Tin Complexes Containing the Nitrate Group: Crystal Structure of Polymeric (2-Aminobenzothiazolato)nitratotin(II)

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The structure of the title compound was solved from *X*-ray diffractometer data by Patterson and Fourier methods and refined by least-squares techniques to *R* 5.9% for 2 166 independent reflections. Crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions: $a = 9.993(5)$, $b = 6.915(4)$, $c = 13.593(6)$ Å, $\beta = 91.9(1)°$, $Z = 4$. Co-ordination around tin can be described as tetrahedral and involves two adjacent NO_3^- anions and two organic molecules. There are two longer Sn–O contacts which complete the co-ordination to six. The nitrate group and the organic ligand both bridge two metal atoms in a rather unusual way, causing the structure to be polymeric.

A FEW examples of structural research on organotin compounds containing the nitrate group as ligand have been reported.[1-3] Recently, we have examined by i.r. spectroscopy and *X*-ray diffraction two organotin(IV) derivatives: μ-oxalato-bis[(di-n-propyl sulphoxide)-nitratodiphenyltin] [4] and tris(dimethyl sulphoxide)-nitratodiphenyltin nitrate,[5] in which nitrate ions act as covalent bidentate ligands and tin exhibits unusual seven-co-ordination.

A crystalline product of formula $[Sn(abt)(NO_3)]$ (abt = deprotonated 2-aminobenzothiazole) has been obtained from the reaction of diphenyltin(IV) dinitrate and 2-aminobenzothiazole (Habt). We now report the *X*-ray crystal-structure determination of this compound.

EXPERIMENTAL

Preparation.—Diphenyltin(IV) dinitrate and Habt were allowed to react in anhydrous acetone, at room temperature under dry nitrogen. After some hours white tabular crystals separated (Found: C, 25.9; H, 1.8; N, 12.9. $C_7H_5N_3O_3SSn$ requires C, 25.5; H, 1.5; N, 12.7%).

Physical Measurements.—I.r. spectra were measured on a Perkin-Elmer 457 instrument by use of KBr disks. *X*-Ray intensity data were collected on a Siemens single-crystal computer-controlled diffractometer by use of Mo-K_α radiation and the ω—2θ scan technique.

Crystal Data.—$C_7H_5N_3O_3SSn$, $M = 329.9$, Monoclinic, $a = 9.993(5)$, $b = 6.915(4)$, $c = 13.593(6)$ Å, $\beta = 91.9(1)°$, $U = 938.7$ Å^3, $D_m = 2.32$, $Z = 4$, $D_c = 2.33$, $F(000) = 632$. Mo-K_α radiation, $\lambda = 0.7107$ Å; $\mu(\text{Mo-}K_\alpha) = 29.4$ cm^{-1}. Space group $P2_1/c$ (from systematic absences).

Cell dimensions were determined from rotation and Weissenberg photographs and refined from diffractometer measurements.

Intensity Data Collection.—A flattened tablet, mean diameter 0.33 mm, was aligned with its [001] axis along the ϕ axis of the diffractometer and all reflections with $2\theta \leqslant 58°$ were collected. Of 2 513 independent reflections measured, 2 166, having $I > 2\sigma(I)$, were considered observed and were used in the analysis.

There was no evidence for decomposition of the sample during the *X*-ray exposure as shown by the intensity of a standard reflection monitored every 20 reflections.

After the usual data reduction the structure amplitudes were put on an absolute scale by comparison with the calculated values. Absorption corrections were not applied in view of the low absorbance of the sample ($\mu\bar{r}$ 0.50).

Structure Determination and Refinement.—The structure was solved by the heavy-atom technique, the initial set of co-ordinates for tin being deduced from a three-dimensional Patterson map. Refinement by block-diagonal anisotropic least-squares gave *R* 6.1%. This was improved to 5.9% by adding the contributions of the four hydrogen atoms of the phenyl ring, which were located from a Fourier difference map and refined isotropically. It was not possible to locate the hydrogen atom bound to N(2) as in the place where it was expected there was only a large region of diffuse electron density (1.2—1.3 eÅ^{-3} out of a background of 0.6—0.9 eÅ^{-3}).

Final positional and thermal parameters are given in Table 1 with their standard deviations. Observed and calculated structure factors and details of i.r. spectrum are listed in Supplementary Publication No. SUP 21286 (13 pp., 1 microfiche).† Atomic scattering factors used throughout the calculations were taken from ref. 6 for non-hydrogen atoms and from ref. 7 for hydrogen atoms.

All calculations were performed on a CDC 6600 computer at the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, using the programs of Immirzi.[8]

RESULTS AND DISCUSSION

I.r. Spectra.—The i.r. spectra of Habt and $[Sn(abt)(NO_3)]$ were examined in the 4 000—250 cm^{-1} region. Three bands >3 100 cm^{-1} were due to NH stretching modes and can be related to the disordered situation of the imino-group proton. The NO_3^- anion shows bands (1 380, 1 020, and 823 cm^{-1}) which correspond to the ν_3, ν_1, and ν_2 modes of an ionic nitrate.[9,10] However this group has been shown to be three-co-ordinating, from the *X*-ray analysis, and this can be explained by considering the three-co-ordinate structure as an extension of the simple ionic structure.[11] On the other hand,

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† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

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there are two weak bands at 1 760 and 1 710 cm^{-1}, which can be assigned to the $\nu_1 + \nu_4$ combination modes, their separation ($\Delta\nu$ 50 cm^{-1}) indicating bidentate behaviour for NO_3^-.[11]

TABLE 1

Fractional atomic co-ordinates and thermal parameters (Å^2),* with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sn	0.2191(1)	0.1110(1)	0.2405(1)	2.88(2)	2.71(2)	3.17(2)	0.25(2)	−0.36(2)	0.73(2)
S	0.6043(2)	0.2041(3)	0.0034(1)	2.31(7)	1.36(7)	1.83(7)	−0.03(6)	0.09(6)	−0.52(5)
O(1)	0.0650(8)	0.2235(13)	0.4012(6)	4.8(4)	4.6(4)	5.2(4)	2.7(3)	−0.9(3)	0.0(3)
O(2)	0.0121(8)	0.3537(14)	0.2637(5)	3.6(3)	6.7(5)	2.5(3)	−0.4(3)	0.8(2)	0.0(3)
O(3)	−0.1023(7)	0.4191(11)	0.3926(5)	3.4(3)	3.7(3)	3.2(3)	1.7(3)	1.1(2)	0.7(3)
N(1)	0.6667(6)	0.4095(9)	0.1594(5)	1.8(2)	1.4(2)	1.8(2)	−0.1(2)	0.2(2)	−0.4(2)
N(2)	0.8507(7)	0.2785(12)	0.0800(6)	1.9(3)	2.9(3)	3.0(3)	0.1(2)	0.3(2)	−0.7(3)
N(3)	−0.0067(7)	0.3309(11)	0.3533(5)	2.2(3)	2.7(3)	2.4(3)	0.3(2)	0.0(2)	−0.1(2)
C(1)	0.2514(8)	0.3758(12)	0.1166(6)	1.7(3)	1.5(3)	3.0(3)	−0.2(2)	0.0(2)	0.6(3)
C(2)	0.3038(8)	0.4724(12)	0.1998(6)	2.2(3)	1.6(3)	2.7(3)	0.2(2)	0.9(3)	−0.1(3)
C(3)	0.4417(8)	0.4865(11)	0.2180(6)	2.5(3)	1.5(3)	2.1(3)	−0.2(2)	0.6(2)	−0.3(2)
C(4)	0.5273(7)	0.4055(10)	0.1506(5)	2.0(3)	0.9(2)	1.8(3)	−0.2(2)	0.2(2)	−0.1(2)
C(5)	0.4738(7)	0.3030(10)	0.0698(5)	2.1(3)	0.8(2)	1.7(3)	0.1(2)	−0.1(2)	−0.1(2)
C(6)	0.3370(8)	0.2884(10)	0.0506(6)	2.3(3)	1.0(2)	2.3(3)	−0.2(2)	−0.3(2)	0.1(2)
C(7)	0.7198(8)	0.3080(11)	0.0881(5)	2.0(3)	1.3(3)	1.9(3)	−0.3(2)	0.3(2)	0.0(2)
				B/Å^2					
H(1)	0.171(10)	0.388(17)	0.109(8)	4(1)					
H(2)	0.250(10)	0.520(16)	0.276(8)	6(2)					
H(3)	0.457(9)	0.527(15)	0.269(7)	3(1)					
H(4)	0.289(10)	0.227(16)	−0.003(7)	3(1)					

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

X-*Ray Structure*.—The most interesting features are: that tin has been reduced from oxidation state (IV) to (II), that the phenyl groups have been removed, the deprotonation of the organic molecule, and the unusual co-ordination of both ligands, NO_3^- and abt. The reduction to tin(II) probably occurred at the expense of a second molecule of Habt, with formation of a benzothiazolone derivative. This hypothesis supported by the presence (in a very small amount) in the reaction mixture of a secondary product containing Sn, NO_3^-, and an organic molecule which has a strong i.r. band at *ca.* 1 650 cm^{-1}, probably due to C=O.

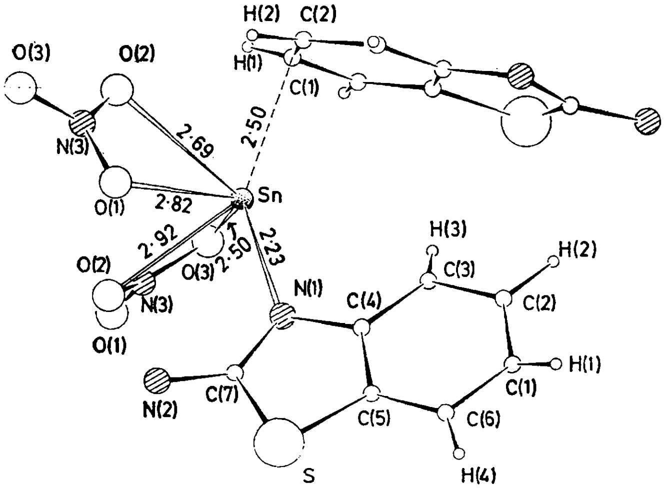

FIGURE 1 Clinographic projection of the structure with interatomic distances in the co-ordination polyhedron

A clinographic projection of the structure is shown in Figure 1. The asymmetric unit comprises one tin atom, one nitrate group, and one abt molecule. Table 2 lists bond distances and angles.

If significant bonding properties are attributed only to contacts <2.70 Å the co-ordination around tin can be described as tetrahedral and involves two oxygen atoms of two adjacent nitrate groups (Sn–O 2.50 and 2.69 Å),

TABLE 2

Bond distances (Å) and angles (°)

(*a*) Distances			
Sn–O(1)	2.82	C(6)–C(1)	1.39
Sn–O(2)	2.69	N(1)–C(4)	1.39
Sn–O(3$^{\mathrm{I}}$)	2.50	N(1)–C(7)	1.32
Sn–O(2$^{\mathrm{I}}$)	2.92	N(2)–C(7)	1.33
Sn–N(1$^{\mathrm{II}}$)	2.23	C(7)–S	1.76
C(1)–C(2)	1.39	S–C(5)	1.75
C(2)–C(3)	1.39	N(3)–O(1)	1.21
C(3)–C(4)	1.39	N(3)–O(2)	1.24
C(4)–C(5)	1.40	N(3)–O(3)	1.26
C(5)–C(6)	1.39		
(*b*) Angles			
O(1)–Sn–O(2)	45.2	C(6)–C(5)–S	128.7
O(1)–Sn–O(3$^{\mathrm{I}}$)	117.0	C(1)–C(6)–C(5)	118.2
O(1)–Sn–O(2$^{\mathrm{I}}$)	74.6	C(5)–S–C(7)	89.4
O(1)–Sn–N(1$^{\mathrm{II}}$)	88.9	S–C(7)–N(1)	115.2
O(2)–Sn–O(3$^{\mathrm{I}}$)	94.3	S–C(7)–N(2)	120.8
O(2)–Sn–O(2$^{\mathrm{I}}$)	76.8	N(1)–C(7)–N(2)	124.0
O(2)–Sn–N(1$^{\mathrm{II}}$)	134.1	C(4)–N(1)–C(7)	110.5
O(3$^{\mathrm{I}}$)–Sn–O(2$^{\mathrm{I}}$)	46.4	C(4)–N(1)–Sn$^{\mathrm{III}}$	123.6
O(3$^{\mathrm{I}}$)–Sn–N(1$^{\mathrm{II}}$)	109.0	C(7)–N(1)–Sn$^{\mathrm{III}}$	124.6
O(2$^{\mathrm{I}}$)–Sn–N(1$^{\mathrm{II}}$)	91.2	O(1)–N(3)–O(2)	119.6
C(2)–C(1)–C(6)	120.1	O(2)–N(3)–O(3)	119.7
C(1)–C(2)–C(3)	121.6	O(1)–N(3)–O(3)	120.6
C(2)–C(3)–C(4)	118.7	N(3)–O(1)–Sn	94.6
C(3)–C(4)–C(5)	119.3	N(3)–O(2)–Sn	100.5
C(3)–C(4)–N(1)	125.0	N(3)–O(3)–Sn$^{\mathrm{IV}}$	106.9
C(5)–C(4)–N(1)	115.6	N(3)–O(2)–Sn$^{\mathrm{IV}}$	87.0
C(4)–C(5)–C(6)	122.0	Sn–O(2)–Sn$^{\mathrm{IV}}$	171.9
C(4)–C(5)–S	109.3		

σ For bond lengths 0.01 Å, and for angles 0.2—0.8°. Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$
II $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$
III $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
IV $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$

the thiazole nitrogen of an abt molecule (Sn–N 2.23 Å), and a point lying on the phenyl ring of a second abt molecule, related to the previous one by the *c* glide (the shortest Sn ··· Ph contact is 2.50 Å). This point is situated about one quarter of the way along the C(1)–C(2) bond [*i.e.* from C(1)]. It is difficult to describe the nature of this contact: it cannot be considered as a σ bond, owing to the presence of the hydrogen atoms on C(1) and C(2) and to the orientation of the ring, nor a π bond, owing to the position of the contact and to the geometry of the ring which maintains the usual aromaticity.

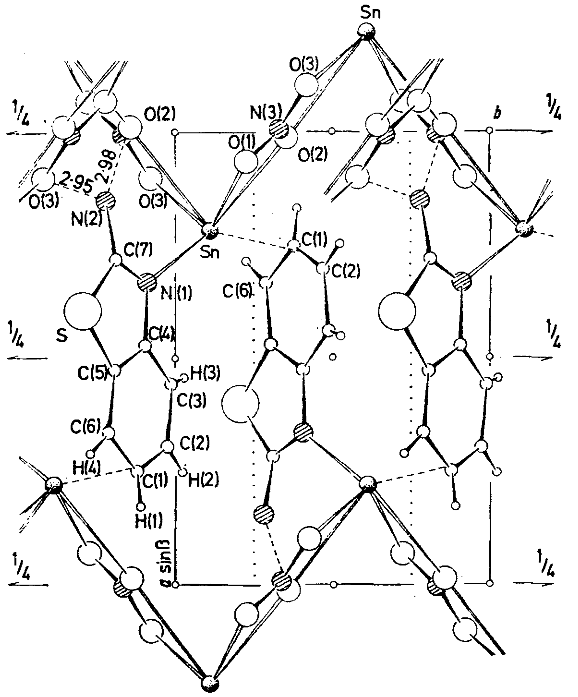

FIGURE 2 Diagrammatic projection of the structure along [001]

If two other oxygen atoms from two NO_3^- ions, situated 2.82 and 2.92 Å from the tin, are regarded as being part of the metal environment, then the co-ordination is completed to six members and becomes more difficult to describe in terms of bonding geometry.

Rather unusual behaviour (with respect to the classification proposed by Addison *et al.*[12]) is shown by the nitrate group, which bridges two metal atoms through two asymmetric bidentate contacts, giving rise to dimers with all the oxygen atoms involved in co-ordination (Figure 2). One oxygen atom [O(2)] is in an asymmetric bridging situation. This type of behaviour by a nitrate group has been observed in some anhydrous metal nitrates,[13,14] but in these compounds the nitrate oxygens co-ordinate to three or more different metal atoms. This is the first example of a three-co-ordinate bridging nitrate group between two metal atoms, behaviour which emphasizes the strong ligand properties of this ion. The nitrate ion is perfectly planar, but shows significant deviations from D_{3h} symmetry. The differences in bond distances and angles within it can be regarded as a consequence of bonding effects, since the N–O bonds involving oxygen atoms more strongly bound to metal are longer than the others. The four Sn–O–N angles are all smaller than usually observed (110°) for bidentate nitrate groups.[15]

The organic molecule also bridges two adjacent metal atoms. The benzothiazole system in it is practically planar, the maximum deviation from the least-squares plane being for C(3) 0.05 Å; N(2) is out of the plane by 0.07 Å. This plane is tilted by 113.3° with respect to the plane of a second organic molecule related to the first one by the *c* glide. The C–S distances (1.75 and 1.76 Å) correspond very closely to pure single bonds.[16] The C–S–C angle (89.4°) is in the range of the values found for sulphur in five-membered rings.[17-19] The values of the N(1)–C(7) (1.32 Å) and N(2)–C(7) (1.33 Å) distances suggest complete π delocalization along the system N(1)–C(7)–N(2); N(1) is coplanar with Sn, C(7), and C(4) and this is evidence for its deprotonation. Our failure in locating the proton bound to N(2) may be due to its disordered distribution in the two positions related to the trigonal hybridization of N(2). This assumption is consistent with the presence of the three i.r. bands in the region 3 400—3 100 cm^{-1} which can be assigned to ν(NH) and with the two nearly equivalent contacts N(2) ··· O(3) $(1 + x, \frac{1}{2} - y, \frac{1}{2} - z)$ 2.95 and N(2) ··· O(2) $(1 + x, y, z)$ 2.98 Å in which the hydrogen atom can be involved (Figure 2).

The bridging nature of the nitrate ions and of the abt ligands causes the whole structure to be polymeric.

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