

THE *trans*-STRENGTHENING OF THE Sn–O BOND IN SIX-COORDINATED COMPLEXES OF TIN(IV): CRYSTAL AND MOLECULAR STRUCTURES OF $\text{SnI}_4 \cdot 2\text{DPSO}$ AND $\text{C}_2\text{H}_5\text{SnI}_3 \cdot 2\text{DPSO}$

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Summary

An X-ray study of $\text{SnI}_4 \cdot 2\text{diphenylsulphoxide}$ and $\text{EtSnI}_3 \cdot 2\text{diphenylsulphoxide}$ indicates octahedral geometry for all the tin atoms in both complexes, the two DPSO ligands being *cis* to each other and in the second complex the ethyl group being *trans* to one of the DPSO ligands. In the second complex, under the influence of the ethyl group lengthening of the *cis* Sn–I bonds by 0.06 Å and shortening of the *trans* Sn–O bond by 0.06 Å occur. The mutual dependence of the Sn–O and O–S bond distances is noted.

Introduction

The phenomenon of strengthening of the Sn–X (X = Hal) bond in the *trans* position to an alkyl group was discovered during an X-ray study of octahedral tin(IV) complexes of the general formula $\text{Me}_n\text{SnX}_{4-n} \cdot 2\text{HMPT}$ ($n = 0, 1$; X = Cl, Br; HMPT = hexamethylphosphoric triamide) [1]. As a continuation of the investigation of this phenomenon, two complexes, $\text{SnI}_4 \cdot 2\text{DPSO}$ (I) and $\text{EtSnI}_3 \cdot 2\text{DPSO}$ (II) (DPSO = diphenylsulphoxide), were synthesized and their crystal and molecular structures determined. The results of these studies are presented below.

Experimental

Crystal preparation

Solutions of SnI_4 and EtSnI_3 were respectively added dropwise to a solution of a calculated amount of DPSO to obtain the complexes. A precipitate formed immediately. The substances were obtained and crystals were grown using a mixture of CH_2Cl_2 /octane as the solvent. M.p.: I, 158–160°C; II, 99–101°C. Elemental analysis:

I Found: C, 27.82; H, 1.95; S, 6.31. Calcd.: C, 27.96; H, 1.96; S, 6.20%.

II Found: C, 33.81; H, 2.51; S, 6.55. Calcd.: C, 33.47; H, 2.70; S, 6.87%.

Crystal data

I: $C_{24}H_{20}I_4S_2O_2Sn$; $M = 1030.8$; a , 21.309(8); b , 9.100(2); c , 15.51(2) Å; U , 3007.57 Å³; $Z = 4$, space group $Pna2_1$.

II: $C_{26}H_{25}I_3S_2O_2Sn$; $M = 931.0$; a , 11.684(4); b , 14.930(3); c , 17.997(4) Å; β , 102.79(2)°, $U = 3061.54$ Å³, $Z = 4$, space group $P2_1/n$.

Data collection and reduction

Crystals of approximate dimensions $0.15 \times 0.15 \times 0.30$ mm³ (I) and $0.25 \times 0.25 \times 0.20$ mm³ (II) were used for data collection. Relative intensities up to $\theta = 25.0^\circ$ were collected with Mo- K_α radiation, using a CAD-4 four-circle automatic diffractometer. 2585 (I) and 4517 (II) unique reflections with $I \geq 3\sigma(I)$ were used for the subsequent analysis. Corrections were made for Lorentz and polarisation effects, but no correction was applied for absorption.

TABLE 1

FINAL FRACTIONAL ATOMIC COORDINATES IN $SnI_4 \cdot 2DPSO$ ($\times 10^4$; for C $\times 10^3$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Sn	3220.6(6)	1585(1)	0
I(1)	3333(1)	-1444(1)	-185(1)
I(2)	2973(1)	4390(2)	616(1)
I(3)	4478(1)	2197(2)	-403(1)
I(4)	2702(1)	2029(2)	-1619(1)
S(1)	4013(2)	236(5)	1658(3)
S(2)	1972(2)	1151(6)	1270(3)
O(1)	3460(6)	1162(16)	1390(8)
O(2)	2257(6)	1033(17)	360(8)
C(11)	448(1)	140(2)	233(1)
C(12)	502(1)	85(3)	267(2)
C(13)	538(1)	173(3)	318(2)
C(14)	521(1)	321(3)	329(2)
C(15)	467(1)	386(3)	297(2)
C(16)	429(1)	288(3)	246(2)
C(21)	372(1)	-97(2)	246(1)
C(22)	368(1)	-242(2)	225(1)
C(23)	343(1)	-347(3)	280(2)
C(24)	323(1)	-294(3)	365(2)
C(25)	327(1)	-144(3)	388(2)
C(26)	353(1)	42(2)	326(1)
C(31)	125(1)	214(2)	109(1)
C(32)	89(1)	231(3)	184(2)
C(33)	31(1)	315(3)	171(2)
C(34)	15(1)	373(3)	91(2)
C(35)	56(1)	356(3)	20(2)
C(36)	114(1)	275(3)	30(2)
C(41)	169(1)	-63(2)	144(1)
C(42)	201(1)	-142(2)	210(1)
C(43)	183(1)	-290(3)	221(2)
C(44)	135(1)	-358(3)	169(2)
C(45)	105(1)	-277(3)	104(2)
C(46)	121(1)	-122(2)	93(1)

Structure determination and refinement

Approximate coordinates of the tin and iodine atoms were determined by direct methods using the "MULTAN-82" program. The remaining atoms were located from conventional and difference Fourier maps. All atoms were given anisotropic temperature factors and full matrix least-squares refinement gave the final $R = 0.037$ (I) and $R = 0.041$ (II) (unit weights for all reflections). All calculations were performed using an "Enraf-Nonius SDP" complex of programs. The scattering factors used were those for neutral atoms. Final fractional atomic coordinates, intramolecular bond distances, angles and the shortest non-valent contacts are given in Tables 1–5.

The interatomic bond distances and angles in the phenyl rings differ from 1.395 Å and 120° by no more than 0.045 Å (estimated standard deviation 0.018 Å) and 4.5° (estimated standard deviation 1.1°). Thus these distances and angles are not given in the tables.

TABLE 2

FINAL FRACTIONAL ATOMIC COORDINATES IN $C_2H_5SnI_3 \cdot 2DPSO$ ($\times 10^5$; for C, $O \times 10^4$)

Atom	x	y	z
Sn	84464(5)	46435(4)	13540(3)
I(1)	71028(6)	47313(5)	–1857(4)
I(2)	95881(7)	41352(5)	28557(4)
I(3)	71731(6)	60177(5)	18833(4)
S(1)	58009(16)	38802(20)	12958(9)
S(2)	90931(18)	24638(18)	14260(11)
O(1)	7152(5)	3707(4)	1526(3)
O(2)	9138(5)	3361(4)	1019(3)
C(1)	10002(8)	5352(8)	1126(7)
C(2)	9790(10)	6205(9)	791(10)
C(11)	5357(8)	3750(7)	2177(6)
C(12)	6171(9)	3502(8)	2831(6)
C(13)	5869(11)	3426(9)	3511(6)
C(14)	4631(10)	3601(9)	3526(7)
C(15)	3850(11)	3871(9)	2873(8)
C(16)	4188(9)	3948(9)	2178(7)
C(21)	5275(7)	2865(6)	826(5)
C(22)	5592(8)	2047(7)	1175(6)
C(23)	5212(9)	1269(7)	775(6)
C(24)	4517(9)	1334(7)	29(6)
C(25)	4213(9)	2153(8)	–304(6)
C(26)	4599(8)	2951(7)	84(5)
C(31)	8494(8)	1715(7)	664(6)
C(32)	7772(8)	2084(7)	14(6)
C(33)	7225(9)	1509(8)	–560(6)
C(34)	7392(9)	610(8)	–493(7)
C(35)	8091(9)	253(8)	156(9)
C(36)	8660(10)	810(8)	748(8)
C(41)	10580(7)	2075(6)	1648(5)
C(42)	10961(9)	1681(8)	2357(7)
C(43)	12148(9)	1382(9)	2532(8)
C(44)	12849(10)	1503(9)	2029(8)
C(45)	12440(9)	1930(10)	1345(8)
C(46)	11276(9)	2224(9)	1145(6)

TABLE 3

BOND DISTANCES (Å) IN $\text{SnI}_4 \cdot 2\text{DPSO}$ AND IN $\text{C}_2\text{H}_5\text{SnI}_3 \cdot 2\text{DPSO}$

$\text{SnI}_4 \cdot 2\text{DPSO}$		$\text{C}_2\text{H}_5\text{SnI}_3 \cdot 2\text{DPSO}$	
Atoms	Distance	Atoms	Distance
Sn–I(1)	2.781(1)	Sn–I(1)	2.869(1)
Sn–I(2)	2.776(1)	Sn–I(2)	2.840(1)
Sn–I(3)	2.806(1)	Sn–I(3)	2.821(1)
Sn–I(4)	2.773(1)	Sn–C(1)	2.218(5)
Sn–O(1)	2.249(6)	Sn–O(1)	2.132(3)
Sn–O(2)	2.189(6)	Sn–O(2)	2.212(3)
S(1)–O(1)	1.510(6)	S(1)–O(1)	1.563(3)
S(1)–C(11)	1.786(9)	S(1)–C(11)	1.785(5)
S(1)–C(21)	1.769(9)	S(1)–C(21)	1.778(5)
S(2)–O(2)	1.540(6)	S(2)–O(2)	1.533(3)
S(2)–C(31)	1.804(9)	S(2)–C(31)	1.788(5)
S(2)–C(41)	1.750(9)	S(2)–C(41)	1.791(4)
		C(1)–C(2)	1.406(9)

The interatomic bond distances and angles in the phenyl rings differ from 1.395 Å and 120° by no more than 0.045 Å (estimated standard deviation 0.018 Å) and 4.5° (estimated standard deviation 1.1°). Thus these distances and angles are not given in the tables.

TABLE 4

ANGLES (°) IN $\text{SnI}_4 \cdot 2\text{DPSO}$ AND IN $\text{C}_2\text{H}_5\text{SnI}_3 \cdot 2\text{DPSO}$

$\text{SnI}_4 \cdot 2\text{DPSO}$		$\text{C}_2\text{H}_5\text{SnI}_3 \cdot 2\text{DPSO}$	
Atoms	Angle	Atoms	Angle
I(1)–Sn–I(2)	164.37(3)	I(1)–Sn–I(2)	166.56(2)
I(1)–Sn–I(3)	95.26(3)	I(1)–Sn–I(3)	94.37(1)
I(1)–Sn–I(4)	94.91(3)	I(1)–Sn–O(1)	85.19(8)
I(1)–Sn–O(1)	84.84(16)	I(1)–Sn–O(2)	86.06(8)
I(1)–Sn–O(2)	82.93(17)	I(1)–Sn–C(1)	95.45(15)
I(2)–Sn–I(3)	94.31(3)	I(2)–Sn–I(3)	92.56(1)
I(2)–Sn–I(4)	95.85(3)	I(2)–Sn–O(1)	83.42(8)
I(2)–Sn–O(1)	82.53(16)	I(2)–Sn–O(2)	84.55(8)
I(2)–Sn–O(2)	87.00(17)	I(2)–Sn–C(1)	94.13(15)
I(3)–Sn–I(4)	98.60(3)	I(3)–Sn–O(1)	89.10(8)
I(3)–Sn–O(1)	91.82(15)	I(3)–Sn–O(2)	166.61(8)
I(3)–Sn–O(2)	177.16(17)	I(3)–Sn–C(1)	103.33(17)
I(4)–Sn–O(1)	169.55(15)	O(1)–Sn–O(2)	77.60(11)
I(4)–Sn–O(2)	83.75(16)	O(1)–Sn–C(1)	167.45(19)
O(1)–Sn–O(2)	85.85(21)	O(2)–Sn–C(1)	89.93(18)
O(1)–S(1)–C(11)	104.9(4)	Sn–C(1)–C(2)	115.9(4)
O(1)–S(1)–C(21)	105.1(4)	O(1)–S(1)–C(11)	102.8(2)
C(11)–S(1)–C(21)	98.9(4)	O(1)–S(1)–C(21)	102.0(2)
O(2)–S(2)–C(31)	103.4(4)	C(11)–S(1)–C(21)	101.1(2)
O(2)–S(2)–C(41)	101.8(4)	O(2)–S(2)–C(31)	103.2(2)
C(31)–S(2)–C(41)	101.1(4)	O(2)–S(2)–C(41)	104.8(2)
Sn–O(1)–S(1)	122.4(3)	C(31)–S(2)–C(41)	99.5(2)
Sn–O(2)–S(2)	125.9(3)	Sn–O(1)–S(1)	124.1(2)
		Sn–O(2)–S(2)	125.0(2)

TABLE 5

THE SHORTEST NON-VALENT CONTACTS (Å) IN $\text{SnI}_4 \cdot 2\text{DPSO}$ AND IN $\text{C}_2\text{H}_5\text{SnI}_3 \cdot 2\text{DPSO}$

$\text{SnI}_4 \cdot 2\text{DPSO}$		$\text{C}_2\text{H}_5\text{SnI}_3 \cdot 2\text{DPSO}$	
Atoms	Distance	Atoms	Distance
I(1)...S(1)	3.551(2)	I(1)...S(1)	3.582(1)
I(1)...O(1)	3.416(6)	I(1)...O(1)	3.428(3)
I(1)...O(2)	3.322(6)	I(1)...O(2)	3.501(3)
I(1)...C(14)	3.913(12)	I(2)...S(2)	3.539(1)
I(1)...C(22)	3.952(10)	I(2)...O(1)	3.350(3)
I(1)...C(24)	3.831(12)	I(2)...O(2)	3.430(3)
I(2)...S(2)	3.778(2)	I(3)...S(1)	3.623(1)
I(2)...O(1)	3.338(6)	I(3)...O(1)	3.509(3)
I(2)...O(2)	3.443(6)		
I(3)...S(1)	3.794(2)		
I(3)...O(1)	3.649(6)		
I(4)...O(2)	3.341(6)		

Results and discussion

The molecular geometries of both complexes, with atomic labelling, are shown in Fig. 1. Tin in both structures has a slightly distorted octahedral environment, with the DPSO ligands positioned *cis* to each other. Let us define the plane passing through oxygen, tin, C(1) (or I(4)) and I(3) atoms in structures I and II as the equatorial plane.

Comparison with the $\text{SnI}_4 \cdot 2\text{DPSO}$ complex allows us to appreciate the influence of the ethyl group on the other ligands of $\text{EtSnI}_3 \cdot 2\text{DPSO}$, so complex I will be described first. The two axial Sn–I bonds (2.781(1), 2.776(1) Å) are approximately equivalent and can be compared with one of the equatorial Sn–I bonds, 2.773(1) Å. The other equatorial Sn–I(3) bond is 0.03 Å longer than these bonds (2.806(1) Å). A similar situation is realized in *cis*- $\text{SnCl}_4 \cdot 2\text{MeCN}$ [2]: three Sn–Cl bond distances are approximately the same (2.339(8), 2.335(8), 2.341(8) Å), while one, Sn–Cl_{eq}, is somewhat longer (2.356(8) Å).

In the complex *cis*- $\text{SnCl}_4 \cdot 2\text{P}(\text{O})\text{Cl}_3$ [3] a similar tendency appears, though the differences in bond lengths are in the limits of estimated standard deviations: both Sn–Cl_{ax} bonds are equal to 2.33(2) Å, and the Sn–Cl_{eq} bonds are equal to 2.31(2) and 2.36(2) Å. Such tetrahalogenide *cis*-complexes as $\text{SnCl}_4 \cdot 2\text{Se}(\text{O})\text{Cl}_2$ [4], $\text{SnCl}_4 \cdot (\text{N}_4\text{O}_5\text{C}_{14}\text{H}_{18})$ [5], $\text{SnCl}_4 \cdot (\text{PhC}(\text{O}))_2\text{NH}$ [6] and $\text{SnBr}_4 \cdot (\text{PhC}(\text{O}))_2\text{NH}$ [7] differ from the structures mentioned above, because their axial Sn–X bonds are significantly longer than the equatorial ones.

In complex II, the Sn–I_{ax} bonds (2.869(1) and 2.840(1) Å) are longer than the Sn–I_{eq} bond (2.821(1) Å). $\text{BuSnCl}_3 \cdot \text{PyC}(\text{H})=\text{NPh}$ [8] is similar to complex II in composition and structure, and in this complex, one of the axial Sn–Cl bonds is practically equal to the equatorial bond, whereas another axial bond exceeds them significantly (2.428(2), 2.426(2) and 2.488(2) Å, respectively).

The phenomenon of weakening of *cis* Sn–X bonds under the influence of an electron-donating alkyl group is well known in the chemistry of the complexes of non-transition elements. This phenomenon is also observed in complex II. The

average Sn–I bond length in this structure is 0.06 Å longer than that in complex I (2.843 and 2.784 Å) and the average axial Sn–I bond distance in the I–Sn–I linear fragment increases by 0.07 Å under the influence of the alkyl group (2.849 and 2.779 Å).

In complex I the SnI_4 fragment is tetrahedrally distorted: all four Sn–I bonds are bent away from the vertices of a regular octahedron towards the DPSO ligands. This is confirmed by the values of the I–Sn–I angles, which exceed 90° ($94.31(3)$ – $98.60(3)$, see Table 4). Such a tendency towards tetrahedral geometry is also found in the structures mentioned above [2–7]. The EtSnI_3 fragment in complex II is also tetrahedrally distorted (see Table 4). The replacement of one iodine ligand by an ethyl group causes additional distortion in complex II (in comparison with I). This additional distortion is confirmed by the observation that the average values of the I(1)–Sn–C(1), I(2)–Sn–C(1) and I(3)–Sn–C(1) angles (97.64°) exceed those of the

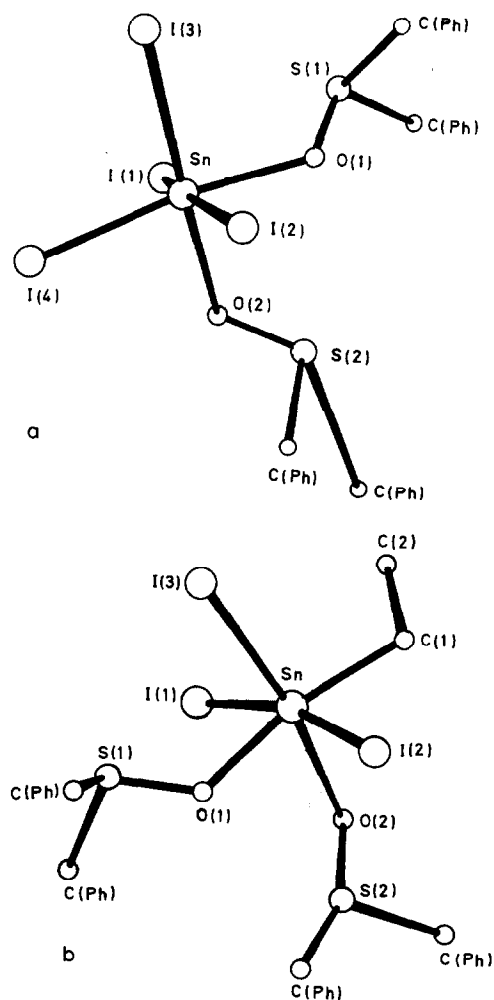


Fig. 1. Coordination about Sn in $\text{SnI}_4 \cdot 2\text{DPSO}$ (a) and in $\text{EtSnI}_3 \cdot 2\text{DPSO}$ (b).

I(1)–Sn–I(4), I(1)–Sn–I(3), I(2)–Sn–I(3), I(2)–Sn–I(4), I(3)–Sn–I(4) angles (95.79°) in complex I.

Being an electron-donating ligand, the ethyl group bends the Sn–I and Sn–O bonds back from itself, which is in accordance with the empirical rules of Gillespie–Nyholm. This distortion is also in good agreement with the idea that the alkyl group occupies the maximum steric angle [9].

The Sn–O bond distances in complex I are non-equivalent: 2.249(6) and 2.189(6) Å, the shorter Sn–O bond distance being *trans* with respect to the longer Sn–I_{eq} bond distance. As for the S–O bond distances, they are also non-equivalent: the O(1)–S(1) distance is 0.03 Å shorter than O(2)–S(2) (1.510(6) and 1.540(6) Å, respectively). So in the four-atom chain I–Sn–O–S, lengthening of the Sn–O bond distance is accompanied by shortening of the Sn–I and O–S bond distances.

The fact that the position *trans* to the ethyl group is occupied by the DPSO ligand and not by halogen, as in complexes MeSnCl₃ · 2HMPT, MeSnBr₃ · 2HMPT [1], MeSnCl₃ · 2DMFA [11] (HMPT = hexamethylphosphoric triamide, DMFA = dimethylformamide), is an important feature of the molecular structure of complex II. In II, the bond distance Sn–O, *trans* to the ethyl group, is equal to 2.132(3) Å, this distance being 0.087 Å shorter than the average value of the Sn–O bond distance in complex I (2.219 Å) and, at any rate, 0.057 Å shorter than the shortest Sn–O bond in complex I (Sn–O(2) 2.189(6) Å). At the same time, the *cis* Sn–O bond distance in complex II is not lengthened, compared with the average value of the Sn–O bond distance in complex I (2.212(3) and 2.219 Å, respectively). This fact must be interpreted as the absence of *cis*-weakening of the Sn–O bond under the influence of the ethyl group in complex II.

In complex II the shorter Sn–O bond distance is also associated with the longer S–O distance, a monotonous dependence existing between the Sn–O and O–S bond distances in the four Sn–O–S fragments in complexes I and II. Such a dependence allows us to come to a conclusion about the connection between the force of the donor–acceptor interaction in complex formation and the degree of the change in the donor molecule. For complex II it is difficult to compare the Sn–O bond distance with the Sn–I bond distance *trans* to it, as was performed for complex I, because of the *cis*-weakening of the Sn–I bond under the influence of the ethyl group.

The shortest non-valent contacts in complexes I and II are listed in Table 5. In the *cis*-complex SnCl₄ · 2SeOCl₂, an Se ... Cl charge-transfer interaction (bond distance 3.01 Å) is observed [4,10]; however, we have not discovered any structural peculiarities in complexes I and II which can be interpreted to be the result of I ... S charge-transfer interactions. Nevertheless, some I ... S contacts are distinctly shorter than the sum of the Van der Waals radii of these atoms, 4.0 Å (Pauling). The I ... O and I ... C contacts are unimportant.

Conclusion

On the basis of the data obtained, we can conclude that in the complex EtSnI₃ · 2DPSO, *trans*-strengthening of the Sn–O bond is observed, besides *cis*-weakening of the Sn–I bond under the influence of the ethyl group. This is confirmed by the data on the change of the O–S bond lengths. *Cis*-weakening of the Sn–O bond is not observed.

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