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Crystal Structure of [Chloro(diethyldithiocarbamato)butyl phenyl]tin(IV)

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Abstract

The crystal structure of the title compound, $SnCl(C_6H_5)(C_4H_9)[S_2CN(C_2H_5)_2]$, was determined and refined to an R factor of 3.2% for 4876 reflections. The molecule contains five-coordinate tin in a distorted trigonal bipyramidal arrangement with the tin atom lying 0.20 Å below the equatorial plane formed by one of the sulphur atoms, S(1), and the donor carbons of the butyl and phenyl groups. The chlorine and the other sulphur atom, S(2), occupy axial sites, making a S(2)–Sn–Cl angle of 156.85(1)°. The Sn–S(2) bond is markedly elongated (2.764(1) Å) compared to the Sn–Cl bond (2.449(1) Å) and the Sn–S(1) bond (2.454(1) Å). The structure resembles those of analogues such as $(C_6H_5)_2Sn$(glygly) in having both hydrocarbon ligands located in the equatorial plane. Crystal data: space group $P\bar{1}$; a = 8.291(2) Å, b = 14.726(3) Å, c = 9.509(2) Å, α = 96.24(2)°, β = 107.02(3)°, γ = 116.70(2)°, Z = 2, R = 3.2% for 4876 independent reflections.

Introduction

X-ray evidence for discrete non-interacting five-coordinate diorganotin(IV) structures, R_2SnX_3, has been reported in the literature for relatively few cases as in Ph_2Sn(SAT) {SAT = 2-(o-hydroxyphenyl)-benzthiazoline dianion} [1], Ph_2Sn(SAB) {SAB = 2-hydroxy-N-(2-hydroxy benzyldine)aniline dianion} [2], Ph_2Sn(glygly) {glygly = glycylglycinato dianion} [3], $Ph_2SnCl_2 \cdot BT$ {BT = benzthiazole} [4], $Ph_2SnCl_2 \cdot$(2,6-Lutidine N-oxide) [5], $Me_2SnCl(S_2CNMe_2)$ [6], $Me_2SnCl[SCH_2CH(NH_2)CO_2Et]$ [7] and the anion in $[Me_2SnCl(terpy)]^+[Me_2SnCl_3]^-$ [8]. These molecules possess trigonal bipyramidal geometry at tin with both the R groups located in the equatorial plane.

In an attempt to determine the effects on structure and bonding when mixed ligand groups reside on tin, we have studied among other model compounds the complex $PhBuSnCl(S_2CNEt_2)$. This complex was predicted on the basis of its Mössbauer spectrum to have a similar C_2Sn skeletal geometry as in $Me_2SnCl(S_2CNMe_2)$ [9]. Its observed quadrupole splitting of 2.66 mm s^{-1} is intermediate between the values for the dialkyltin (2.9 mm s^{-1}) and diphenyltin (2.3 mm s^{-1}) analogues. However, it has been pointed out that the observed splittings for the diphenyltin derivatives are also consistent with an alternative isomeric *cis*-structure, with one phenyl group axially disposed and the other situated in the equatorial plane [10]. To the extent that deviations from ideal geometry and experimental errors impinge on the tolerance limit (±0.4 mm s^{-1}) of the additive model for the interpretation of electric field gradients in five-coordinate organotin systems, a degree of uncertainty also accompanies the Mössbauer structural characterization of the mixed alkyl–aryl complex, $PhBuSnCl(S_2CNEt_2)$. It was therefore of interest to ascertain its structure from single crystal study.

Experimental

The title compound was synthesised as reported previously [9]. Single crystals suitable for X-ray crystallography were obtained by recrystallization from benzene. The compound is soluble in the common dense organic solvents, and its exact density could, as a consequence, not be determined.

Cell Measurements and Data Collection

Cell dimensions and space group data (Table I) were obtained by standard methods at room temperature on an Enraf-Nonius four-circle CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation. The θ–2θ scan technique was used, as previously described [11], to record the intensities

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TABLE I. Crystallographic Details for [SnClPhBu(S_2CNEt_2)].

formula wt.	436
crystal system	triclinic
a; b; c (Å)	8.291(2); 14.726(3); 9.509(2)
α, β; γ (deg)	96.24(2); 107.02(3); 116.70(2)
V, Å^3	952
space group	$P\bar{1}$
Z	2
ρ(calcd.), g cm^{-3}	1.52
Crystal dimensions, mm	
$(10\bar{1})$ to $(\bar{1}01)$	0.40
(010) to $(0\bar{1}0)$	0.45
(001) to $(00\bar{1})$	0.55
μ(MoKα), cm^{-1}	16.9
transmission coefft., max/min	0.670/0.512
scan type	$\theta - 2\theta$

for all nonequivalent reflections for which $1.5° < 2\theta < 62°$. Scan widths were calculated as (A + B tan θ)°, where A is estimated from the mosaicity of the crystal and B allows for the increase in peak width due to Kα1–Kα2 splitting. The values of A and B were 0.6 and 0.35 respectively.

The intensities of three standard reflections showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects and for absorption. Of the 7154 independent intensities, there were 4876 with $F_0^2 > 3\sigma(F_0^2)$, where $\sigma(F_0^2)$ was estimated from counting statistics [12]. These data were used in the final refinement of the structural parameters.

Structure Determination and Refinement

A three-dimensional Patterson synthesis was used to determine the heavy atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier syntheses. Full-matrix least squares refinement was carried out as previously described [11]. Anisotropic temperature factors were introduced for the non-hydrogen atoms. Further Fourier difference functions permitted location of the non-methyl hydrogen atoms, which were included in the refinement for four cycles of least squares and then held fixed. The model converged with R = 3.2% and R_w = 3.6%. A final Fourier difference map was featureless. The thermal parameters and lists of observed and calculated structure factors are available from the editor. The principal programs used are as described previously [11].

Results and Discussion

Final positional parameters for the atoms are given in Table II. Intramolecular bond distances and angles are given in Table III, and least-squares planes data in Table IV. The digits in parentheses in tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Atomic numbering and a stereoview of the molecule are shown in Fig. 1, while Fig. 2 shows the molecular packing diagram

TABLE II. Final Positional Parameters (Å) for [SnClPhBu(S_2CNEt_2)].

Atom	x	y	z
Sn	0.27334(3)	0.31348(2)	0.07607(2)
Cl	0.5208(1)	0.48697(8)	0.2591(1)
S(1)	0.0927(1)	0.39694(6)	−0.0445(1)
S(2)	−0.0584(1)	0.16948(6)	−0.1776(1)
N	−0.2255(4)	0.2763(2)	−0.2960(3)
C(N)	−0.0814(4)	0.2785(2)	−0.1867(3)
C(M1)	−0.2476(5)	0.3705(3)	−0.3013(5)
C(E1)	−0.1438(7)	0.4350(3)	−0.3901(6)
C(M2)	−0.3698(6)	0.1801(3)	−0.4255(5)
C(E2)	−0.5388(7)	0.1083(4)	−0.3898(7)
C(1)	0.1688(4)	0.2346(2)	0.2335(3)
C(2)	0.2121(5)	0.2921(3)	0.3778(4)
C(3)	0.1388(5)	0.2400(3)	0.4790(4)
C(4)	0.0269(5)	0.1319(3)	0.4375(4)
C(5)	−0.0128(6)	0.0740(3)	0.2955(5)
C(6)	0.0562(6)	0.1254(3)	0.1929(4)
C(B1)	0.4514(5)	0.2908(3)	−0.0326(4)
C(B2)	0.6326(7)	0.3005(4)	0.0660(7)
C(B3)	0.6194(7)	0.2280(5)	0.1709(7)
C(B4)	0.5371(13)	0.1211(5)	0.1107(10)
H(11M)	−0.382(4)	0.349(2)	−0.347(4)
H(12M)	−0.201(4)	0.414(3)	−0.199(4)
H(21M)	−0.306(5)	0.144(3)	−0.458(4)
H(22M)	−0.417(5)	0.197(3)	−0.517(4)
H(2)	0.296(4)	0.370(2)	0.407(4)
H(3)	0.166(5)	0.281(3)	0.579(4)
H(4)	−0.024(4)	0.097(2)	0.510(4)
H(5)	−0.084(4)	0.001(3)	0.271(4)
H(6)	0.027(5)	0.087(3)	0.094(4)
H(11E)	−0.180(5)	0.383(3)	−0.496(4)
H(12E)	−0.009(5)	0.469(3)	−0.336(4)
H(13E)	−0.176(5)	0.488(3)	−0.401(5)
H(21E)	−0.609(5)	0.139(3)	−0.345(4)
H(22E)	−0.501(5)	0.076(3)	−0.311(4)
H(23E)	−0.632(5)	0.056(3)	−0.485(4)
H(11B)	0.486(5)	0.349(3)	−0.088(5)
H(12B)	0.383(6)	0.212(3)	−0.094(5)
H(21B)	0.716(6)	0.382(3)	0.148(5)
H(22B)	0.717(5)	0.298(3)	−0.002(4)
H(31B)	0.762(5)	0.257(3)	0.247(4)
H(32B)	0.559(5)	0.244(3)	0.237(4)

TABLE III. Interatomic Bond Distances (Å) and Angles (°) for [$SnClPhBu(S_2CNEt_2)$].

a) Bond distances			
Sn–Cl	2.449(1)	C(M2)–C(E2)	1.490(1)
Sn–S(1)	2.454(1)	C(1)–C(2)	1.384(1)
Sn–S(2)	2.764(1)	C(1)–C(6)	1.383(1)
Sn–C(1)	2.138(1)	C(2)–C(3)	1.403(1)
Sn–C(B1)	2.148(1)	C(3)–C(4)	1.368(1)
S(1)–C(N)	1.742(1)	C(4)–C(5)	1.377(1)
S(2)–C(N)	1.708(1)	C(5)–C(6)	1.396(1)
N–C(N)	1.319(1)	C(B1)–C(B2)	1.454(2)
N–C(M1)	1.483(1)	C(B2)–C(B3)	1.529(2)
N–C(M2)	1.479(1)	C(B3)–C(B4)	1.372(2)
C(M1)–C(E1)	1.491(1)	C(B4)–C(B4)	3.628(4)[a]
b) Bond angles			
Cl–Sn–S(1)	88.13(1)	S(1)–C(N)–N	119.07(6)
Cl–Sn–S(2)	156.85(1)	S(2)–C(N)–N	122.71(6)
Cl–Sn–C(1)	97.98(2)	N–C(M1)–C(E1)	112.48(8)
Cl–Sn–C(B1)	98.65(3)	N–C(M2)–C(E2)	111.88(8)
S(1)–Sn–S(2)	68.85(1)	Sn–C(1)–C(2)	120.54(5)
S(1)–Sn–C(1)	113.93(2)	Sn–C(1)–C(6)	120.71(6)
S(1)–Sn–C(B1)	116.28(3)	C(2)–C(1)–C(6)	118.75(7)
S(2)–Sn–C(1)	93.80(2)	C(1)–C(2)–C(3)	120.18(7)
S(2)–Sn–C(B1)	89.82(3)	C(2)–C(3)–C(4)	120.60(8)
C(1)–Sn–C(B1)	127.27(3)	C(3)–C(4)–C(5)	119.51(8)
Sn–S(1)–C(N)	91.06(3)	C(4)–C(5)–C(6)	120.27(8)
Sn–S(2)–C(N)	81.83(2)	C(1)–C(6)–C(5)	120.66(8)
C(N)–N–C(M1)	122.48(6)	Sn–C(B1)–C(B2)	117.33(8)
C(N)–N–C(M2)	121.48(7)	C(B1)–C(B2)–C(B3)	117.66(2)
C(M1)–N–C(M2)	115.96(6)	C(B2)–C(B3)–C(B4)	120.5(2)
S(1)–C(N)–S(2)	118.22(4)		

[a] Symmetry transformation: 1 − x, −y, −z.

TABLE IV. Coefficients of Least Squares Planes AX + BY + CZ = D for [$SnClPhBu(S_2CNEt_2)$].

Plane	Atoms	A	B	C	D	Distance of atoms from plane (Å)
I	Sn–S(1)–S(2)	0.699	0.418	−0.580	1.243	Sn, S(1), S(2) all 0.00, Cl 0.11, N 0.08, C(N) 0.04, C(M1) 0.08, C(M2) 0.21
II	S(1)–S(2)–C(N)	0.726	0.412	−0.551	1.150	S(1), S(2), C(N) all 0.00, Sn 0.09, Cl 0.24, N −0.01, C(M1) −0.04, C(M2) 0.08
III	S(1)–C(1)–C(B1)	−0.244	−0.674	−0.697	−2.903	S(1), C(1), C(B1) all 0.00, Sn −0.20
Interplanar angles (deg)		I, II	I, III	II, III		
		2.3	87.3	85.9		

in the unit cell. As is evident from the packing (Fig. 2), the structure consists of relatively isolated complex molecules, the closest intermolecular approach (3.628(4) Å) being between the methyl carbon atoms of the butyl groups of neighbouring molecules. From both Table III and Fig. 1 it can be seen that the configuration about the tin atom is pentacoordinated distorted trigonal bipyramid. The three atoms S(1), C(1) and C(B1) lie on the equatorial plane (Fig. 1) of the bipyramid, with the tin atom located 0.20 Å below this plane (Table IV). The sum of the ligand–Sn–ligand angles in the trigonal girdle of the compound is 357.48(8)° instead of the ideal 360°, due to the displacement of Sn out of the plane. The Cl and S(2) atoms occupy apical positions. The Sn–S(2) bond is markedly elongated (2.764(1) Å) compared to the Sn–S(1) bond (2.454(1) Å). This makes the dithiocarbamate coordination unsymmetrical. The Sn–C(1) bond distance of 2.138(1) Å compares favourably to the mean value found in other five-coordinate diphenyltin structures [1–5], and is only slightly shorter than the Sn–C(B1) bond (2.148(1) Å). The structure determination of the analogous Me_2-$SnCl(S_2CNMe_2)$ complex is of lower accuracy (R = 13.7%) [6], but the bond lengths are similar within

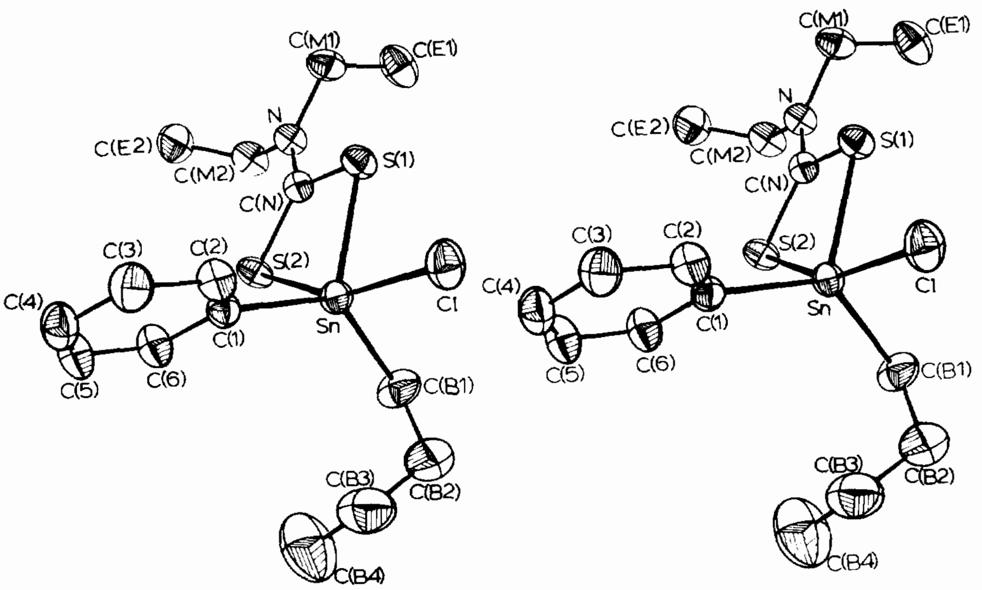

Fig. 1. A stereoview of the [$PhBuSnCl(S_2CNEt_2)$] molecule.

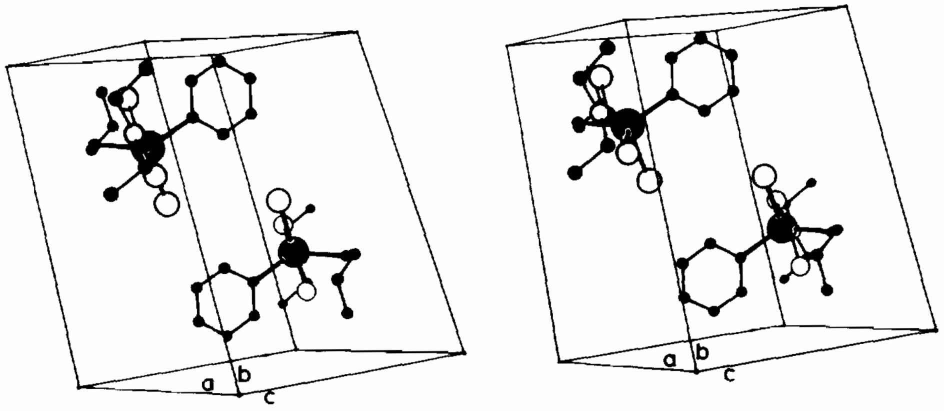

Fig. 2. Molecular packing in [$PhBuSnCl(S_2CNEt_2)$].

experimental error, except within the SnS_2C fragments of the dithiocarbamate ligands (Fig. 3). The Cl–Sn–S(2) bond angle at 156.85(1)° is larger than the value for the Me_2Sn complex by about 2° but there are no other important angular differences. For both complexes the C–Sn–C angle in the equatorial plane is 127–128°. By way of comparison, a narrowing of the C–Sn–C angle to 119.5° occurs in $Me_2SnCl[SCH_2CH(NH_2)CO_2Et]$ [7], where the 'bite angle' of the cysteinato ligand ($\sphericalangle S_{eq}$–Sn–N_{ax} = 80.1°) is substantially larger than that of the dithiocarbamate ligand ($\sphericalangle$S(1)–Sn–S(2) = 68.2–68.8°). Indeed, the limited structural flexibility of the dithiocarbamate ligand (Fig. 3) may explain the apparent insensitivity of the C–Sn–C bond angle to the steric size of the R groups on tin in going from $Me_2SnCl(S_2CNMe_2)$ to the title compound.

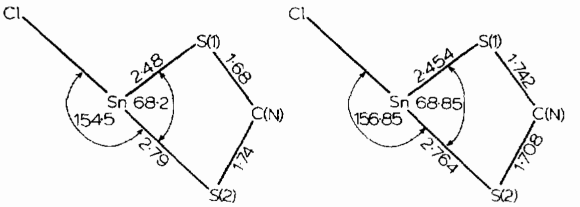

Fig. 3. Angular and bond distance variations in the $ClSnS_2C$ fragments of (a) [$Me_2SnCl(S_2CNMe_2)$] and (b) [$PhBuSnCl(S_2CNEt_2)$].

Acknowledgements

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