THE X-RAY STRUCTURE OF (O-ISOPROPYLDITHIOCARBONATO)-TRIPHENYLTIN(IV); AN EXAMPLE OF S- AND O-XANTHATE COORDINATION

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(Received April 23rd, 1986)

Summary

The compound $Ph_3Sn(S_2CO^iC_3H_7)$, crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters a 7.5075(9), b 35.376(5), c 8.293(2) Å, β 97.76(1)°, $Z = 4$. Refinement on 3162 reflections [with $I \geqslant 2.5\sigma(I)$] converged with final R 0.037 and R_w 0.050. The tin atom is coordinated by three phenyl groups and a sulphur atom derived from the xanthate ligand. There is an additional intermolecular $Sn \cdots O$ interaction of 2.950 (3) Å indicating a S- and O-chelating mode of coordination by the xanthate ligand.

Introduction

A wide variety of coordination modes of the xanthate ligand (^-S_2COR; for R = ethyl: exa, R = isopropyl: iprxa) are known for tin(IV) derivatives. In $Sn(exa)_4$ [1], the presence of both monodentate and bidentate xanthate ligands define an approximate octahedral geometry about the tin atom. Similar coordination geometries have been found in the *cis*-halotinxanthates, $Sn(exa)_2X_2$ (X = Cl [2], Br, I [3]), in which the two xanthate ligands chelate the tin atoms with almost symmetric Sn–S bond distances. The substitution of the halogens in $Sn(exa)_2X_2$ by CH_3 groups, as in $Me_2Sn(exa)_2$ [4], results in a marked distortion of the tin atom environment. This distortion is manifested by the Me–Sn–Me angle of 130.1(3)° and the presence of asymmetrically binding xanthates (av. Sn–S 2.5 and 3.1 Å). However, ^{119}Sn NMR studies have shown that, in solution, the tin atom in $Me_2Sn(exa)_2$ is essentially four-coordinate [4]. Similarly, for the isopropylxanthate ligand in solid $Ph_2Sn(iprxa)Cl$ [5], a coordination mode intermediate between bidentate and monodentate behaviour is observed (Sn–S 2.5 and 2.8 Å), so that it was of interest to

investigate the coordination geometry of the tin atom when the chloride in $Ph_2Sn(iprxa)Cl$ was replaced by a futher phenyl group.

Experimental

$Ph_3Sn(iprxa)$ was prepared by the addition of an aqueous solution of a one molar equivalent of potassium isopropylxanthate to a stirred solution of Ph_3SnCl (Kodak Ltd, 0.4 g, 25 ml CH_2Cl_2). The mixture was stirred for 0.5 h, separated, the organic layer dried over Na_2SO_4, and the volume reduced to yield an oil which solidified on standing. Colourless crystals suitable for X-ray diffraction studies were obtained by the slow evaporation of a CH_2Cl_2/hexane solution.

$Ph_3Sn(iprxa)$, m.p. 82–83°C; in the C–O, C–S, and M–S regions of the infrared spectrum (KBr disc) strong characteristic xanthate absorptions were observed at 1230, 1035, and 455 cm^{-1}, respectively.

Intensity data were collected at room-temperature on an Enraf–Nonius CAD4F diffractometer fitted with Mo-$K_{\bar{a}}$ radiation (graphite monochromator) with the use of the ω-2θ scan technique. No decomposition of the crystal occurred during the data collection. The data were corrected for Lorentz and polarization effects and for absorption [6], max. and min. transmission factors 0.7692 and 0.5707 respectively. Of the 5497 reflections measured, 3827 were unique and of these, 3162 satisfied the $I \geqslant 2.5\sigma(I)$ criterion of observability.

Crystal data. $C_{22}H_{22}OS_2Sn$, M 485.2, monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a 7.5075(9), b 35.376(5), c 8.293(2) Å, β 97.76(1)°, V 2182.3 Å^3, D_m 1.46, Z 4, D_x 1.477 g cm^{-3}, $F(000)$ 976, μ(Mo-$K_{\bar{a}}$) 13.37 cm^{-1}, λ 0.71073 Å, no. parameters/no. variables = 13.4.

The structure was solved from the interpretation of the Patterson synthesis and refined by a full-matrix least-squares procedure in which the function $\Sigma w\Delta^2$ was minimized [6]. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions. A weighting scheme, $w = [\sigma^2(F) + g|F|^2]^{-1}$, was introduced and the refinement continued until convergence; final $R = 0.037$, $R_w = 0.050$ for $g = 0.0024$. The analysis of variance showed no special features and the maximum residual electron
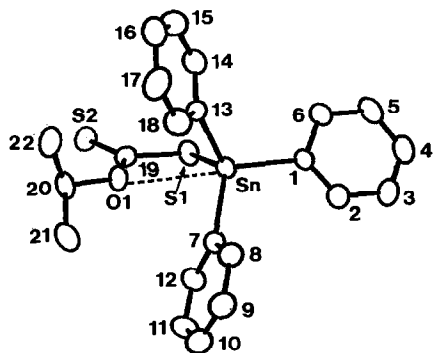

Fig. 1. The molecular structure of $Ph_3Sn(iprxa)$ showing the numbering scheme employed; atoms not otherwise indicated are carbon atoms.

TABLE 1

FRACTIONAL ATOMIC COORDINATES FOR Ph$_3$Sn(iprxa)

Atom	x	y	z
Sn	0.47075(4)	0.13421(1)	0.02903(4)
S(1)	0.7377(1)	0.1138(1)	0.2099(2)
S(2)	0.7548(2)	0.0603(1)	0.4834(2)
C(19)	0.6361(6)	0.0883(1)	0.3535(6)
O(1)	0.4645(4)	0.0962(1)	0.3447(4)
C(20)	0.3528(7)	0.0773(2)	0.4567(6)
C(21)	0.2250(8)	0.1082(2)	0.4949(9)
C(22)	0.2661(10)	0.0439(2)	0.3756(10)
C(1)	0.5927(6)	0.1634(2)	−0.1533(5)
C(2)	0.5582(7)	0.2004(2)	−0.1879(7)
C(3)	0.6397(10)	0.2199(2)	−0.3037(8)
C(4)	0.7538(9)	0.2018(2)	−0.3877(8)
C(5)	0.7923(8)	0.1646(3)	−0.3592(7)
C(6)	0.7126(8)	0.1441(2)	−0.2421(7)
C(7)	0.3062(6)	0.1733(2)	0.1361(6)
C(8)	0.1382(7)	0.1835(2)	0.0507(7)
C(9)	0.0341(8)	0.2087(2)	0.1194(8)
C(10)	0.0838(8)	0.2233(2)	0.2682(8)
C(11)	0.2404(9)	0.2144(2)	0.3546(8)
C(12)	0.3557(8)	0.1893(2)	0.2876(7)
C(13)	0.3320(6)	0.0839(2)	−0.0549(6)
C(14)	0.4194(8)	0.0539(2)	−0.1052(7)
C(15)	0.3263(11)	0.0213(2)	−0.1608(10)
C(16)	0.1458(12)	0.0192(2)	−0.1645(8)
C(17)	0.0549(8)	0.0485(2)	−0.1153(10)
C(18)	0.1451(7)	0.0816(2)	−0.0582(8)

density peak in the final difference map was 0.40 eÅ^{-3} located in the vicinity of the tin atom. The scattering factors for neutral tin were from ref. 7 (the values were corrected for $\Delta f'$ and $\Delta f''$) and those for the remaining atoms were from SHELX [6]. Fractional atomic coordinates are listed in Table 1 and the numbering scheme used is shown in Fig. 1. Tables of anisotropic thermal parameters, hydrogen atom parameters, all bond lengths and angles, and structure factors are available from the authors.

Description of structure

The crystal structure of Ph$_3$Sn(iprxa) is comprised of discrete molecular units, there being no intermolecular distances significantly less than those expected from normal Van der Waals contacts. The immediate environment of the tin atom involves three carbon atoms derived from each of the phenyl groups and a sulphur atom of the iprxa ligand. The geometry about the tin atom may be considered as tetrahedral with the most obvious deviation from an ideal tetrahedral arrangement being manifested in the C(1)–Sn–S(1) angle of 100.6(1)°. The distortion of the tin atom geometry appears to be due to the presence of an additional Sn · · · O interaction. The xanthate ligand is orientated so that the sulphur atom, S(2), is directed away from the tin atom with the result that the oxygen atom, O(1), is in

TABLE 2

INTERATOMIC BOND DISTANCES(Å) AND ANGLES (°) FOR Ph₃Sn(iprxa)

Atoms	Distance	Atoms	Distance
Sn–C(1)	2.136(4)	S(1)–C(19)	1.748(5)
Sn–C(7)	2.126(5)	S(2)–C(19)	1.636(5)
Sn–C(13)	2.130(5)	C(19)–O(1)	1.310(5)
Sn–S(1)	2.445(1)	Sn · · · O(1)	2.950(3)

Atoms	Angle	Atoms	Angle
C(1)–Sn–C(7)	108.1(2)	C(13)–Sn–S(1)	106.1(1)
C(1)–Sn–C(13)	114.2(2)	Sn–S(1)–C(19)	100.0(1)
C(1)–Sn–S(1)	100.6(1)	S(1)–C(19)–S(2)	120.8(3)
C(7)–Sn–C(13)	113.2(2)	S(1)–C(19)–O(1)	111.6(3)
C(7)–Sn–S(1)	114.2(1)	S(2)–C(19)–O(1)	127.5(4)

close proximity of the tin atom. The Sn · · · O(1) distance of 2.950(3) Å is significantly less than the sum of the Van der Waals radii for Sn and O of 3.7 Å [8] (see Table 2). Inclusion of the O(1) atom in the coordination sphere results in the overall geometry being trigonal bipyramidal with two phenyl groups in axial positions.

The Sn–C bond distances of ca. 2.13 Å are as expected. The C(19)–S(2) bond distance of 1.636(5) Å is significantly shorter than the C(19)–S(1) bond length of 1.748(3) Å which reflects the non-coordinating position of the S(2) atom.

Discussion

Clearly the substitution of the chloride atom in Ph₂Sn(iprxa)Cl [5] by another phenyl group results in a major change in the mode of coordination of the xanthate ligand. In Ph₂Sn(iprxa)Cl [5], the xanthate ligand chelates the tin atom via the two sulphur atoms, albeit with dissimilar Sn–S bond distances of 2.450(2) and 2.826(1) Å. In contrast, the xanthate ligand in Ph₃Sn(iprxa) appears to function as a S and O donor ligand.

In 1980 Tsipsis et al. [9] noted that in all metal xanthates in which a xanthate moiety behaves as a monodentate ligand the orientation of the xanthate ligand was

TABLE 3

CENTRAL-ATOM–OXYGEN DISTANCES (Å) WHERE THE XANTHATE LIGAND IS ROTATED ABOUT THE C–S(1) BOND

Compound [a]	A · · · O	Sum of Van der Waals radii [8]	Ref.
(η-C₅H₅)Ni(PPh₃)exa	3.302	3.1	9
[Cd(exa)₃]⁻	2.956(8)	3.1	10
[Te(exa)₃]⁻	3.278(8)	3.6	11
Sn(exa)₄	3.348, 3.184	3.7	1
Sn(oxin)₂(exa)₂	3.183, 3.262	3.7	12
Ph₃Sn(iprxa)	2.950(3)	3.7	this work
PPh₃Au(mexa)	2.959(3)	3.2	13

[a] oxin = 8-hydroxyquinolate; mexa = O-methylxanthate.

such that the oxygen atom, rather than the non-bonding sulphur atom, was located nearest to the central atom. For their compound, $(\eta\text{-}C_5H_5)Ni(PPh_3)(exa)$, the Ni $\cdots$ O distance of 3.303 Å was considered too long to indicate any bonding between these atoms. We have now re-examined all those metal xanthate structures where such a rotation about the C–S(1) bond is observed. The results are summarized in Table 3. With the exception of the nickel complex of Tsipsis et al [9], the A $\cdots$ O distances are shorter than the sum of their respective Van der Waals radii. In some instances the difference is small and possibly not significant. However, for $Ph_3Sn(iprxa)$, the difference is ca. 0.7 Å which indicates a relatively strong interaction between the Sn and O(1) atoms. This observation provides an interesting example in which a chelating xanthate ligand is found to coordinate via a sulphur atom and an oxygen atom in contrast to the commonly observed S, S-chelation.

Acknowledgements

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