B–halogeno–dithio-ligand complexes in the preceding series of papers, there is, of course, no stereochemically active lone pair.* The geometries of the tin environments of (1) and (2) are given in Table 3, together with those of a number of other bis(unidentate ligand)-bis(1,1-dithiolato)tin complexes for comparison. Given the reasonably constant nature of the bidentate ligands in all cases, and wide variations in the metal–unidentate ligand distances, it might be expected that a trend of some sort might be seen in the bidentate ligand parameters. Considerable variations are observed; these, however, are seemingly random. An alternative method of handling *cis*-[M(bidentate ligand)$_2$(unidentate ligand)$_2$] structural parameters is in terms of the angular co-ordinates ϕ and θ following the repulsion model of Kepert.[7] The stereochemistries of the complexes of Table 3 are reformulated accordingly in Table 4; these considerations show that the bidentate ligands are rotated about the molecular pseudo-two-fold axis so that θ_A has small positive values and θ_B is *ca.* −70° in accord with the calculations of the model. The asymmetry of chelation of the dithiochelates in (1) and (2) [s/t of Table 3: 0.97(1), 0.96(2)] is also in agreement

TABLE 2

Xanthate ligand geometries in (1) and (2)

	(1)	(2)/a	(2)/b
(*a*) Distances/Å			
C(1)–S(1)	1.708(8)	1.709(6)	1.711(6)
C(1)–S(2)	1.690(9)	1.674(6)	1.685(6)
C(1)–O	1.305(10)	1.319(7)	1.310(7)
O–C(2)	1.49(1)	1.463(8)	1.455(8)
C(2)–C(3)	1.52(1)	1.48(1)	1.50(1)
(*b*) Angles/°			
Sn–S(1)–C(1)	84.8(3)	86.1(2)	86.2(2)
Sn–S(2)–C(1)	83.0(3)	82.9(2)	83.1(2)
S(1)–C(1)–S(2)	121.0(5)	121.4(3)	120.8(3)
S(1)–C(1)–O	121.8(7)	115.0(4)	114.6(4)
S(2)–C(1)–O	117.1(6)	123.7(4)	124.5(4)
C(1)–O–C(2)	119.5(6)	119.0(5)	120.3(5)
O–C(2)–C(3)	105.2(7)	108.5(6)	107.2(6)

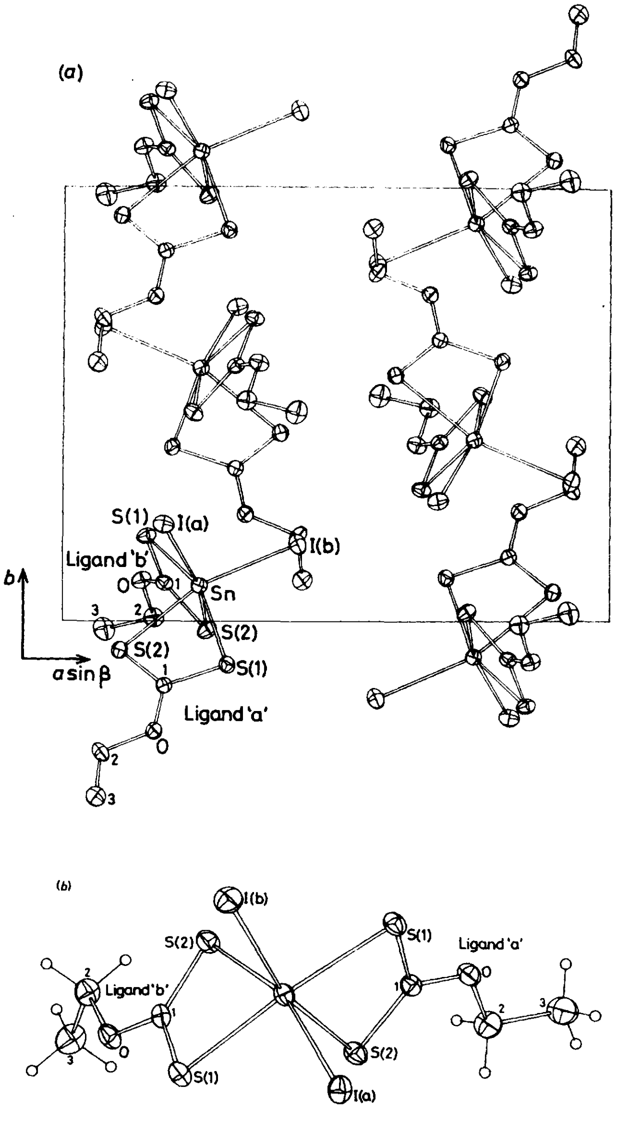

FIGURE 3 (*a*) Unit-cell contents of $[\mathrm{Sn(S_2COEt)_2I_2}]$, (2), projected down *c*; (*b*) a single molecule of (2) projected down its pseudo-two-fold axis

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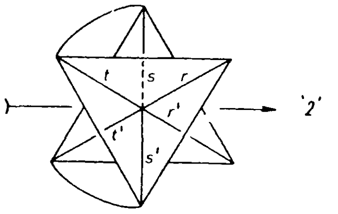
* We wish to correct a statement to the contrary in ref. 6, final paragraph.

TABLE 3

Comparative geometries of the tin environments in *cis*-bis(unidentate)bis(1,1-dithiolato)tin(IV) complexes. Geometrical parameters are defined as shown, primed atoms being generated by the intramolecular pseudo-two-fold rotor



Compound	Distances			Angles								
	r	*s*	*t*	*rs*	*rt*	*st*	*rr'*	*ss'*	*tt'*	*rs'*	*rt'*	*st'*
$[Sn(S_2COEt)_2Br_2]$ [a]	2.53_7	2.520	2.58_8	97.5_5	90.1_9	70.7_6	95.3_4	162.4_8	88.1_7	94.2_3	164.6_0	96.3_6
$[Sn(S_2COEt)_2I_2]$ [a]	2.75_0	2.52_5	2.64_2	101.7	91.4	69.6	98.6	155.2	82.9	94.1	162.4	91.9
$[Sn(S_2CNEt_2)_2Ph_2]$ [b]	2.18	2.58	2.71	101.6	91.6	67.6	101.4	154.9	89.9	94.3	159.5	93.1
$[Sn(S_2CNEt_2)_2(SCSNEt_2)_2]$ [c]	2.50_2	2.52_9	2.55_4	99.9	91.7	70.6	81.1	156.3	97.8	98.2	165.6	93.4
$[Sn(S_2COEt)_2(SCSOEt)_2]$ [d]	2.49_4	2.55_1	2.62_2	95.7	92.3	69.9	92.6	154.7	88.1	101.8	169.9	93.6

[a] This work. [b] P. F. Lindley and P. Carr, *J. Cryst. Mol. Struct.*, 1974, **4**, 173. [c] C. S. Harreld and E. O. Schlemper, *Acta Crystallogr., Sect. B*, 1971, **27**, 1964. [d] Ref. 4.

with similar structures and the predictions of the repulsion model.

TABLE 4

Angular co-ordinates (in terms of ref. 7) for the compounds of Table 3

Compound	*b*	$\phi_A/°$	$\phi_B/°$	$\phi_A/°$	$\theta_E/°$	$\theta_B/°$
Regular octahedron	1.41	90	135	45	0	−90
$[Sn(S_2COEt)_2Br_2]$	1.16	99	136	48	2	−69
$[Sn(S_2COEt)_2I_2]$	1.14	102	139	49	5	−68
$[Sn(S_2CNEt_2)_2Ph_2]$	1.11	103	140	51	5	−65
$[Sn(S_2CNEt_2)_2(SCSNEt_2)_2]$	1.16	102	131	41	1	−73
$[Sn(S_2COEt)_2(SCSOEt)_2]$	1.14	103	136	46	0	−78

EXPERIMENTAL

The preparation [4] and manipulation of tin(II) xanthate was carried out under an atmosphere of pure, dry nitrogen. The apparatus used was that described for the preparation of iron(II) halides.[8] Tin(IV) xanthate and bis(ethyl xanthato)bis(oxinato)tin(IV) were prepared as described elsewhere.[4] Light petroleum refers to that fraction of b.p. 40—60 °C.

Bis(O-*ethyl xanthato*)*dihalogenotin*(IV).—*Method* 1. To a solution of tin(II) ethyl xanthate (1 g) in chloroform (30 cm^3) was slowly added an equimolar amount of iodine, bromine, or chlorine, dissolved in chloroform. After stirring the solution for 30 min, the solvent was evaporated under reduced pressure, to give an oil, which solidified on scratching with a glass rod. The solid was then recrystallized from light petroleum.

Analyses for the chloro-, bromo-, and iodo-complexes, $[Sn(S_2COEt)_2X_2]$, with calculated values in parentheses, were: C 16.7 (16.7), 13.9 (13.8), 11.9 (11.7); H 2.4 (2.3), 2.0 (1.9), 1.6 (1.6); S 30.0 (29.7), 24.6 (24.6), 20.6 (20.9); X 16.5 (16.4), 31.0 (30.7), 41.3% (41.3%).

Method 2. A mixture of ethyl dixanthogen (1 g) and tin(II) chloride (0.8 g) or tin(II) bromide (1.1 g), in chloroform (75 cm^3), was refluxed for 1 h. After filtering, the filtrate was evaporated under reduced pressure, to give an oil, which solidified on scratching with a glass rod. The solid was then recrystallized from light petroleum. The i.r. spectra of the materials were identical to those obtained by Method 1.

Method 3. To tin(IV) halide (1 g) in benzene (50 cm^3) were added 2 mole equivalents of potassium ethyl xanthate. The mixture was stirred for 1 h and then filtered {for $[Sn(S_2COEt)_2I_2]$, form (B), the filtrate was allowed to stand for several days}. The benzene was then evaporated under reduced pressure, and the resulting oil was solidified by scratching with a glass rod. The product was then recrystallized from light petroleum.

Analyses for $[Sn(S_2COEt)_2I_2]$, forms (A) and (B), with calculated values in parentheses, were: C 11.7, 12.1 (11.7); H 1.7, 1.8 (1.6); S 21.0, 20.1 (20.9); I 40.8, 40.3 (41.3); Sn 19.4, 19.4 (19.3%). The i.r. spectra of the dichloride and of the dibromide were identical to those prepared by Method 1.

Method 4. To a solution of tin(IV) ethyl xanthate (2 g) in benzene (50 cm^3) was added a benzene solution of tin(IV) chloride (0.9 g) or tin(IV) iodide (2.1 g) and the mixture stirred for 1 h. The benzene solution was then evaporated under reduced pressure to give an oil, which solidified on scratching with a glass rod. The product was then recrystallized from light petroleum. The i.r. spectra of the materials were identical to those obtained by Method 1.

Method 5. To tin(IV) xanthate (1 g) in benzene (40 cm^3) was added iodine (0.42 g), bromine (0.27 g), or chlorine (0.12 g) dissolved in benzene. The mixture was then stirred for 2 h (for the iodo-complex the mixture was allowed to stand overnight). The solution was then evaporated under reduced pressure to give an oil which solidified by scratching with a glass rod. The solid was then recrystallized from light petroleum. The i.r. spectra were identical to those of the analogous products prepared by Method 1.

Method 6. To a solution of $[Sn(S_2COEt)_2(C_9H_6NO)_2]$ (1.6 g) in benzene was added a benzene solution of tin(IV) chloride (0.7 g) or tin(IV) iodide (1.6 g) and the resulting mixture stirred for 2 h. The precipitate was collected, washed twice with benzene, and finally with light petroleum to give a yellow solid [Analysis: C, 32.7 (32.7); H, 1.9 (1.8); N, 4.0 (4.2); I, 37.9% (38.4%)]. The filtrate was evaporated under reduced pressure and the resulting oil was solidified by scratching with a glass rod. The solid was then recrystallized from light petroleum. The i.r.

spectra were identical to those of the compounds prepared by Method 1.

Bis(O-*ethyl xanthato*)*thiotin*(IV).—To tin(IV) halide (1 g) in benzene (50 cm^3) were added 3 mole equivalents of potassium ethyl xanthate. The mixture was stirred for 1 h and then filtered. The solvent was evaporated under reduced pressure, to give an oil, which solidified on addition of light petroleum. The product was then washed with boiling light petroleum, which removed the dihalogeno-complex. The solid was then recrystallized from chloroform–light petroleum as yellow crystals containing 1 molecule occluded chloroform per dimer (Found: C, 17.6; H, 2.6; Cl, 12.6; S, 34.4; Sn, 27.9. $C_{13}H_{21}Cl_3O_4S_{10}Sn_2$ requires C, 17.2; H, 2.3; Cl, 11.7; S, 35.4; Sn, 26.2%).

TABLE 5

Non-hydrogen atom co-ordinates for (1)

Atom	*x*	*y*	*z*
Sn	0.000 00(—)	0.199 65(5)	0.250 00(—)
Br	0.101 54(7)	0.300 79(5)	0.482 96(15)
S(1)	0.110 0(2)	0.176 9(1)	−0.012 8(3)
S(2)	0.120 9(2)	0.089 6(1)	0.394 1(4)
C(1)	0.166 5(6)	0.112 1(5)	0.174 0(13)
O	0.245 0(4)	0.076 1(3)	0.150 9(9)
C(2)	0.290 9(7)	0.096 1(5)	−0.034 9(13)
C(3)	0.386 5(7)	0.054 1(5)	0.007 7(16)

Instrumentation.—Ultraviolet absorption spectra were obtained using a Varian Techtron 635D spectrophotometer. Infrared spectra were determined as KBr discs using a Perkin-Elmer 457 spectrophotometer. The spectra in the 200 cm^{-1} region were obtained on a Perkin-Elmer 180 spectrophotometer at Monash University by arrangement with Dr. G. B. Deacon. Infrared and visible–u.v. spectral details are tabulated in Supplementary Publication No. SUP 22984 (19 pp.).*

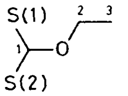
Analyses.—Analyses were performed by the Australian Microanalytical Service.

Crystallography.—*Crystal data.* (1), $C_6H_{10}Br_2O_2S_4Sn$, $M = 520.8$, Monoclinic, space group $C2/c$ (C_{2h}^{6}, no. 15), $a = 14.27(1)$, $b = 16.894(8)$, $c = 6.360(5)$ Å, $\beta = 100.41(5)°$, $U = 1\,508(1)$ Å^3, $D_m = 2.29(1)$, $Z = 4$, $D_c = 2.29$ g cm^{-3}, $F(000) = 984$, μ(Mo) = 78 cm^{-1}. Specimen: twinned flake, 0.09 × 0.05 × 0.22 mm, $2\theta_{max.} = 50°$, $n = 1\,965$, $n_o = 1\,342$. Values of R, R', S are 0.037, 0.049, 2.6 respectively.

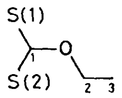
(2), $C_6H_{10}I_2O_2S_4Sn$, $M = 614.8$, Monoclinic, space group $P2_1/n$ (C_{2h}^{5}, no. 14), $a = 14.026(6)$, $b = 11.210(4)$, $c = 10.203(4)$ Å, $\beta = 91.96(3)°$, $U = 1\,603(1)$ Å^3, $D_m = 2.50(1)$, $Z = 4$, $D_c = 2.55$ g cm^{-3}, $F(000) = 1\,128$, μ(Mo) = 55 cm^{-1}. Specimen: pseudo-spherical polyhedron, *ca.* 0.30 mm diameter, $2\theta_{max.} = 50°$, $n = 2\,823$, $n_o = 2\,512$. Values of R, R', S are 0.030, 0.043, 1.6 respectively.

Abnormal features. Crystals of compound (2) were twinned and not easily separated. The specimen used for the above analysis yielded poor agreement for reflections *hk*0, *hk*5; in fact the overlap of the reflections in these two zones was so precise that refinement was possible with their inclusion by the adoption of an independent refinable scale factor, with no further abnormalities. In both structures hydrogen atoms were included in the refinement, constrained at tetrahedral estimates.

Atom numbering is as follows; the two ligands in (2) are numbered a, b and hydrogen atoms are designated according to the parent carbon, suffixed A, B, C. [In order to maintain a *cis* orientation of S(1) to both halide atoms, the ethyl group is defined *cis* to S(1) in (1) and *trans* in (2).]



(1)



(2)

TABLE 6

Non-hydrogen atom co-ordinates for (2)

	Ligand 'a'			Ligand 'b'		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sn	0.249 52(3)	0.082 52(4)	0.913 26(4)			
I	0.183 60(3)	0.222 74(4)	1.113 33(4)	0.428 52(3)	0.177 94(5)	0.898 13(5)
S(1)	0.300 7(1)	−0.100 0(1)	1.042 5(2)	0.152 9(1)	0.196 2(1)	0.741 4(1)
S(2)	0.104 8(1)	−0.066 8(1)	0.934 1(2)	0.263 5(1)	−0.020 2(1)	0.682 1(2)
C(1)	0.185 9(4)	−0.148 4(5)	1.018 3(5)	0.186 1(4)	0.087 6(5)	0.634 2(5)
O	0.167 5(3)	−0.253 3(4)	1.070 1(4)	0.144 3(3)	0.094 2(4)	0.517 6(4)
C(2)	0.071 1(5)	−0.302 3(6)	1.054 7(8)	0.166 7(5)	0.007 9(6)	0.416 7(6)
C(3)	0.062 6(6)	−0.404 7(7)	1.145 3(9)	0.075 9(6)	−0.018 7(7)	0.341 3(7)

Tables 5 and 6 give the non-hydrogen atom co-ordinates. Structure-factor amplitudes, thermal parameters, hydrogen-atom parameters, and least-squares planes are in SUP 22984.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.