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STRUCTURAL CHARACTERIZATION OF A SEVEN-COORDINATED ORGANOTIN(IV) COMPLEX: TRIS(DIMETHYL SULPHOXIDE)-NITRATODIPHENYLTIN(IV) NITRATE

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Summary

A seven-coordinated organotin(IV) compound has been obtained and its IR spectroscopic properties and X-ray crystal structure are reported. Crystals are monoclinic ($P2_1/c$) with unit-cell dimensions: a 16.017(9), b 10.365(5), c 15.994(8) Å, β 96.1(1)°, $Z = 4$. The structure has been determined from diffractometer data (Cu-K_α radiation) by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares procedure to an R value of 0.093 for 4298 independent reflections. The structure consists of monomeric seven-coordinated cations $[Sn(C_6H_5)_2NO_3\{(CH_3)_2SO\}_3]^+$ and NO_3^- anions. Coordination around tin is pentagonal bipyramidal with the bidentate nitrate group and the three dimethyl sulphoxide molecules in the equatorial positions and the two phenyl rings at the apices. Literature on seven-coordinated tin(IV) compounds and nitratotin(IV) complexes is quoted and discussed.

Introduction

The study of the title compound has been undertaken as part of a research program on the structural properties of adducts of nitrato complexes of organotin(IV) with oxygen ligands containing donor groups as: $\geq$C=O, $\geq$S=O, $\equiv$P=O, $\equiv$As=O, $\equiv$N→O. The aim of this research is to provide additional information on the tin—ligand interactions, particularly with reference to the possibility of achieving high coordination numbers for the metal, which can be favoured by the short bite of the nitrate ion. This program has so far included: μ-oxalatobis-[(di-n-propyl sulphoxide)nitratodiphenyltin] [1] and nitratotriphenyl(triphenylphosphine oxide)tin [2]; moreover, the ligand properties of the dimethyl sulph-

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oxide in organotin compounds have been examined in the two polymorphs of *cis*-dichloro-*cis*-bis(dimethyl sulphoxide)-*trans*-diphenyltin [3].

The present paper deals with the synthesis, the IR-spectroscopic properties and the X-ray analysis of tris(dimethyl sulphoxide)nitratodiphenyltin(IV) nitrate. A preliminary account of the principal features of this structure has already been given [4].

Experimental

The compound was prepared by adding hot dimethyl sulphoxide in a dry nitrogen atmosphere to a solution of dinitratodiphenyltin(IV) in anhydrous acetone. After some days at room temperature, colourless crystals, slightly unstable in air, of formula $C_{18}H_{28}N_2O_9S_3Sn$ separated. (Found: C, 34.0; H, 4.2; N, 4.2; Sn, 19.0. Calcd.: C, 34.3; H, 4.5; N, 4.4; Sn, 18.8%.)

Preliminary cell dimensions and systematic extinctions were determined from rotation and Weissenberg photographs. The refined cell dimensions, which are given with other crystallographic data in Table 1, and the intensities were obtained on a "Siemens" AED automated single-crystal diffractometer. All the 5014 accessible reflections with 2θ less than 140° were measured with Cu-K_α radiation ($\lambda = 1.54178$ Å), the $\omega - 2\theta$ scanning technique being employed. 4298 reflections were considered as "observed" having $I > 2\sigma(I)$. There was some evidence for decomposition of the sample during X-ray exposure, as shown by the decrease of the intensity of a standard reflection measured every twenty reflections. A correction for this crystal decay was applied by means of a computer program which uses the intensity of the standard reflection as an internal scaling of the data set. The usual Lorentz-polarization factors were applied, but no absorption correction was made.

Solution and refinement of the structure

The coordinates of the tin atom were obtained from a Patterson synthesis. The electron density distribution, calculated with the tin phases, gave the positions of the three sulphur atoms, while the remaining atoms other than hydrogen were located from a series of Fourier syntheses, using the heavy-atom method.

Refinement of the structure was carried out by block-diagonal least-squares, first with isotropic and then with anisotropic thermal parameters (anisotropic parameters were not used for the oxygen atoms of the uncoordinated nitrate group).

Convergence was achieved after ten cycles to a conventional R $(\Sigma(|F_o| - |F_c|)/\Sigma|F_o|)$ of 10.2%. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, in which the weight for each reflection was unity. At this stage a difference Fourier map showed a peak of height equivalent to a carbon atom, but too near to S(3), and explicable only with a disordering of S(3) itself. A further refinement, assuming this disorder (the occupancies were fixed at 0.80 and 0.20 respectively) improved R to 9.3%. The final difference Fourier synthesis showed some well-defined electron density peaks in regions corresponding to the expected positions of the hydrogen atoms, but the subsequent isotropic refinement for these atoms was not successful, so they were not further considered.

TABLE 1

CRYSTALLOGRAPHIC DATA

$[Sn(C_6H_5)_2(NO_3)\{(CH_3)_2SO\}_3]NO_3$. Mol. wt 631.3. Monoclinic, space group $P2_1/c$ (from systematic absences) a 16.017(9); b 10.365(5); c 15.994(8) Å; β 96.1(1)°; V 2640.1 Å^3; Z 4, D_{obs} 1.57 g cm^{-3}, D_{calc} 1.59 g cm^{-3}; $\mu(Cu\text{-}K_\alpha)$ = 106.8 cm^{-1}; $F(000)$ = 1280.

The final atomic parameters are given in Table 2. A list of observed and calculated structure factors can be obtained from the authors on request.

Scattering factors were taken from Cromer and Mann [5]. For all calculations the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale was used.

Results and discussion

The structure consists of discrete seven-coordinated $[Sn(C_6H_5)_2NO_3\{(CH_3)_2SO\}_3]^+$ cations and NO_3^- anions, held together by weak Van der Waals interactions. As illustrated in Fig. 1, which represents a clinographic projection of the structure of the cation, five oxygen and two carbon atoms build a pentagonal bipyramidal arrangement around tin, with the carbon atoms occupying the

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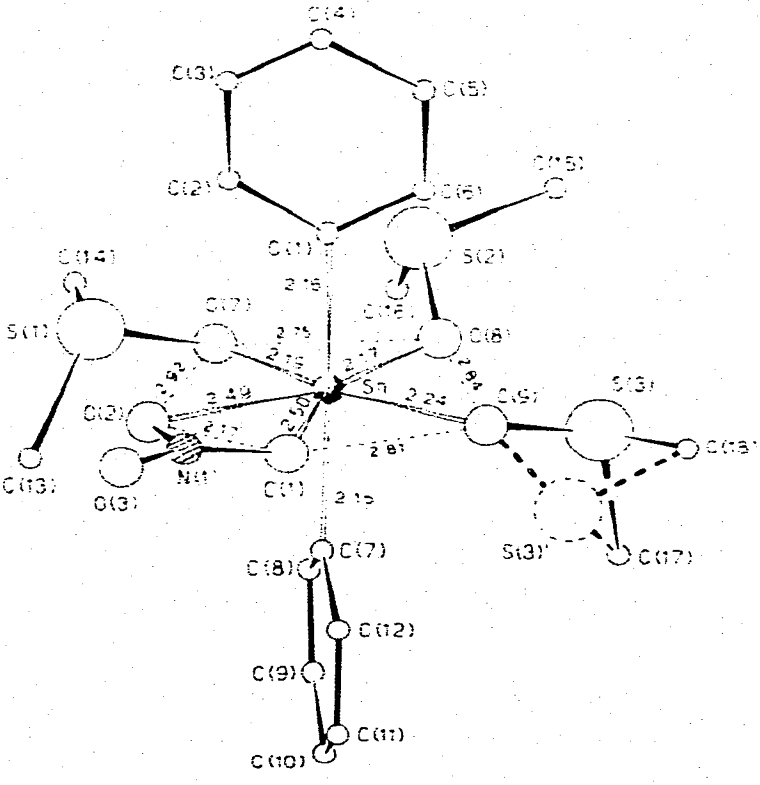

Fig. 1. Clinographic projection of the structure of the cation $[Sn(C_6H_5)_2NO_3\{(CH_3)_2SO\}_3]^+$.

TABLE 2

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS ($Å^2$)[a] (Standard deviations occurring in the last significant figure are given in parentheses.)

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sn	0,2106(1)	0,1282(1)	0,1917(1)	1,98(3)	2,72(3)	3,60(4)	−0,01(3)	0,71(3)	0,03(3)
S(1)	0,4009(2)	0,1750(4)	0,1092(3)	2,5(1)	3,6(2)	5,3(2)	−0,2(1)	1,6(1)	−0,1(1)
S(2)	0,3465(2)	0,0552(4)	0,3508(3)	3,2(1)	3,3(2)	4,8(2)	0,1(1)	−0,2(1)	0,5(1)
S(3)	0,0772(3)	−0,0046(5)	0,3222(3)	3,6(2)	3,7(2)	4,9(2)	−0,6(2)	1,5(2)	0,3(2)
S(3)'	0,028(1)	−0,010(2)	0,253(1)	2,5(6)	4,1(8)	3,7(8)	−1,1(6)	0,7(5)	−0,2(6)
O(1)	0,0938(6)	0,2389(9)	0,1040(6)	3,1(4)	3,7(4)	5,3(5)	0,1(3)	1,1(4)	−0,2(4)
O(2)	0,2164(6)	0,2477(9)	0,0576(6)	3,7(4)	3,9(5)	4,9(5)	0,3(4)	1,4(4)	0,7(4)
O(3)	0,1119(9)	0,3527(13)	−0,0077(8)	8,2(8)	6,9(8)	5,9(7)	2,4(6)	0,1(6)	2,4(6)
O(4)	0,428(1)	−0,380(2)	0,134(1)	11,2(5)					
O(5)	0,488(1)	−0,317(2)	0,035(1)	11,2(4)					
O(6)	0,468(1)	−0,208(2)	0,147(1)	11,7(4)					
O(7)	0,3435(5)	0,1156(9)	0,1713(6)	2,1(3)	4,2(5)	4,9(5)	0,2(3)	1,3(3)	0,1(4)
O(8)	0,2619(5)	0,0198(9)	0,3010(9)	2,8(4)	3,4(4)	4,6(5)	−0,1(3)	0,3(3)	1,0(4)
O(9)	0,0925(5)	0,0903(9)	0,2505(6)	2,9(4)	3,3(4)	5,2(5)	−0,3(3)	1.7(3)	0,5(4)
N(1)	0,1403(7)	0,2805(11)	0,0507(7)	3,2(5)	3,5(5)	4,2(6)	0,3(4)	0,5(4)	0,1(4)
N(2)	0,453(1)	−0,282(2)	0,087(1)	4,4(7)	6,5(9)	12,7(13)	−1,3(6)	3,5(8)	−4,9(9)
C(1)	0,226(1)	0,311(1)	0,256(1)	3,1(5)	3,3(6)	3,5(6)	0,0(5)	0,6(4)	−0,1(5)
C(2)	0,276(1)	0,409(1)	0,225(1)	4,8(7)	3,2(6)	5,9(9)	−1,0(6)	0,4(6)	−0,3(6)
C(3)	0,283(1)	0,529(2)	0,265(1)	7,2(10)	3,8(7)	5,1(8)	−1,2(7)	0,1(7)	0,3(6)
C(4)	0,241(1)	0,550(2)	0,335(1)	6,9(10)	3,4(7)	7,4(10)	−0,2(7)	−0,2(8)	−1,3(7)
C(5)	0,192(1)	0,454(2)	0,367(1)	7,6(10)	5,0(9)	4,8(8)	0,1(8)	0,8(8)	−1,3(7)
C(6)	0,184(1)	0,334(1)	0,326(1)	4,2(7)	4,0(7)	5,2(8)	0,0(6)	1,4(6)	−0,6(6)
C(7)	0,182(1)	−0,041(1)	0,116(1)	2,8(5)	3,6(6)	3,2(6)	−0,2(4)	0,4(4)	0,3(5)
C(8)	0,246(1)	−0,138(2)	0,119(1)	4,3(7)	4,0(7)	5,2(8)	0,2(6)	1,4(6)	−0,9(6)
C(9)	0,228(1)	−0,253(2)	0,075(1)	6,1(9)	3,7(7)	6,6(10)	0,2(7)	0,9(8)	−0,8(7)
C(10)	0,151(1)	−0,269(2)	0,029(1)	6,2(9)	4,1(8)	6,2(9)	−0,5(7)	0,6(7)	−1,4(7)
C(11)	0,089(1)	−0,173(2)	0,026(1)	5,5(8)	4,5(8)	5,1(8)	−0,9(7)	−0,7(7)	−0,1(7)
C(12)	0,106(1)	−0,060(1)	0,073(1)	3,9(6)	3,7(7)	4,5(7)	−0,3(5)	−0,1(5)	0,1(6)
C(13)	0,382(1)	0,086(2)	0,013(1)	5,1(8)	7,2(10)	4,3(8)	−1,0(7)	1,0(6)	−1,4(7)
C(14)	0,503(1)	0,112(2)	0,147(1)	2,4(5)	4,8(8)	8,4(10)	−0,5(5)	1,0(6)	−0,4(8)
C(15)	0,324(1)	0,026(2)	0,457(1)	8,0(11)	7,4(12)	3,8(8)	1,6(10)	0,8(7)	−0,3(8)
C(16)	0,414(1)	−0,078(2)	0,336(1)	4,4(8)	5,8(10)	8,8(12)	2,5(7)	1,1(8)	0,3(9)
C(17)	0,059(2)	−0,158(2)	0,278(2)	8,0(13)	2,2(8)	8,6(15)	−0,6(8)	4,2(12)	0,1(8)
C(18)	−0,028(1)	0,034(2)	0,341(1)	3,1(7)	3,7(8)	7,6(12)	−0,5(6)	3,6(8)	0,0(8)

[a] Anisotropic thermal parameters are in the form: $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE 3

COMPARISON BETWEEN SEVEN-COORDINATED TIN(IV) COMPOUNDS (BOND DISTANCES IN A)

Compound	Stoichiometry	Polyhedron	Equatorial bonds	Apical bonds
Tris(tropolonato)monochlorotin chloroform solvate [12]	MX_6Y	Pentagonal bipyramid	Sn—O 2.138(6), 2.130(6), 2.162(7) 2.128(6), 2.168(7)	Sn—Cl 2.362(4) Sn—O 2.050(6)
Tris(tropolonato)monohydroxotin hydrate methanol solvate [12]	MX_6Y	Pentagonal bipyramid	Sn—O 2.148(5), 2.139(5), 2.180(6) 2.132(5), 2.220(7)	Sn—O 2.057(5) Sn—O(OH) 1.974(6)
Methyltin trinitrate [13]	MX_6Y	Pentagonal bipyramid	Sn—O 2.331(6), 2.148(6), 2.240(6) 2.130(6), 2.298(6)	Sn—C 2.092(6) Sn—O 2.105(6)
Aquotin(ethylenediaminetetraacetate) [14]	MX_4Y_2Z	Undefinable	Sn—O 2.093(3), 2.074(3), 2.075(3), 2.088(3), 2.124(3) Sn—N 2.329(3), 2.296(3)	
μ-oxalatobis[(di-n-propyl sulphoxide)-nitratodiphenyltin] [1]	$MX_2Y_2Z_2W$	Pentagonal bipyramid	Sn—O(NO_3) 2.388(6), 2.408(6) Sn—O(oxal) 2.282(5), 2.248(5) Sn—O(PSO) 2.178(6)	Sn—C 2.115(7) 2.116(8)
Dimethyldiisothiocyanato-(terpyridyl)tin [15]	$MX_3Y_2Z_2$	Pentagonal bipyramid	Sn—N(terp) 2.570(4), 2.479(3), 2.497(3) Sn—N(NCS) 2.280(4), 2.285(4)	Sn—C 2.091(5) 2.119(5)
Tris(dimethyl sulphoxide)nitrato-diphenyltin nitrate	$MX_3Y_2Z_2$	Pentagonal bipyramid	Sn—O(DMSO) 2.17(1), 2.19(1), 2.24(1) Sn—O(NO_3) 2.49(1), 2.50(1)	Sn—C 2.15(1) 2.16(1)

apical positions. Two of the five equatorial oxygen atoms belong to a bidentate nitrate group, the other three to the dimethyl sulphoxide molecules. These five atoms lie at the vertices of a pentagon centred on tin; they are nearly coplanar, with none of them displaced more than 0.05 Å out of the mean least-squares plane and with the sum of the O—O—O angles = 539.7° (theoretical 540°). Of the five interligand O···O contacts in the pentagonal girdle, four are ranging from 2.75 to 2.92 Å (2.80 Å representing the sum of Van der Waals radii), the fifth contact, involving the two oxygen atoms from the bidentate NO_3^-, is much shorter, 2.17 Å, and this value corresponds fairly well to the normal bite for the covalent nitrate group.

As pointed out by Gillespie [6], the geometry of a seven-coordinated species can be described in terms of three basic polyhedra: the 1 : 3 : 3 capped octahedron C_{3v}, the 1 : 4 : 2 monocapped trigonal prism C_{2v} and the 1 : 5 : 1 pen-

TABLE 4

BOND DISTANCES (Å) AND ANGLES (°) (Standard deviations occurring in the last significant figure are given in parentheses) [a]

S(1)—O(7)	1.55(1)	S(3)′—C(17)	1.65(3)	C(3)—C(4)	1.38(3)
S(1)—C(13)	1.80(2)	S(3)′—C(18)	1.80(3)	C(4)—C(5)	1.40(3)
S(1)—C(14)	1.80(2)	O(1)—N(1)	1.27(1)	C(5)—C(6)	1.41(2)
S(2)—O(8)	1.54(1)	O(2)—N(1)	1.26(1)	C(6)—C(1)	1.39(2)
S(2)—C(15)	1.80(2)	O(3)—N(1)	1.24(2)	C(7)—C(8)	1.44(2)
S(2)—C(16)	1.78(2)	O(4)—N(2)	1.35(3)	C(8)—C(9)	1.39(2)
S(3)—O(9)	1.55(1)	O(5)—N(2)	1.11(3)	C(9)—C(10)	1.37(3)
S(3)—C(17)	1.75(2)	O(6)—N(2)	1.24(3)	C(10)—C(11)	1.41(2)
S(3)—C(18)	1.78(2)	C(1)—C(2)	1.41(2)	C(11)—C(12)	1.41(2)
S(3)′—O(9)	1.47(2)	C(2)—C(3)	1.40(2)	C(12)—C(7)	1.35(2)

O(1)—Sn—O(2)	51.7(3)	O(2)—N(1)—O(3)	120(1)
O(2)—Sn—O(7)	77.0(3)	O(4)—N(2)—O(6)	94(2)
O(7)—Sn—O(8)	78.3(3)	O(4)—N(2)—O(5)	112(2)
O(8)—Sn—O(9)	80.5(3)	O(5)—N(2)—O(6)	135(2)
O(9)—Sn—O(1)	72.5(3)	O(7)—S(1)—C(13)	106.7(7)
C(1)—Sn—C(7)	172.1(5)	O(7)—S(1)—C(14)	102.7(7)
C(7)—Sn—O(1)	87.5(4)	C(13)—S(1)—C(14)	99.9(8)
C(7)—Sn—O(2)	86.9(4)	O(8)—S(2)—C(15)	101.2(8)
C(7)—Sn—O(7)	91.1(4)	O(8)—S(2)—C(16)	104.9(7)
C(7)—Sn—O(8)	94.1(4)	C(15)—S(2)—C(16)	100.5(9)
C(7)—Sn—O(9)	87.4(4)	O(9)—S(3)—C(17)	108(1)
C(1)—Sn—O(1)	84.6(4)	O(9)—S(3)—C(18)	102(1)
C(1)—Sn—O(2)	87.7(4)	C(17)—S(3)—C(18)	99(1)
C(1)—Sn—O(7)	93.3(4)	O(9)—S(3)′—C(17)	118(1)
C(1)—Sn—O(8)	93.3(4)	O(9)—S(3)′—C(18)	105(1)
C(1)—Sn—O(9)	99.8(4)	C(17)—S(3)′—C(18)	102(1)
Sn—O(7)—S(1)	136.3(6)	C(6)—C(1)—C(2)	120(1)
Sn—O(8)—S(2)	122.1(5)	C(1)—C(2)—C(3)	120(2)
Sn—O(9)—S(3)	129.1(5)	C(2)—C(3)—C(4)	119(2)
Sn—O(9)—S(3)′	139.9(9)	C(3)—C(4)—C(5)	122(2)
Sn—O(1)—N(1)	94.3(7)	C(4)—C(5)—C(6)	119(2)
Sn—O(2)—N(1)	94.9(7)	C(5)—C(6)—C(1)	120(1)
Sn—C(1)—C(2)	121(1)	C(12)—C(7)—C(8)	121(1)
Sn—C(1)—C(6)	119(1)	C(7)—C(8)—C(9)	118(1)
Sn—C(7)—C(8)	117(1)	C(8)—C(9)—C(10)	120(2)
Sn—C(7)—C(12)	123(1)	C(9)—C(10)—C(11)	122(1)
O(1)—N(1)—O(3)	121(1)	C(10)—C(11)—C(12)	118(2)
O(1)—N(1)—O(2)	119(1)	C(11)—C(12)—C(7)	121(1)

[a] Bond distances in the coordination polyhedron are given in Table 3 and Fig. 1.

tagonal bipyramid D_{5h}. It has been shown that these three polyhedra describe a reaction cycle illustrating the idealized relationships based on edge stretching [7], the energy differences between them being relatively small [6,8]. The choice of the polyhedron for a given complex is dictated by a number of factors, including ligand—ligand repulsions, crystal packing forces, steric constraints of multidentate ligands and the electronic structure of the metal [9,10]. Lewis and Lippard [9] have summarized the distributions of the structurally-known seven-coordinated structures among the three basic polyhedra. Out of twenty two structures, nine are pentagonal bipyramidal, nine capped trigonal prismatic and four capped octahedral.

Seven-coordination for tin is quite interesting since it is rare, especially in R_2Sn^{IV} derivatives; the known examples concern mainly RSn^{IV} compounds [11]. As far as we know, only six crystal structures are available at the time of writing and they are listed, together with bond distances in the coordination polyhedra, in Table 3. As already observed in other metal complexes, ligands such as tropolonato or nitrato are well adapted to achieve coordination numbers greater than six for metals, as a consequence of their relatively small bite. The geometry of these compounds can be classed unambiguously as pentagonal bipyramidal with only the exception of aquotin(ethylenediaminetetraacetate) [14] (for which a description in terms of one of the above three polyhedra does not seem possible from the least-squares planes) and this configuration is rather surprising for μ-oxalatobis[(di-n-propyl sulphoxide)nitratodiphenyltin] [1] in which the great variety of ligands (four different) would favour the configuration of lowest symmetry, i.e. the capped trigonal prism. However, it can be thought that in this case, as in the compound studied in the present work, the pentagonal bipyramidal arrangement is the favoured configuration for two reasons:

(i) The presence, in the pentagonal girdle, of all equal atoms (this assumption holds for all the tabulated compounds);

(ii) The apparent necessity of maintaining two short Sn—C bonds at apical sites thus forcing the arrangement of the other ligands [15].

It is worth noting that none of the seven-coordinated tin compounds shows the MX_5Y_2 stoichiometry for which the D_{5h} configuration would be favoured by energy minimization [8]. On the other hand, it has pointed out by Drew and Wilkins [10] that the stoichiometry seems to be a factor of secondary importance in fixing the geometry of seven-coordinated species.

Table 4 lists bond distances and angles, while Table 5 gives all the vibrational bands, registered as in Nujol mulls as well as in KBr disks.

The Sn—O bond lengths involving the sulphoxide molecules (2.17, 2.19, 2.24 Å) are close to normal single bonds, those involving the nitrate ion (2.49, 2.50 Å) are relevantly longer. This difference can be explained by the bidentate behaviour of the nitrate group which cannot approach as close to metal as can the unidentate dimethyl sulphoxide ligand. Both these lengths can be compared with the corresponding ones observed in μ-oxalatobis[(di-n-propyl sulphoxide)nitratodiphenyltin] [1] (Sn—O(PSO) = 2.178(6); Sn—O(NO_3) = 2.388(6), 2.408(6) Å), while shorter values for Sn—O(NO_3) lengths have been observed in methyltin trinitrate (2.11—2.33 Å) [13].

The Sn—C bonds are slightly longer than those found in the other seven-coor-

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TABLE 5

INFRARED ABSORPTION BANDS (cm^{-1})

Nujol	KBr	Assignments
—	3060 m	ν(CH)(phenyl)
—	3040 m	
—	2990 m	ν(CH)(methyl)
—	2910 m	
1760 w	1760 w	
1740 w	—	$\nu_1 + \nu_3$
1730 w	—	
1570 w	1570 w	ν(CC)
1470 s	1475 m	$\nu(NO)_{as} + \nu(CC)$
1430 (sh)	1430 (sh)	ν(CC)
1370 s	1380 vs	ν(NO)
1320 (sh)	1315 mw	phenyl
1280 s	1280 sh	$\nu(NO)_s$
1180 w	1180 w	β(CH)
1070 mw	1075 w	
1065 (sh)	—	
1040 (sh)	1025 (sh)	$\delta(CH) + \nu(NO)$
1015 (sh)	1020 m	
—	995 (sh)	
980 s	980 s	ν(SO)
960 (sh)	—	
950 (sh)	—	ν(SO)
925 s(br)	940 s	
822 mw	822 m	$\delta(NO_2)$
805 mw	—	
—	740 ms	γ(CH)
733 ms	735 (sh)	
710 (sh)	713 vw	ν(CS)
690 m	692 ms	ϕ(CC)
465 (sh)	—	ring vibration
460 (sh)	460 m	
450 m	—	
412 m	415 m	ν(SnO)
350 m	335 mw	δ(CSO)
305 (sh)	305 vw	
290 (sh)	285 m	ν(SnC)

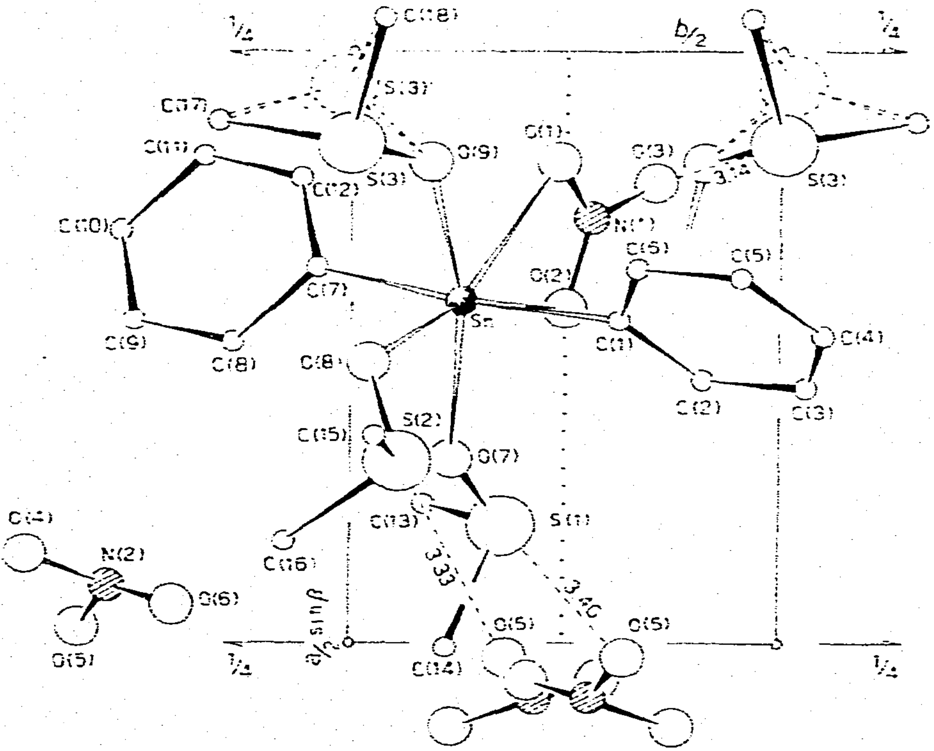

Fig. 2. Diagrammatic projection of the structure along [001].

TABLE 7

COMPARISON OF NITRATE VIBRATIONAL BANDS IN TIN COMPOUNDS (The spectra for the first two compounds were registered in nujol mulls, for the others the KBr technique was used)

Compound	$\nu_1 + \nu_4$	$\nu(NO)_{as}$	ν_3	$\nu(NO)_s$	ν_1	ν_2	$\nu_{as} - \nu_s$	Ligand behaviour
Nitratotriphenyl(triphenylphosphine oxide)tin(IV) [2]	1765vw 1705vw	1475s	1370m	1290vs	1010m	810mw	185	Unidentate
Nitratotriphenylstannyltin(II) [22]	1755w 1745(sh)	1435(sh)	—	1300vs	1020m	820vw 812m	135	Bridging three-coordinate
Nitratotris(triphenylstannyl)tin(IV) [20]	—	1485s	—	1300s	1020m	820vw	185	Bidentate
μ-Oxalatobis[(di-n-propyl sulphoxide)-nitratodiphenyltin(IV)] [1]	1763w	1495m	1375s	1275m	998(sh)	830(sh) 822w	220	Bidentate
(2-Aminobenzothiazolato)-nitratotin(II) [23]	1760w 1710w	1460(sh)	1380s	1320(sh)	1020m	830(sh) 823m	140	Bridging three-coordinate
Tris(dimethyl sulphoxide)nitrato-diphenyltin(IV) nitrate	1760w 1740w 1730w	1470s	1370s	1280w	1020m	822mw 805mw	190	Bidentate ionic

TABLE 6

COMPARISON OF NITRATOTIN(IV) COMPLEXES (BOND DISTANCES IN Å, ANGLES IN °)

Compound	Coordination number	Ligand behaviour	M—O(1)	M—O(2)	N—O(1)
$Sn(NO_3)_4$ [16]	8	symmetrically bidentate	2.139(7) 2.145(6) 2.151(7) 2.154(7)	2.195(7) 2.172(8) 2.174(7) 2.158(11)	1.29(1) 1.29(1) 1.28(1) 1.30(1)
$Sn(CH_3)(NO_3)_3$ [13]	7	unsymmetrically bidentate	2.148 2.130 2.105	2.331 2.298 2.240	1.302 1.293 1.299
$Sn(OH_2)(CH_3)_3(NO_3)$ [17]	7	unidentate	2.22(3)	—	1.33(2)
$Sn(CH_3)_2(NO_3)_2$ [18]	6	unsymmetrically bidentate	2.17(1) 2.15(1)	2.42(1) 2.70(2)	1.31(2) 1.35(2)
$[Sn(C_2O_4)_{1/2}(C_6H_5)_2(NO_3)\{(C_3H_7)_2SO\}]_2$ [1]	7	symmetrically bidentate	2.388(6)	2.408(6)	1.275(8)
$[Sn(OH)(CH_3)_2(NO_3)]_2$ [19]	5	unidentate	2.30(3)	—	1.30(3)
$Sn(NO_3)[(C_6H_5)_3Sn]_3$ [20]	5	symmetrically bidentate	2.58(3)	2.59(2)	1.10(3)
$Sn(C_6H_5)_3(NO_3)[(C_6H_5)_3PO]$ [2]	5	unidentate	2.22(2)	—	1.30(3)
$[Sn(C_6H_5)_2(NO_3)\{(CH_3)_2SO\}_3]NO_3$	7	symmetrically bidentate	2.49(1)	2.50(1)	1.26(1)

dinated tin compounds (Table 3) but little or no meaning can be attached to this lengthening as it has pointed out that this kind of length is slightly influenced by the coordination number at tin and by the nature of the ligands [3,15].

There are two kinds of NO_3^- groups in the structure: one is covalently chelating to metal, the other is not involved in coordination. In this last ion the variations in bond lengths and angles and the large thermal parameters indicate some disorder. Table 6 lists all the structurally known nitratotin(IV) complexes. A detailed inspection of this table suggests the following considerations:

(i) The nitrate group is a versatile ligand, for which several modes of coordination have been proposed [21]. Among the tabulated compounds there are examples of unidentate (3), symmetrically (7) and unsymmetrically (5) bidentate nitrates;

(ii) As mentioned earlier, the nitrate group is able to give metal complexes with high coordination numbers. Out of the nine compounds of the table, five, including the present one, show coordination numbers greater than six;

(iii) The Sn—O lengths show a great deal of scatter about the average values, ranging from 2.11 to 2.70 Å, but these lengths do not increase with increase of the number of ligands. The factor which seems to have influence on these distances is the presence of bulky ligands.

(iv) Bond distances and angles within the NO_3 group indicate deviations from D_{3h} symmetry and this can be regarded as a consequence of bonding effects, since the N—O bond involving the oxygen atom more strongly coordinated to metal, is longer than the other N—O lengths and the O—N—O angle opposite this bond is narrower than the other two angles.

N—O(2)	N—O(3)	O(1)—N—O(2)	O(1)—N—O(3)	O(2)—N—O(3)	M—O(1)—N	M—O(2)—N
1.28(1)	1.18(1)	112.7(8)	124.3(9)	123.0(9)		
1.29(1)	1.20(1)	113.1(7)	123.4(8)	123.5(8)		
1.31(1)	1.16(1)	111.5(8)	124.1(8)	124.4(8)		
1.28(1)	1.17(1)	111.8(8)	122.7(9)	125.5(9)		
1.263	1.190					
1.267	1.187					
1.249	1.182					
1.26(2)	1.18(2)	134(2)	104(2)	118(2)	127(2)	—
1.22(2)	1.26(3)	123(1)	113(1)	124(1)	101.5(8)	90.8(8)
1.23(2)	1.21(2)	122(1)	121(1)	117(1)	103.2(9)	80.7(9)
1.255(8)	1.219(7)	115.6(4)	121.6(6)	122.8(6)	95.3(3)	95.7(3)
1.27(3)	1.20(3)	118(3)	119(3)	123(3)	112(2)	—
1.21(3)	1.14(2)	107(2)	127(2)	126(2)	108(2)	103(2)
1.22(3)	1.22(3)	116(2)	120(1)	124(2)	117(1)	—
1.27(1)	1.24(2)	119(1)	120(1)	121(1)	94.9(7)	94.3(7)

(v) The M—O—N angle at the coordinated oxygen is always larger than 110° (112—127°) when the nitrate acts as unidentate as a consequence of steric hindrance, while it is narrower than 110° (81—108°) when NO_3^- is bidentate.

The infrared absorption bands of the two nitrate groups are in agreement with the X-ray analysis results. In particular, the ionic NO_3^- is well evident in the Nujol spectrum as well in the KBr one, while the absorptions of the covalently-bound nitrate appear only in the Nujol spectrum and their frequency values are characteristic of a bidentate behaviour [21]. In Table 7 the NO_3^- vibrations of the present compound are compared with those of the other nitratotin complexes so far examined by X-ray diffraction. On the basis of the criterion that the splittings of the ν_3 band and of the $\nu_1 + \nu_4$ combination band are greater for the bidentate than for the unidentate nitrate [24,25], the observed values, with only the exception of nitratotriphenyl(triphenylphosphine oxide)tin(IV), are in agreement with the structural situation as found from X-ray analysis. For the triphenylphosphine oxide derivative the values are more indicative of bidentate than unidentate behaviour, in contrast to the X-ray results [2]. For some compounds, frequencies assignable to ionic nitrate (ca. 1370 cm^{-1}) are observed, even when the NO_3^- group is covalently bound.

The dimethyl sulphoxide molecules coordinate to metal through their oxygen atoms as is also suggested by the infrared spectrum, in which the absorption band assigned to the S=O stretching vibration is shifted towards lower frequency values upon complex formation (Table 5). The nature of this shift ($\Delta\nu$ —130 cm^{-1}) has been interpreted in terms of oxygen coordination of the S=O link towards

TABLE 8

INTERMOLECULAR CONTACTS (Å) LESS THAN 3.52 Å (Standard deviations occurring in the last significant figure are given in parentheses)

O(4)···C(9)	3.50(3)	O(3)···S(3^{iii})	3.14(1)
O(6)···C(14)	3.36(3)	O(3)···C(18^{iii})	3.33(2)
O(6)···C(16)	3.50(3)	O(4)···C(15^{iv})	3.48(3)
O(1)···C(11^{i})	3.47(2)	O(4)···C(3^{v})	3.42(3)
O(1)···C(17^{ii})	3.42(3)	O(5)···C(16^{v})	3.45(3)
O(1)···C(18^{ii})	3.38(2)	O(5)···S(2^{vi})	3.33(2)
O(2)···C(15^{iii})	3.41(2)		

The different equivalent positions are labelled as follows:

i = $\bar{x}, \bar{y}, \bar{z}$
ii = $\bar{x}, 1/2 + y, 1/2 - z$
iii = $x, 1/2 - y, -1/2 + z$
iv = $x, \bar{y} - 1/2, -1/2 + z$
v = $x, y - 1, z$
vi = $1 - x, y - 1/2, 1/2 - z$

the metal ions [3,26,27]. The configuration of the dimethyl sulphoxide groups is pyramidal, as expected, with S—O and S—C lengths in the ranges usually found [28]. One of these three groups is affected by disorder involving only the sulphur atom which is distributed into two positions with occupancies of 0.80 and 0.20. This situation, which is probably due to packing effects, is analogous to that observed in polymorph II of *cis*-dichloro-*cis*-bis(dimethyl sulphoxide)-*trans*-diphenyltin [3], but it is different from that found in polymorph I of the above-mentioned compound [3] and in μ-oxalatobis[(di-n-propyl sulphoxide)nitratodiphenyltin] [1], in which, besides sulphur, the carbon atoms are too disordered. In all these compounds disordering does not involve the oxygen atom bonded to tin.

The two benzene rings are planar with no significant departure from the regular geometry; the metal atom is displaced by 0.08 Å out of the C(1)···C(6) plane and by 0.10 Å out of the C(7)···C(12) plane. The C—Sn bonds are nearly perpendicular to the equatorial plane, the angles which they form being 94.4° for C(1)—Sn and 93.4° for C(7)—Sn. The reciprocal orientation of the two benzene rings is defined by the dihedral angle which they form (73.4°).

The intermolecular distances less than 3.52 Å are listed in Table 8; they involve the oxygen atoms of the two nitrate ions and the sulphur or carbon atoms from the cation ligands. The most significant of these distances are illustrated in Fig. 2, which shows a diagrammatic projection of the whole structure along [001]. Assuming Pauling's radii (S, 1.85, C, 1.70, O, 1.40 Å) [29] only the O(3)···S(3) (x, ½ − y, z − ½) contact appears to be significantly shorter than the Van der Waals value, but this shortening (3.14 Å with respect to the theoretical 3.25 Å) is in good agreement with the suggestion that the radius for sulphur should be about 1.70 Å [30,31,32].

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References

1 A. Mangia, C. Pelizzi and G. Pelizzi, J. Chem. Soc. Dalton, (1973) 2557.
2 M. Nardelli, C. Pelizzi and G. Pelizzi, J. Organometal. Chem., 112 (1976) 263.

3 L. Coghi, M. Nardelli, C. Pelizzi and G. Pelizzi, Gazz. Chim. Ital., 105 (1975) 1187.
4 L. Coghi, C. Pelizzi and G. Pelizzi, Gazz. Chim. Ital., 104 (1974) 1315.
5 D.T. Cromer and J.B. Mann, Acta Crystallogr. A, 24 (1968) 321.
6 R.J. Gillespie, Canad. J. Chem., 38 (1960) 818.
7 E.L. Muetterties and L.J. Guggenberger, J. Amer. Chem. Soc., 96 (1974) 1748.
8 E.L. Muetterties and C.M. Wright, Quart. Rev. Chem. Soc. 21 (1967) 109.
9 D.F. Lewis and S.J. Lippard, Inorg. Chem., 11 (1972) 621.
10 M.G.B. Drew and J.D. Wilkins, J. Chem. Soc. Dalton, (1973) 2664.
11 R. Okawara and M. Wada, Advan. Organometal. Chem., 5 (1967) 137.
12 J.J. Park, D.M. Collins and J.L. Hoard, J. Amer. Chem. Soc., 92 (1970) 3636.
13 G.S. Brownlee, A. Walker, S.C. Nyburg and J.T. Szymanski, Chem. Commun., (1971) 1073.
14 F.P. Van Remoortere, J.J. Flynn and F.P. Boer, Inorg. Chem., 10 (1971) 2313.
15 D.V. Naik and W.R. Scheidt, Inorg. Chem., 12 (1973) 272.
16 C.D. Garner, D. Sutton and S.C. Wallwork, J. Chem. Soc. A, (1967) 1949.
17 R.E. Drew and F.W.B. Einstein, Acta Crystallogr. Sect. B, 28 (1972) 345.
18 J. Hilton, E.K. Nunn and S.C. Wallwork, J. Chem. Soc. Dalton, (1973) 173.
19 A.M. Domingos and G.M. Sheldrick, J. Chem. Soc. Dalton, (1974) 475.
20 G. Pelizzi, J. Organometal. Chem., 87 (1975) C1 and data to be published.
21 C.C. Addison, N. Logan, S.C. Wallwork and C.D. Garner, Quart. Rev., 25 (1971) 289.
22 M. Nardelli, C. Pelizzi and G. Pelizzi, J. Organometal. Chem., 85 (1975) C43.
23 M. Nardelli, C. Pelizzi and G. Pelizzi, J. Chem. Soc. Dalton, (1975) 1595.
24 N.F. Curtis and Y.M. Curtis, Inorg. Chem., 4 (1965) 804.
25 A.B.P. Lever, E. Mantovani and B.S. Ramaswamy, Canad. J. Chem. 49 (1971) 1957.
26 J. Reedijk, A.H.M. Fleur and W.L. Groeneveld, Rec. Trav. Chim. Pays-Bas, 88 (1969) 1115.
27 W.L. Reynolds, Progr. Inorg. Chem., 12 (1970) 1.
28 P. Biscarini, L. Fusina, G.D. Nivellini, A. Mangia and G. Pelizzi, J. Chem. Soc. Dalton, (1974) 1846.
29 L. Pauling, Nature of the Chemical Bond, Cornell University Press, Ithaca, New York, 1960.
30 J. Donohue, J. Amer. Chem. Soc. 72 (1950) 2701.
31 D. van der Helm, A.E. Lessor Jr. and L.L. Merritt Jr., Acta Crystallogr., 13 (1960) 1050.
32 M. Nardelli, G.Fava Gasparri, G.Giraldi Battistini and P. Domiano, Acta Crystallogr., 20 (1966) 349.