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Crystal structure of bis(*O*-isopropyldithiocarbonato)-diphenyltin(IV)

Neil Donoghue and Edward R.T. Tiekink

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001 (Australia)

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Abstract

The crystal structure of the title compound, $[Ph_2Sn(S_2CO^iPr)_2]$, shows the Sn atom to exist in a skew-trapezoidal planar geometry defined by two asymmetrically coordinated isopropylxanthate ligands (Sn–S(1) 2.482(1), Sn–S(2) 3.179(1) Å and Sn–S(3) 2.500(1), Sn–S(4) 3.067(1) Å) and two phenyl groups that lie over the weaker Sn–S interactions giving a C–Sn–C angle of 128.6(1)°.

Introduction

The xanthate ligand, ^-S_2COR, is known to adopt a variety of coordination modes, ranging from monodentate coordination, in which only one S atom is involved in bonding to the central atom, to bidentate chelation in which equivalent central atom to S bonds are formed. More interesting, however, is an intermediate mode of coordination often found in Main Group xanthate complexes in which both a strong and weak central atom to S bond is formed. Attempts to account for this mode have focused on (i) the stereochemical effect of lone-pairs of electrons found in many of the Main Group xanthate complexes [1], and (ii) the dominance of different canonical forms of the xanthate ligand depending on the Lewis acidity of the central atom [2–4].

Some of the structurally characterised tin(IV) xanthates also feature this intermediate mode of coordination, and as the Sn atom does not possess a stereochemically active lone-pair of electrons, one of the possible explanations cited above is precluded [1]. The absence of (i) as a factor makes tin(IV) xanthates attractive species for testing the hypotheses embodied in (ii) [2–4]. So far three mononuclear organotin xanthates, namely $[Ph_3Sn(S_2CO^iPr)]$ [5], $[Ph_2Sn(S_2CO^iPr)Cl]$ [6] and $[Me_2Sn(S_2COEt)_2]$ [7], have been investigated. In the case of the first two compounds, containing phenyltin functions, there is an opportunity to examine the effect on the xanthate coordination of replacing an electropositive phenyl group in $[Ph_3Sn(S_2CO^iPr)]$ or an electronegative Cl group in $[Ph_2Sn(S_2CO^iPr)Cl]$ by a

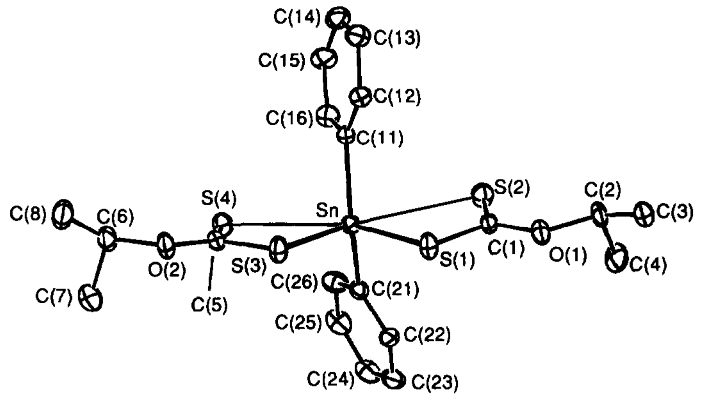

Fig. 1. Molecular structure and crystallographic numbering scheme employed for $[Ph_2Sn(S_2CO^iPr)_2]$.

second S_2CO^iPr ligand. Thus we have determined the crystal structure of $[Ph_2Sn(S_2CO^iPr)_2]$.

Results and discussion

The molecular structure of $[Ph_2Sn(S_2CO^iPr)_2]$ is shown in Fig. 1 and selected interatomic parameters are listed in Table 1. The crystal structure is made up of discrete molecules, with no significant intermolecular interactions. The Sn atom

Table 1
Selected interatomic parameters (Å, deg.) for $[Ph_2Sn(S_2CO^iPr)_2]$

Sn-S(1)	2.482(1)	Sn-S(3)	2.500(1)
Sn-S(2)	3.179(1)	Sn-S(4)	3.067(7)
S(1)-C(1)	1.747(3)	S(3)-C(5)	1.733(3)
S(2)-C(1)	1.652(3)	S(4)-C(5)	1.663(3)
C(1)-O(1)	1.320(4)	C(5)-O(2)	1.320(3)
O(1)-C(2)	1.475(3)	O(2)-C(6)	1.480(3)
Sn-C(11)	2.125(2)	Sn-C(21)	2.132(2)
S(1)-Sn-S(2)	62.5(1)	S(1)-Sn-S(3)	84.0(1)
S(1)-Sn-S(4)	147.7(1)	S(1)-Sn-C(11)	109.9(1)
S(1)-Sn-C(21)	105.5(1)	S(2)-Sn-S(3)	145.5(1)
S(2)-Sn-S(4)	149.7(1)	S(2)-Sn-C(11)	79.3(1)
S(2)-Sn-C(21)	85.4(1)	S(3)-Sn-S(4)	64.0(1)
S(3)-Sn-C(11)	107.0(1)	S(3)-Sn-C(21)	112.8(1)
S(4)-Sn-C(11)	84.5(1)	S(4)-Sn-C(21)	85.0(1)
C(11)-Sn-C(21)	128.6(1)	Sn-S(1)-C(1)	97.5(1)
Sn-S(2)-C(1)	76.0(1)	Sn-S(3)-C(5)	95.0(1)
Sn-S(4)-C(5)	77.9(1)	S(1)-C(1)-S(2)	123.7(2)
S(1)-C(1)-O(1)	108.9(2)	S(2)-C(1)-O(1)	127.5(2)
C(1)-O(1)-C(2)	121.7(2)	S(3)-C(5)-S(4)	123.3(2)
S(3)-C(5)-O(2)	110.6(2)	S(4)-C(5)-O(2)	126.1(2)
C(5)-O(2)-C(6)	120.8(2)	Sn-C(11)-C(12)	120.1(2)
Sn-C(11)-C(16)	120.5(2)	C(12)-C(11)-C(16)	119.3(2)
Sn-C(21)-C(22)	120.0(2)	Sn-C(21)-C(26)	120.6(2)
C(22)-C(21)-C(26)	119.4(2)		

exists in a skew-trapezoidal planar geometry defined by two asymmetrically coordinating xanthate ligands and two phenyl substituents. The phenyl groups lie over the weaker Sn–S bonds and define a C(11)–Sn–C(21) angle of 128.6(1)°. While the individual S_2CO chromophores are planar, the Sn atom and four S atoms deviate significantly from planarity; the dihedral angle between the least-squares plane defining each S_2CO group is 13.0°.

The degrees of asymmetry in the mode of coordination of each xanthate ligand, while comparable, are not equivalent. The first ligand forms Sn–S(1) and Sn–S(2) bond distances of 2.482(1) and 3.179(1) Å, respectively, and the other forms Sn–S(3) and Sn–S(4) bonds at 2.500(1) and 3.067(1) Å, respectively. These differences yield values of 0.697 and 0.567 Å, respectively for Δ(Sn–S), and are reflected in the associated C–S bond distances. As expected, the C–S bond distances for the S atoms bound strongly to the Sn centre are longer than the shorter C–S bonds that involve the S atoms forming the weaker bonds to the Sn atom. Furthermore, the greater the degree of asymmetry in the mode of coordination of the xanthate ligand the greater is the difference in the C–S values, i.e. 0.95 and 0.70 Å, respectively. The remaining parameters defining the xanthate ligands are normal, and agree well with previous examples.

The availability of three crystal structures containing phenyltin moieties and isopropylxanthate ligands allows a comparison of the variation of the coordination mode of the xanthate ligand as the Lewis acidity of the Sn centre is altered. In our investigations we have kept the alkyl substituent on the xanthate ligand constant in order to avoid any additional factors, such as electronic or steric requirements of the ligand, that might influence the interpretation of the various possible coordination modes. Crystallographic investigations of related xanthate [e.g. 8], dithiocarbamate [e.g. 9] and carboxylate [10] complexes, have shown that very different structures, including different coordination numbers and stereochemistries for the central atom, may arise as a result of a change in the nature of the remote terminal R substituent on the ligand. This point is best illustrated by the case of the two dithiophosphate complexes related to the title compound, $[Ph_2Sn(S_2P(OEt)_2)_2]$ [11] and $[Ph_2Sn(S_2P(O^iPr)_2)_2]$ [12]. In the former complex, the dithiophosphate ligand is coordinated in the monodentate mode (Sn–S(1) 2.49(1), Sn–S(2) 3.23(1) Å and Sn–S(3) 2.481(9), Sn–S(4) 3.20(1) Å) and the C–Sn–C angle is 135(1)°, whereas in the isopropyl ester the Sn atom is located on a crystallographic centre of inversion constraining the C–Sn–C to 180°. Furthermore, in $[Ph_2Sn(S_2P(O^iPr)_2)_2]$ the two Sn–S distances are almost equivalent, at 2.678(1) and 2.689(1) Å [12].

The structures available for comparison may be related to that of the triphenyltin species $[Ph_3Sn(S_2CO^iPr)]$ [5]. In this compound the tetrahedral Sn geometry is defined by three phenyl substituents and a S atom derived from a monodentate $^-S_2CO^iPr$ ligand; the Sn–S separation is 2.445(1) Å. The orientation of the xanthate ligand in this structure was of much interest because the O atom, rather than the non-coordinated S atom, was directed towards the Sn atom. This separation of 2.956(8) Å was interpreted as indicating a rare example of a *S,O*-coordination mode for the xanthate ligand [5]. Subsequent studies [13] seem to indicate that the weak central atom to O(xanthate) interactions probably arise as a result of crystal packing effects rather than any other factor. Nevertheless, for $[Ph_3Sn(S_2CO^iPr)]$ an essentially monodentate coordination for the $^-S_2CO^iPr$

ligand was found. Replacement of one phenyl group in [$Ph_3Sn(S_2CO^iPr)$] by a chloride ligand, to yield [$Ph_2Sn(S_2CO^iPr)Cl$] [6], has a profound effect on the structure. The Sn atom is now best described as being five-coordinate, with a distorted trigonal bipyramidal geometry. The equatorial plane is defined by the two phenyl substituents and one S atom of the asymmetrically chelating ligand such that Sn–S(1) is 2.450(2) Å (i.e. equal within experimental error to the Sn–S(1) bond length in [$Ph_3Sn(S_2CO^iPr)$] [5]). The axial positions are occupied by the second S atom (Sn–S(2) 2.826(1) Å) and the Cl substituent; Sn–Cl 2.426(1) Å and S(2)–Sn–Cl 156.3(1)°. While the Sn–S(2) bond distance is long compared to the sum of the covalent radii for Sn and S of 2.42 Å, it is well within the sum of the van der Waals radii for these atoms (4.0 Å). The presence of the Cl atom in [$Ph_2Sn(S_2CO^iPr)Cl$] has the effect of increasing the Lewis acidity of the Sn centre and thereby enables the close association of the second S atom, which is non-bonding in [$Ph_3Sn(S_2CO^iPr)$] [5]. If on the other hand one phenyl group in [$Ph_3Sn(S_2CO^iPr)$] is replaced by a somewhat less electronegative ligand, i.e. $^-S_2CO^iPr$, as in the title compound, the coordination mode of the xanthate ligand is intermediate between the two types displayed in the [$Ph_3Sn(S_2CO^iPr)$] [5] and [$Ph_2Sn(S_2CO^iPr)Cl$] [6] complexes.

The different coordination modes found for the $^-S_2CO^iPr$ ligands can be rationalized in terms of the valence bond approach, described previously [4], in which it is assumed that Sn–bound *d* orbitals play no significant role in bonding. As the Lewis acidity of the Sn centre is increased, i.e. in the order $Ph_2SnCl > Ph_2Sn(S_2CO^iPr) > Ph_3Sn$, non-dative canonical forms tend to dominate the overall resonance structure, leading to equivalent Sn–S bond distances.

A final structure for comparison is that of the dimethyltin analogue, [$Me_2Sn(S_2COEt)_2$] [7]. Although the R group of the xanthate ligand has been changed, the structural variation seen for the dithiophosphate complexes cited above [11,12] is not apparent. The molecular structure found for [$Me_2Sn(S_2COEt)_2$] [7] is essentially similar to that found for the diphenyltin analogue, although the molecule has crystallographic symmetry such that the Sn atom and the two $^-S_2COEt$ ligands lie on a mirror plane. It is noteworthy that the degree of asymmetry in the Sn–S bonds is comparable for the two compounds, although this may reflect the different electronic profile of the two R groups of the xanthate ligands.

Experimental

Synthesis

[$Ph_2Sn(S_2CO^iPr)_2$], a known compound [6], was prepared by the addition of an aqueous solution of a 2.1 molar equivalent of potassium isopropylxanthate to a stirred solution of [Ph_2SnCl_2] (Aldrich, 1.0 g, 50 ml CH_2Cl_2). The mixture was stirred for 2 h, and the organic layer separated, dried over $MgSO_4$, and evaporated to yield a white solid. This was recrystallized from CH_2Cl_2/ethanol (yield 0.65 g, 41%) to give crystals suitable for X-ray diffraction studies; m.p. 93–94 °C. In the infrared spectrum (Perkin-Elmer 1700X FT) characteristic xanthate absorptions were observed in the regions 1219, 1022, 450 cm^{-1} assigned to ν(C–O), ν(C–S) and ν(Sn–S), respectively.

Table 2

Crystal data and refinement details for $[Ph_2Sn(S_2CO^iPr)_2]$

Formula	$C_{20}H_{24}O_2S_4Sn$
Mol. wt.	543.3
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	7.672(2)
b, Å	16.147(3)
c, Å	19.021(5)
β, deg.	97.00(2)
V, Å^3	2338.8
Z	4
D_c, g cm^{-3}	1.543
$F(000)$	1096
μ, cm^{-1}	13.42
T, K	293
No. of data collected	4339
No. of unique data	3064
No. of unique reflections used with $I \geqslant 2.5\sigma(I)$	2590
R	0.021
k	2.83
g	0.003
R_w	0.024
Residual ρ_{max}, e Å^{-3}	0.22

Table 3

Fractional atomic coordinates ($\times 10^5$ for Sn, $\times 10^4$ for other atoms) for $[Ph_2Sn(S_2CO^iPr)_2]$

Atom	x	y	z
Sn	37286(2)	13874(1)	21638(1)
S(1)	3028(1)	1144(1)	3387(1)
S(2)	6882(1)	1468(1)	3412(1)
S(3)	467(1)	1383(1)	1855(1)
S(4)	2378(1)	1543(1)	584(1)
O(1)	5138(2)	1099(1)	4503(1)
O(2)	−1077(2)	1622(1)	625(1)
C(1)	5163(4)	1237(2)	3820(2)
C(2)	6737(4)	1170(2)	5015(2)
C(3)	6085(4)	1245(2)	5720(2)
C(4)	7888(4)	428(2)	4959(2)
C(5)	525(3)	1521(2)	955(2)
C(6)	−1373(4)	1749(2)	−152(1)
C(7)	−1551(5)	915(2)	−515(2)
C(8)	−3010(4)	2264(2)	−273(2)
C(11)	4584(3)	2628(2)	2061(1)
C(12)	4044(4)	3238(2)	2490(2)
C(13)	4600(4)	4045(2)	2424(2)
C(14)	5679(4)	4252(2)	1927(2)
C(15)	6246(4)	3648(2)	1502(2)
C(16)	5710(4)	2831(2)	1566(2)
C(21)	4928(3)	271(2)	1864(1)
C(22)	4778(3)	−441(2)	2247(2)
C(23)	5527(4)	−1173(2)	2043(2)
C(24)	6433(4)	−1185(2)	1465(2)
C(25)	6622(4)	−475(2)	1095(2)
C(26)	5864(4)	257(2)	1285(2)

Crystallography

Intensity data for a colourless crystal (0.20 × 0.32 × 0.38 mm) of $[Ph_2Sn(S_2CO^iPr)_2]$ were measured at 293 K on an Enraf–Nonius CAD4F diffractometer fitted with graphite monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å. The $\omega:2\theta$ scan technique was used to measure data up to a maximum Bragg angle of 22.5°. The data set was corrected for Lorentz and polarization effects and for absorption by an analytical procedure [14]; maximum and minimum transmission factors were 0.798 and 0.680, respectively. Relevant crystal data are given in Table 2.

The structure was solved by a Patterson synthesis and refined by a full-matrix least-squares procedure based on F [14]. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions. After the inclusion of a weighting scheme of the form $w = [\sigma^2(F) + |g| F^2]^{-1}$, the refinement was continued until convergence; final refinement details are listed in Table 2. The analysis of variance showed no special features, indicating that an appropriate weighting scheme had been applied. Fractional atomic coordinates are listed in Table 3 and the numbering scheme employed is shown in Fig. 1 which was drawn with ORTEP [15] at 25% probability ellipsoids. Scattering factors were as incorporated in the SHELX76 program [14] and the refinement was performed on a SUN4/280 computer. Lists of thermal parameters, hydrogen-atom parameters, all bond distances and angles, and observed and calculated structure factors are available from E.R.T.T.

Acknowledgements

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