Characterisation of an Intermediate in the Oxidation of a Tin(II) Carboxylate. An Example of a Pentagonal Pyramidal Six-co-ordinate Tin(II) Atom

By Paul F. R. Ewings, Philip G. Harrison,* Trevor J. King, and Alan Morris

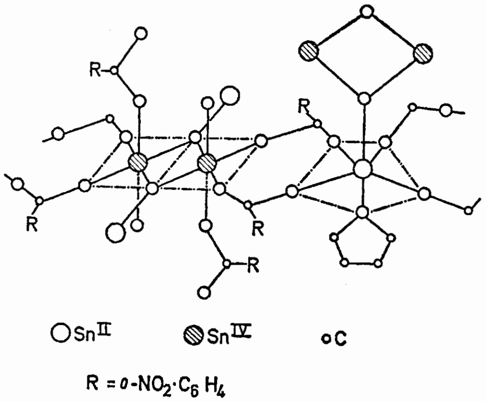
(*Department of Chemistry, University of Nottingham, University Park, Nottingham* NG7 2RD)

Summary The compound $Sn_2(O_2C{\cdot}C_6H_4{\cdot}NO_2\text{-}o)_4O$,THF is polymeric, consisting of octahedrally co-ordinated tin(IV) atoms connected by carboxylate bridges to tin(II) atoms which are also six-co-ordinate, but having a pentagonal pyramidal geometry.

We have previously noted the ease with which derivatives of bivalent tin are oxidised.[1] The products of such oxidation, however, have so far not been identified. Dehnicke has synthesised tin(IV) dihalide oxides, SnX_2O ($X = F$, Cl, Br, I), by the thermal decomposition of $SnF_2(NO_3)_2$ or the reaction of Cl_2O or ozone with SnX_4 ($X = Cl$, Br, I), which may be regarded as the ultimate result of the oxidation of tin(II) halides.[2] These compounds are considered to be polymeric with Sn–O–Sn–O chains.[3] We report on the constitution of a partial oxidation product of tin(II) bis-(*o*-nitrobenzoate) (I), the first characterised intermediate in the oxidation of a tin(II) compound.

Crystals of the composition $Sn_2(O_2C{\cdot}C_6H_4{\cdot}NO_2\text{-}o)_4O$,THF, obtained from the molecular oxygen oxidation of (I) in THF–benzene, are monoclinic, space group $P2_1/c$, $a =$ 13·426, $b =$ 14·666, $c =$ 22·029 Å, $\beta =$ 111·51°, $Z =$ 4.2138 independent reflections (Cu-K_α radiation) were collected using a Hilger-Watt four-circle diffractometer. The positions of the tin atoms were located from the three-dimentional Patterson function, and the structure refined by successive Fourier syntheses. The conventional '*R*' factor is now 6·74, and refinement is continuing. The structure consists of a three-dimensional polymeric network (see Figure), with one tin atom being in the +4 oxidation state, and the other in the +2 state, all metal atoms in each oxidation state being equivalent.

All carboxylate residues connect the tin(II) atoms to the tin(IV) atoms, whilst two oxygen atoms bridge two tin(IV) atoms forming a lozenge-shaped distannoxane ring [r(Sn–O) = 2·03, 2·07 Å; ∠O–Sn–O = 80°]. Oxygen atoms from carboxylate residues make up a slightly distorted octahedron about each tin(IV) atom. The co-ordination about the tin(II) atoms is extremely unusual, being the first example of pentagonal pyramidal co-ordination at tin. The five equatorial positions are occupied by oxygen atoms from four carboxylate groups and the solvating THF molecule [r(Sn–O) = 2·40—2·59 Å] in an almost planar arrangement (sum of the angles subtended at tin = 356°). Six-co-ordination at the tin(II) atom is completed by co-ordination of a distannoxane ring oxygen *via* an axial site [r(Sn–O) = 2·12 Å]. By inference, therefore, the tin(II) lone pair of electrons is located in the remaining axial position. This compound represents only the second example of such geometry (the complex trisoxalato-antimoniate anion $[\mathrm{Sb(C_2O_4)_3}]^{3-}$ has a similar structure).[4] In all other known examples of six-co-ordination at tin(II)[5] the lone pairs apparently occupy equatorial positions.



FIGURE

We thank the S.R.C. and Albright & Wilson for support.

(*Received*, 8*th November* 1973; *Com.* 1544.)

---

[1] P. G. Harrison and S. R. Stobart, *Inorg. Chim. Acta*, **1973**, **6**, **306**; and refs. therein.

[2] K. Dehnicke, *Z. anorg. Chem.*, **1961**, **308**, 72; 1965, **338**, 279; *Chem. Ber.*, 1965, **98**, 280, 290.

[3] H. S. Cheng and R. H. Herber, *Inorg. Chem.*, **1971**, **10**, **1315**.

[5] F. P. van Remoortere, J. J. Flynn, F. P. Boer, and P. P. North, *Inorg. Chem.*, **1971**, **10**, 1511; K. G. Shields, R. C. Seccombe, and C. H. L. Kennard, *J.C.S. Dalton*, **1973**, **741**.