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Tin-119 NMR Studies of Alkyl and Aryl Haloxanthates of Tin(IV): The Crystal and Molecular Structure of Diphenyl(*O*-isopropylxanthato)chlorotin(IV)

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Abstract

Tin-119 NMR data are reported for the two series of compounds of the type $R_2Sn(S_2COR')_2$ and $R_2SnX(S_2COR')$ [where R = CH_3, C_6H_5, R′ = C_2H_5, i-C_3H_7, and X = Cl, Br]. In solution both types of compounds appear to have a coordination number less than six. The crystal structure of $\phi_2SnCl(S_2CO\text{-i-}C_3H_7)$ shows that the tin atom is penta-coordinated in a distorted trigonal bipyramidal environment. The iprxa ligand coordinates the tin atom with asymmetric Sn–S bonds of 2.450(2) and 2.826(1) Å. The unit cell of $\phi_2SnCl(S_2CO\text{-i-}C_3H_7)$ is monoclinic, $P2_1/c$, a = 12.206(4), b = 10.825(3), c = 19.374(3) Å and β = 133.32(2)°, Z = 4. The structure was refined by conventional least squares methods with final values of R 0.038 and R_w 0.042 for 3112 unique reflections.

Introduction

Recent tin-119 NMR studies on a series of adducts of tin(IV) halides have demonstrated that the tin-119 chemical shift is sensitive to the coordination number of the tin atom in solution [1, 2] with the four coordinate systems having chemical shifts at higher frequencies relative to those of six coordinate tin species. On this basis tin-119 NMR spectroscopy has indicated that the tin atom in the compounds $Sn(exa)_2$ and $Sn(exa)_2X_2$ [where exa = *O*-ethylxanthato and X = Cl, Br, I] are six coordinate in dichloromethane solution [3]. The halo-tin xanthates $SnX(xan)_3$ and $SnX_3(xan)$ have been identified in solution by tin-119 NMR spectroscopy; $SnX(xan)_3$ has been assigned a six coordinate structure and $SnX_3(xan)$ four coordinate [X = Br] and five coordinate [X = Cl] structures [3]. However, as yet none of these species have been isolated in the solid state.

The position of the tin-119 resonance for $Me_2Sn(exa)_2$ suggests that this compound is essentially four coordinate in solution with exa functioning as a monodentate ligand [4]. Its crystal structure however, shows a distorted octahedral environment about the tin atom in the solid state in which the chelating exa ligands display gross asymmetry in their mode of coordination [4]. We have now extended the tin-119 NMR spectroscopy studies to the series $R_2SnX(S_2COR')$ and $R_2Sn(S_2COR')_2$ [where R = CH_3, C_6H_5; R′ = C_2H_5-i-C_3H_7; X = Cl, Br] and report the crystal structure of a member of the latter series, *i.e.* $(C_6H_5)_2SnCl(iprxa)$ [where iprxa = *O*-isopropylxanthato]. The structure determination was undertaken in order to investigate the nature of the coordination about the tin atom in the solid state and to establish whether in solution the effective coordination of the tin atom is reduced as was observed in $Me_2Sn(exa)_2$ [4].

Experimental

Preparations

The complexes $R_2SnX(xan)$ and $R_2Sn(xan)_2$ were prepared by addition of one and two mol equivalents of Kxan, respectively, to the appropriate R_2SnX_2 compound in dichloromethane solution (Table I). Interestingly none of these preparations led to the formation of $R_4Sn_2X_2O$ species as was obtained from the analogous preparation of $Me_2SnCl(exa)$ [5].

Crystallography

Data Collection

Suitable crystals for X-ray diffraction studies were grown by the slow evaporation of a dichloromethane solution of the compound. Intensity data were collected on an Enraf-Nonius CAD-4F four circle diffractometer. Accurate cell dimensions and an orientation matrix were obtained by a least squares procedure on the setting angles of 25 reflections. The ω:2θ scan technique and MoKα (graphite monochromator) radiation were used to measure the intensities of 5443 reflections of which

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TABLE I. Melting Points (°C), ν(C–O) Frequencies (cm^{-1}) and Tin-119 (ppm) Chemical Shifts for Selected Organotin Compounds.

Compound	Melting point (°C)	ν(C–O) (cm^{-1})	δ(^{119}Sn) (ppm)
Me_2SnBr(exa)	97–99	1250	−150
Me_2SnBr(iprxa)	74–77	1253	−155
Me_2SnCl(exa)	102	1260	−124
Me_2SnCl(iprxa)	86.5–88	1260	−126
$Me_2Sn(exa)_2$^{a}	105–106	1238, 1205	−224
$Me_2Sn(iprxa)_2$	≤40	1230	−222
ϕ_2SnBr(exa)	99–102	1280, 1255	−286
ϕ_2SnBr(iprxa)	137–138.5	1265	−290
ϕ_2SnCl(exa)	98.5–99.5	1255	−276
ϕ_2SnCl(iprxa)	133.5–134.5	1270	−276
$\phi_2Sn(exa)_2$	90–91	1215	−314
$\phi_2Sn(iprxa)_2$	84–85	1230	−300
Me_2SnBr_2^{b}			72
Me_2SnCl_2^{b}			137
ϕ_2SnBr_2^{b}			−75
ϕ_2SnCl_2^{b}			−33

^{a}Ref. [4]. ^{b}Commercial sources.

4110 were unique and 3112 satisfied the $I \geqslant 2\sigma(I)$ criterion of observability; no significant decomposition of the crystal occurred during the data collection. Corrections were applied for Lorentz and polarization effects and for absorption [6] (max. and min. transmission factors 0.7988 and 0.6406).

Crystal Data

ϕ_2SnCl(iprxa): $C_{16}H_{17}ClOS_2Sn$, M = 443.6, monoclinic, $P2_1/c$ (C_{2h}^5, No. 14), a = 12.206(4), b = 10.825(3) and c = 19.374(3) Å, β = 133.32(2)°, U = 1865.0 Å^3, D_{meas} = 1.59 (aqueous zinc bromide solution), $Z = 4$, D_{calc} = 1.580 Mg m^{-3}, $F(000)$ = 880, MoKα (graphite monochromator) radiation λ = 0.71069 Å, $1 \leqslant \theta \leqslant 27.5°$, μ = 1.60 mm^{-1}, no. parameters/no. variables = 16.

Solution and Refinement of Structure

The position of the Sn atom was located from the three-dimensional Patterson synthesis and all non-hydrogen atoms were located from subsequent difference maps. Initially their positional and individual isotropic thermal parameters were refined, R 0.104 where $R = \Sigma\Delta/\Sigma|F_o|$. The structure was refined using a full-matrix least squares procedure in which the function, $\Sigma w\Delta^2$ was minimized, where w was the weight applied to each reflection and $\Delta = ||F_o| - |F_c||$. Anisotropic thermal parameters were introduced and subsequently hydrogen atoms included in the model at their calculated positions. A weighting scheme, $w = [\sigma^2(F) + 0.0005|F|^2]^{-1}$ was applied and refinement continued until convergence; R 0.038 and R_w 0.042 where $R_w = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|$. The analysis of variance showed no special features and the maximum residual electron density peak in the final difference map was 0.7 eÅ^{-3} located near the sulphur atom involved in the weak Sn–S interaction.

The scattering factors used for all atoms were those listed by Sheldrick [7]. Structure determination and refinement were performed using the SHELX-76 [7] program system and the University of Melbourne's CYBER 170-730 computer system.

The fractional atomic coordinates and their estimated standard deviations are listed in Table II and the numbering scheme used is shown in Fig. 1.

TABLE II. Fractional Atomic Coordinates for ϕ_2SnCl(iprxa). (e.s.d.s in parentheses in this and all other tables).

Atom	x/a	y/b	z/c
Sn	0.10036(3)	0.14885(3)	0.22004(2)
Cl	0.1623(2)	−0.0550(1)	0.2034(1)
S(1)	0.2428(2)	0.2374(1)	0.1855(1)
S(2)	0.0901(1)	0.4097(1)	0.2150(1)
C(1)	0.1955(5)	0.3859(4)	0.1914(3)
O(1)	0.2531(4)	0.4700(3)	0.1753(3)
C(2)	0.2253(7)	0.6037(5)	0.1762(4)
C(3)	0.1098(11)	0.6436(6)	0.0760(6)
C(4)	0.3705(10)	0.6636(7)	0.2289(8)
C(5)	0.2093(5)	0.1423(4)	0.3649(3)
C(6)	0.2904(6)	0.0390(5)	0.4181(4)
C(7)	0.3568(7)	0.0330(7)	0.5135(5)
C(8)	0.3392(8)	0.1261(7)	0.5514(5)
C(9)	0.2597(9)	0.2270(7)	0.5000(5)
C(10)	0.1935(7)	0.2375(6)	0.4059(4)
C(11)	−0.1366(6)	0.1430(4)	0.1030(4)
C(12)	−0.1964(8)	0.0894(7)	0.0194(5)
C(13)	−0.3560(11)	0.0841(9)	−0.0565(5)
C(14)	−0.4432(9)	0.1328(8)	−0.0454(7)
C(15)	−0.3838(7)	0.1898(8)	0.0400(6)
C(16)	−0.2287(6)	0.1936(6)	0.1126(4)

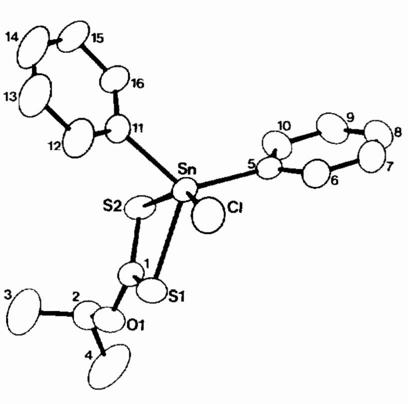

Fig. 1. The numbering scheme used for ϕ_2SnCl(iprxa). Atoms otherwise not indicated are carbons.

Listings of anisotropic thermal parameters, hydrogen atom parameters, and the observed and calculated structure factors have been deposited with the Editors.

Results and Discussion

Tin-119 chemical shifts for the complexes R_2-SnX(xan) and R_2Sn(xan)$_2$, in dichloromethane solution, cover a comparatively small range between −124 and −314 ppm and are at lower frequencies than shifts observed for related compounds which are thought to be four coordinate in solution, (Table I), but at substantially higher frequencies than those associated with six coordinate tin species. Variation of X from Cl to Br shows a low frequency shift as expected for the decreased electronegativity of the halogen which in turn increases the shielding about the tin nucleus. The positions of the tin-119 resonances for variation of R group from CH_3 to C_6H_5 are at lower frequencies in line with the relative electron donating properties of these substituents.

Description of Structure

Relevant interatomic distances and angles are given in Tables III and IV respectively. The crystals consist of discrete molecules of ϕ_2SnCl(iprxa) as is shown in Fig. 2, there being no significant intermolecular interactions. The tin atom is pentacoordinated with a distorted trigonal bipyramidal environment. An approximate trigonal plane is defined by the atoms S(1), C(5) and C(11) with both the S(2) and Cl atoms occupying those sites which approximate to the axial positions of the trigonal bipyramidal polyhedra. The restricted bite angle of the iprxa ligand [S(1)–Sn–S(2) 67.8(5)°] causes considerable distortion from the ideal value of 90°.

TABLE III. Bond Distances (Å) for ϕ_2Sn(iprxa)Cl.

Atoms	Distance	Atoms	Distance
Sn–Cl	2.426(1)	C(7)–C(8)	1.35(1)
Sn–S(1)	2.450(2)	C(8)–C(9)	1.34(1)
Sn–S(2)	2.826(1)	C(9)–C(10)	1.402(9)
S(1)–C(1)	1.739(5)	C(10)–C(5)	1.394(8)
S(2)–C(1)	1.657(5)	Sn–C(11)	2.124(5)
C(1)–O(1)	1.313(5)	C(11)–C(12)	1.367(9)
O(1)–C(2)	1.490(6)	C(12)–C(13)	1.43(1)
C(2)–C(3)	1.48(1)	C(13)–C(14)	1.33(1)
C(2)–C(4)	1.46(1)	C(14)–C(15)	1.41(1)
Sn–C(5)	2.127(4)	C(15)–C(16)	1.382(9)
C(5)–C(6)	1.376(7)	C(16)–C(11)	1.375(7)
C(6)–C(7)	1.421(9)		

TABLE IV. Bond Angles (°) for ϕ_2Sn(iprxa)Cl.

Atoms	Angle	Atoms	Angle
Cl–Sn–S(1)	88.53(6)	C(3)–C(2)–C(4)	113.3(7)
Cl–Sn–S(2)	156.25(6)	Sn–C(5)–C(6)	119.5(4)
Cl–Sn–C(5)	100.1(1)	Sn–C(5)–C(10)	121.5(4)
Cl–Sn–C(11)	98.8(1)	C(5)–C(6)–C(7)	119.1(5)
S(1)–Sn–S(2)	67.8(5)	C(6)–C(7)–C(8)	120.8(7)
S(1)–Sn–C(5)	117.1(1)	C(7)–C(8)–C(9)	120.6(7)
S(1)–Sn–C(11)	115.1(1)	C(8)–C(9)–C(10)	120.5(7)
S(2)–Sn–C(5)	93.0(1)	C(9)–C(10)–C(5)	120.0(6)
S(2)–Sn–C(11)	89.9(1)	C(10)–C(5)–C(6)	119.0(5)
C(5)–Sn–C(11)	124.5(2)	Sn–C(11)–C(12)	120.3(4)
Sn–S(1)–C(1)	90.7(2)	Sn–C(11)–C(16)	119.1(4)
Sn–S(2)–C(1)	80.2(2)	C(11)–C(12)–C(13)	118.6(7)
S(1)–C(1)–O(1)	111.6(3)	C(12)–C(13)–C(14)	119.8(8)
S(2)–C(1)–O(1)	127.1(3)	C(13)–C(14)–C(15)	122.5(7)
S(1)–C(1)–S(2)	121.3(3)	C(14)–C(15)–C(16)	116.6(5)
C(1)–O(1)–C(2)	120.5(4)	C(15)–C(16)–C(11)	121.9(6)
O(1)–C(2)–C(3)	106.8(5)	C(16)–C(11)–C(12)	120.6(6)
O(1)–C(2)–C(4)	105.2(5)		

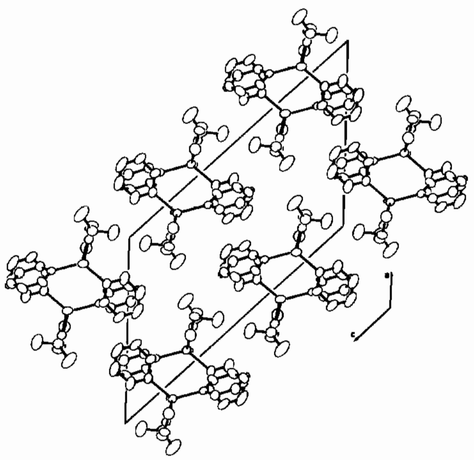

Fig. 2. A [010] projection of the unit cell contents of ϕ_2-SnCl(iprxa).

The iprxa ligand chelates the tin atom with asymmetric Sn–S distances of 2.450(2) and 2.826(1) Å, this asymmetry being reflected in the associated C–S bonds of 1.739(5) and 1.657(5) Å. The Sn–C bond distances are comparable to those observed in related structures. The Sn–Cl distance of 2.426(1) Å is substantially longer than the corresponding bond distances of 2.376(2) and 2.374(1) Å in Sn(exa)$_2$Cl$_2$ [8].

The crystal structure of ϕ_2SnCl(iprxa) is so far the only known example of a Sn(IV) xanthate complex in which the tin atom is other than six coordinate in the solid state. The structure of a related dimethyldithiocarbamate complex, $(CH_3)_2$-

SnCl(dmdtc) [9], has been reported in which the tin atom also exists in a distorted trigonal bipyramidal geometry. The organo substituents occupy equatorial positions, as in ϕ_2SnCl(iprxa), and the dmdtc ligand displays a similar mode of coordination as does the iprxa ligand.

The asymmetry observed in the mode of the Sn–S coordination in ϕ_2SnCl(iprxa) of about 0.38 Å is intermediate between 0.62 Å in $Me_2Sn(exa)_2$ [4] and 0.05–0.12 Å in $Sn(exa)_2L_2$, [where L = Cl [8], Br [10], I [10] and exa [11]]. The solid state structures of ϕ_2SnCl(iprxa) and $Me_2Sn(exa)_2$ [4] have a common feature in that in both structures long and short Sn–S bonds are observed. It is probable that in solution these long Sn–S bonds are labile with the result that the xanthate ligands become essentially monodentate and impart a lower effective coordination number about the tin atom.

Instrumentation

Tin-119 NMR spectra were recorded at room temperature on a JEOL FX-100 spectrometer using an external ^{7}Li lock and were referenced against external Me_4Sn.

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