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Crystal structure of dimethyltin dichloride–dibenzylsulfoxide

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Abstract

Dimethyltin dichloride–dibenzylsulfoxide, $[(CH_3)_2SnCl_2 \cdot O{=}S(CH_2C_6H_5)_2]$, crystallizes in the orthorhombic $P2_12_12_1$ space group with a sub-structure of dimensions a 8.007(2), b 12.134(3), c 19.595(5) Å; $Z = 4$. A superstructure lattice with a 64.06(2) Å ($a \times 8$) could not be fully characterized. The geometry of the five-coordinated tin atom is *cis*-trigonal bipyramidal with the methyl groups equatorial [Sn–C 2.109(16), 2.128(15) Å; C–Sn–C 136.4(9)°], and the sulfoxide [Sn–O 2.319(10) Å] and one chloride [Sn–Cl 2.464(6) Å] apical [Cl–Sn–O 173.9(4)°]. The complex is an unusual example of a monomeric five-coordinate 1 : 1 adduct of a dialkyltin dichloride with a monodentate Lewis base.

Introduction

In the solid dialkyltin dichlorides [1–5] normally form infinite chains with the tin atom unsymmetrically bridged by two chlorine atoms, whereas diaryltin dichlorides [6–9] are present as discrete molecules. However, steric and electronic factors can influence the overall structure, and thus one modification of crowded dicyclohexyltin dichloride consists of only weakly linked molecules [10], and methylphenyltin dichloride forms a tetrameric chain [11]. The tin–chlorine bridges in diorganotin dichlorides are expected to be disrupted upon complexation with neutral monodentate nitrogen- or oxygen-donor ligands, and crystal structure determinations have revealed a five-coordinate geometry for the 1 : 1 adducts of diphenyltin dichloride [12–14]. The 1 : 1 adducts of dimethyltin dichloride with 0.5pyrazine [14,15], water · 18-crown-6 [16], diphenylcyclopropenone [17], tetramethylurea [18,19], 2,6-lutidine *N*-oxide [20] and methylphenylsulfine [21] are, in fact, six-coordinate [22] chlorine-bridged dimers. Other dialkyltin dichlorides form monomeric 1 : 1 adducts with bi- or tri-dentate ligands [23–26], with a coordination of six or seven, and a monomeric

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five-coordinate 1 : 1 adduct of a dialkyltin dichloride has not been observed until now [27,28].

Both dimethyltin dichloride and diphenyltin dichloride form 1 : 1 and 1 : 2 adducts with monodentate sulfoxides [29–31], and it seemed to us possible that structural determination of a 1 : 1 adduct of dimethyltin dichloride with a sulfoxide ligand might reveal novel behaviour, and this expectation was realized in the case of dimethyltin dichloride–dibenzylsulfoxide, whose crystal structure is described below.

Experimental

Single crystals of dimethyltin dichloride–dibenzylsulfoxide [30] were obtained by slow evaporation of a chloroform solution containing dimethyltin dichloride and dibenzylsulfoxide in 1/1 molar ratio. Diffraction data were collected on a Nicolet R3 automated four-circle diffractometer. Crystals of $[(CH_3)_2SnCl_2 \cdot O{=}S(CH_2C_6H_5)_2]$ were coated with epoxy cement to prevent hydrolysis. Initial photographic characterization revealed the presence of a super-structure lattice with an eight-fold increase in the *a*-axis. However, the sub-structure so dominated the diffraction pattern that it proved impossible to collect sufficient super-structure data to process the true structure, which contains eight independent complex molecules. Hence, the structure reported represents the composite of eight independent molecules. The structural parameters reported are subject to errors inherent in averaging over eight molecules. While it is certain that the structure is correct in terms of the intramolecular connectivity, individual parameters should be regarded as only approximate.

Table 1

Crystallographic data for $[(CH_3)_2SnCl_2 \cdot O{=}S(CH_2C_6H_5)_2]$

Crystal data			
Formula	$C_{16}H_{20}Cl_2OSSn$	Z	4
Formula wt	449.97	D(calcd), g cm^{-3}	1.570
Crystal system	orthorhombic	Color	colorless
Space group	$P2_12_12_1$	Size, mm	0.31 × 0.31 × 0.34
a, Å	8.007(2) [a]	μ(Mo-K_α), cm^{-1}	17.3
b, Å	12.134(3)	T, K	294
c, Å	19.595(5)	T_{max}/T_{min}	1.163
V, Å^3	1903.8(10)		
Data collection			
Diffractometer	Nicolet R3m	Rflns collected	1969
Radiation	Mo-K_α	Observed rflns	1034 ($3\sigma F_0$)
Wavelength, Å	0.71073	Std rfns	3 stds/197 rflns
2θ limits, deg	$4 \leq 2\theta \leq 52$	Decay, %	< 1
Refinement			
$R(F)$, %	7.73	Δ/σ	0.13
$R(wF)$, %	8.94	$\Delta(\rho)$, e Å^{-3}	1.06
GOF	1.579	NO/NV	9.89

[a] Sub-structure value (super-structure a axis is 64.06(2) Å). See text.

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	*U*
Sn	2201(4)	770(4)	213(2)	110(2) [a]
S	5554(13)	−1139(19)	−35(6)	122(9) [a]
Cl(1)	1450(12)	−1058(15)	524(7)	128(7) [a]
Cl(2)	−647(21)	1444(18)	442(10)	172(10) [a]
O	4884(39)	80(54)	84(16)	159(25) [a]
C(1)	2256(63)	894(41)	−923(25)	111(16)
C(2)	3231(82)	1567(53)	990(30)	159(26)
C(3)	7007(77)	−1486(51)	686(26)	130(20)
C(4)	7158(67)	−864(44)	−639(26)	114(17)
C(5)	5501(41)	−956(21)	1725(16)	139(22)
C(6)	4600	−1225	2311	105(16)
C(7)	4275	−2326	2466	90(14)
C(8)	4850	−3158	2035	121(19)
C(9)	5751	−2890	1449	90(14)
C(10)	6077	−1789	1294	48(8)
C(11)	5508(50)	−1221(30)	−1727(23)	148(25)
C(12)	4799	−935	−2353	140(22)
C(13)	4923	144	−2592	157(24)
C(14)	5757	938	−2206	257(49)
C(15)	6466	652	−1580	162(26)
C(16)	6342	−428	−1341	112(18)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Corrections for absorption were applied to the data. The structure was solved by heavy-atom methods. Chemically sensible phenyl rings could be refined only with rigid hexagonal constraints (C–C = 1.395 Å). The Sn, Cl, S and O atoms were refined anisotropically, the C atoms isotropically, and the H atoms were treated as idealized contributions (C–H = 0.96 Å). SHELXTL (5.1) software was used for all computations (G. Sheldrick, Nicolet XRD, Madison, WI). Crystallographic data are listed in Table 1. Table 2 gives the atomic coordinates, and Table 3 the bond distances and angles. Structure factor tables, anisotropic thermal parameters and hydrogen atoms coordinates are available from the authors.

Table 3

Bond distances (Å) and angles (°) for $[(CH_3)_2SnCl_2 \cdot O{=}S(CH_2C_6H_5)_2]$ [a]

Sn–Cl(1)	2.392(6)	Sn–C(2)	2.109(16)
Sn–Cl(2)	2.464(6)	S–O	1.488(21)
Sn–O	2.319(10)	S–C(3)	1.876(21)
Sn–C(1)	2.128(15)	S–C(4)	1.779(19)
Cl(1)–Sn–Cl(2)	91.6(3)	O–Sn–C(2)	83.3(9)
Cl(1)–Sn–O	83.6(4)	C(1)–Sn–C(2)	136.4(9)
Cl(2)–Sn–O	173.9(4)	O–S–C(3)	105.5(7)
Cl(1)–Sn–C(1)	108.2(6)	O–S–C(4)	104.6(8)
O–Sn–C(1)	87.8(9)	C(3)–S–C(4)	94.6(9)
Cl(1)–Sn–C(2)	113.0(6)	Sn–O–S	135.6(6)
Cl(2)–Sn–C(2)	95.3(7)		

[a] The parameters shown are those obtained by sub-structure averaging over eight independent molecules.

Results and discussion

Dimethyltin dichloride forms with dibenzylsulfoxide a discrete 1 : 1 adduct, whose structure is depicted in Fig. 1. No intermolecular tin–chlorine or tin–oxygen contacts of < 4 Å are present in the unit cell. The tin atom is five-coordinate and its geometry is *cis*-trigonal bipyramidal; the tin–carbon bonds [2.109(16), 2.128(15) Å] subtend an angle of 136.4(9)° at the metal. The axial tin–chlorine bond [2.464(9) Å] is longer than the equatorial bond [2.392(6) Å], but the bond lengths are otherwise not much different from those of the tin–chloride bonds in other diorganotin dichloride Lewis acids [1–11] and their 1 : 1 complexes [12–21]. The sum of angles in the equatorial plane is 357.6(21)°, and the tin atom is displaced from the plane in the direction of the axial chlorine by 0.22 Å; some distortion from idealized geometry is also seen in the non-linear Cl–Sn–O skeleton [173.9(4)°].

Dimethyltin compounds have been much studied because of the simplicity of the $(CH_3)_2Sn$ unit, and tin is frequently six-coordinate in dimethyltin compounds [27,28]. For example, the 1 : 1 adducts of dimethyltin dichloride [14–21] are six-coordinate, as are [32] the dimethylchlorotin monochelates [33–35]; indeed, chlorine bridging invariably helps to complete the coordination sphere of tin. There are a few unambiguous examples of monomeric, five-coordinated dimethyltin compounds; they include dimethyltin glycylmethionate [36], dimethylchlorotinethyl-L-cysteinate [37,38] and two dimethylstannoles [39,40]. The dimethyltin angles found in the glycylmethionate (123.8° [36]), cysteinate (119.5° [37,38]) and in 2,2-dimethyl-1,3-dithia-2-stannacyclopentane (121.73° [40]) are close to the ideal sp^2 angle of 120°, and the inability of tin to expand its coordination number to six can be associated with its decreased Lewis acidity arising from the sulfide linkage. The title compound is also monomeric as its chlorine atoms do not engage in bridging; bond distances and angles involving the tin atom are normal, but an important difference between this and the five-coordinate dimethyltin mercaptides is in the size of the dimethyltin angle. The 136.4(9)° angle in the title adduct is larger than that in the parent Lewis acid (123.5° [1]), but smaller than that in its six-coordinate adducts, viz., 153.2, 154.4° (water · 18-crown-6 [16]), 142.2° (diphenylcyclopropenone [17]), 146.6° (tetramethylurea [18,19], 145.3° (2,6-dimethylpyridine *N*-oxide [20]) and 153.4°

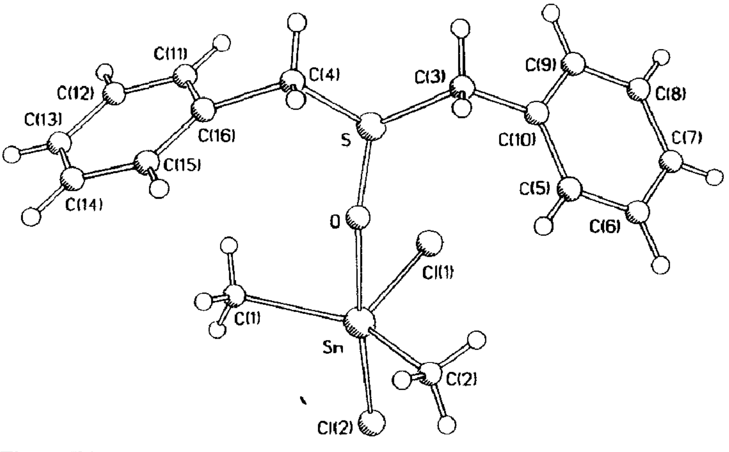

Fig. 1. Dimethyltin dichloride–dibenzylsulfoxide.

Table 4

Structural data for organotin–sulfoxide complexes

Complex	Sn···O (Å)	O=S (Å)	S–C (Å)	Sn–O–S (°)	O–S–C (°)	C–S–C (°)	Ref.
$Me_2SnCl_2\cdot 2OSMe_2$	2.32	1.61	1.75, 1.85	117	100, 103	98	51,52
	2.38	1.51	1.78, 1.84	112	102, 103	97	
$Me_2SnCl_2\cdot 2OSMe_2$	2.27	1.56	1.77, 1.82	125.2	103.5, 104.9	100.4	41
	2.31	1.58	1.81, 1.81	119.0	103.3, 103.8		
$Me_2SnBr_2\cdot 2OSMe_2$	2.22	1.56	1.74, 1.85	125	100, 101	97	41
$MeSnCl_2CH_2Cl_2SnMe\cdot OSMe_2$ [a]	2.555	1.527	1.79, 1.79	131.1	105.3, 105.8	97.7	53
$MeSnCl_2CH_2ClSnMe_2\cdot OSMe_2$ [a]	2.572	1.526	1.80, 1.82	130.6	103.4, 106.3	97.7	53
$Cl_3SnCH_2SnCl_3$	2.109	1.550	1.770, 1.784	128.7	100.5, 103.0	100.2	53
$\cdot 4OSMe_2$		1.547	1.726, 1.753	123.0	102.7, 105.1	97.1	
$Ph_2SnCl_2\cdot 2OSMe_2$							54,55
Form I	2.280	1.521	1.75, 1.77	126.5	104.4, 105.9	98.5	
	2.355	1.539	1.81, 1.81	142.0	101.1, 106.2	100.6	
Form II	2.281	1.521	1.75, 1.77	124.5	104.2, 104.9	99.1	
	2.295	1.503	1.75, 1.80	133.7	104.3, 105.1	97.7	
$[Ph_3SnCl]_2\cdot {}^nPrSOCH$	2.447	1.448	1.887, 1.985	128.8	102.7, 105.9	103.8	56
$=CHSOPr^n$			1.901		100.5		
$2[Ph_2SnNO_3\cdot OS^nPr_2]^+$	2.178	1.430	1.80, 1.86	147.4	108.2, 109.6	101.8	57
$C_2O_4^{2-}$		1.409	1.69, 1.84	158.3	104.4, 114.7	103.0	
$[Ph_2SnNO_3\cdot 3OSMe_2]^+$	2.19	1.55	1.80, 1.80	136.3	102.7, 106.7	99.9	58
NO_3^-	2.17	1.54	1.78, 1.80	122.1	101.2, 104.9	100.5	
	2.24	1.55	1.75, 1.78	129.1	102, 108	99	
		1.47	1.65, 1.80	139.9	105, 118	101	
$(CH_3)_2SnCl_2\cdot OS(CH_2C_6H_5)_2$	2.319(10)	1.488(21)	1.779(19), 1.876(21)	135.6(6)	104.6(8), 105.5(7)	94.6(9)	this work

[a] The Me_2SO ligand bridges the $Sn–CH_2–Sn$ unit in the adduct.

(methylphenylsulfine [21]). The angle in these six-coordinate adducts is, in turn, smaller than that in the 1 : 2 oxygen- [41–47] and the weakly-basic sulfur-donor [48] adducts. The dimethyltin angles thus increase in the sequence $(CH_3)_2SnCl_2$ (123.3°), $(CH_3)_2SnCl_2\cdot O{=}S(CH_2C_6H_5)_2$ [136.4(9)°], $[(CH_3)_2SnCl_2\cdot L]_2$ (142.2–153.4°) and $(CH_3)_2SnCl_2\cdot 2L$ (ca. 180°), where L = oxygen-donor ligand.

A sulfoxide can be represented by two canonical forms, $R_2S{=}O$ and $R_2S^+\cdots O^-$. Coordination to a metal or the presence of electron-releasing R groups would favor the dipolar form. The crystal structure of dibenzylsulfoxide is unknown, but the sulfur–oxygen bond [49] of the related sulfoxide, diphenylsulfoxide is 1.47 Å [50]. Coordination to an organotin compound would be expected to lengthen the sulfur–oxygen bond, and if the structure of diphenylsulfoxide is taken as the basis for comparison, such shortening is observed in a majority of organotin–sulfoxide complexes [41,51–58] (Table 4). The long sulfur–oxygen bond of 1.488(21) Å in the title adduct suggests some contribution from the $R_2S^+\cdots O^-$ form.

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References

1 A.G. Davies, H.J. Milledge, D.C. Puxley and P.J. Smith, J. Chem. Soc., Dalton Trans., (1970) 2862.
2 N.G. Bokii, Yu.T. Struchkov and A.K. Prokof'ev, J. Struct. Chem. (Engl. Transl.), 13 (1972) 619.
3 N.W. Alcock and J.F. Sawyer, J. Chem. Soc., Dalton Trans., (1977) 1090.
4 J.F. Sawyer, Acta Cryst. C, 44 (1988) 633.
5 K.C. Molloy, K. Quill and I.W. Nowell, J. Organomet. Chem., 289 (1985) 271.
6 P.T. Greene and R.F. Ryan, J. Chem. Soc. (A), (1971) 2549.
7 J.L. Baxter, E.M. Holt and J.J. Zuckerman, Organometallics, 4 (1985) 255.
8 N.G. Bokii, Yu.T. Struchkov, V.V. Korol'kov and T.P. Tolstaya, Sov. J. Coord. Chem. (Engl. Transl.), 1 (1975) 965.
9 N.G. Bokii and Yu.T. Struchkov, Sov. J. Coord. Chem. (Engl. Transl.), 4 (1978) 107.
10 P. Ganis, G. Valle, D. Furlani and G. Tagliavini, J. Organomet. Chem., 302 (1986) 165.
11 M.M. Amini, E.M. Holt and J.J. Zuckerman, J. Organomet. Chem., 327 (1987) 147.
12 P.G. Harrison and K.C. Molloy, J. Organomet. Chem., 152 (1978) 63.
13 A.L. Rheingold, S.W. Ng and J.J. Zuckerman, Organometallics, 3 (1984) 233.
14 D. Cunningham, P. McArdle, J. McManus, T. Higgins and K. Molloy, J. Chem. Soc., Dalton Trans., (1988) 2621.
15 E. Rivarola, M. Camalli and F. Caruso, Inorg. Chim. Acta, 126 (1987) 1.
16 M.M. Amini, A.L. Rheingold, R.W. Taylor and J.J. Zuckerman, J. Am. Chem. Soc., 106 (1984) 7289.
17 S.W. Ng, C.L. Barnes, M.B. Hossain, D. van der Helm, J.J. Zuckerman and V.G. Kumar Das, J. Am. Chem. Soc., 104 (1982) 5359.
18 G. Valle, S. Calogero and U. Russo, J. Organomet. Chem., 288 (1982) C79.
19 S. Calogero, G. Valle and U. Russo, Organometallics, 3 (1984) 1205.
20 S.W. Ng, C.L. Barnes, D. van der Helm and J.J. Zuckerman, Organometallics, 2 (1983) 600.
21 R.J.F. Jans, G. van Koten, K. Vrieze, B. Kojic-Prodic, A.L. Spek and J.L. de Boer, Inorg. Chim. Acta, 105 (1985) 193.
22 S.W. Ng and J.J. Zuckerman, J. Chem. Soc., Chem. Commun., (1982) 475.
23 G. Pelizzi, P. Tarasconi, C. Pelizzi, K.C. Molloy and P. Waterfield, Main Group Met. Chem., 10 (1987) 353.
24 G. Pelizzi, P. Tarasconi, F. Vitali and C. Pelizzi, Acta Cryst. C, 43 (1987) 1505.
25 L. Prasad, Y. Le Page and F.E. Smith, Acta Cryst. B, 38 (1982) 2890.
26 L. Prasad, Y. Le Page and F.E. Smith, Inorg. Chim. Acta, 68 (1983) 45.
27 J.A. Zubieta and J.J. Zuckerman, Prog. Inorg. Chem., 24 (1978) 251.
28 P.J. Smith, J. Organomet. Chem. Libr., 12 (1982) 97.
29 A. Abras, A.L. Filgueiras and J.M.K. Baba, J. Inorg. Nucl. Chem., 43 (1981) 2249.
30 W. Kitching, C.J. Moore and D. Doddrell, Aust. J. Chem., 22 (1969) 1149.
31 V.G. Liengme, R.S. Randall and J.R. Sams, Can. J. Chem., 50 (1972) 3212.
32 S.W. Ng, Chen Wei, V.G. Kumar Das, J.-P. Charland and F.E. Smith, J. Organomet. Chem., 364 (1989) 343.
33 D.W. Allen, I.W. Nowell, J.S. Brooks and R.W. Clarkson, J. Organomet. Chem., 219 (1981) 29.
34 S.K. Lee and B.K. Nicholson, J. Organomet. Chem., 309 (1986) 257.
35 K. Furue, T. Kumura, N. Yasuoka, N. Kasai and M. Kakudo, Bull. Chem. Soc. Japan, 43 (1970) 1661.
36 H. Preut, B. Mundus, F. Huber and R. Barbieri, Acta Cryst. C, 42 (1986) 536.
37 G. Domazetis, M.F. Mackay, R.J. Magee and B.D. James, Inorg. Chim. Acta, 34 (1979) L247.
38 G. Domazetis and M.F. Mackay, J. Cryst. Mol. Struct., 9 (1979) 57.
39 H.W. Roesky, Z. Naturforsch. B, 31 (1976) 680.
40 A.S. Secco and J. Trotter, Acta Cryst. C, 39 (1983) 451.
41 L.A. Aslanov, V.M. Ionov, W.M. Attiya, A.B. Permin and V.S. Petrosyan, J. Struct. Chem. (Engl. Transl.), 19 (1978) 91.
42 G. Valle, G. Plazzogna and R. Ettorre, J. Chem.Soc., Dalton Trans., (1985) 1271.
43 M.E. Kamwaya and L.E. Khoo, Acta Cryst. C, 41 (1985) 1027.
44 M.E. Kamwaya and L.E. Khoo, J. Fiz. Mal., 6 (1985) 39.
45 E.A. Blom and B.R. Penfold, J. Chem. Soc. (A), (1969) 914.
46 G.-E. Matsubayashi and K. Nakatsu, Inorg. Chim. Acta, 64 (1982) L163.
47 A.L. Rheingold, S.W. Ng and J.J. Zuckerman, Inorg. Chim. Acta, 86 (1984) 179.

48 G. Valle, R. Ettorre, U. Vettori, V. Peruzzo and G. Plazzogna, J. Chem. Soc., Dalton Trans., (1987) 815.

49 S.C. Abrahams, Acta Cryst., 10 (1957) 417.

50 P. Biscarini, L. Fusina, G.D. Nivellini, A. Mangia and G. Pelizzi, J. Chem. Soc., Dalton Trans., (1973) 159.

51 N.W. Isaacs, C.H.L. Kennard and W. Kitching, J. Chem. Soc., Chem. Commun., (1968) 820.

52 N.W. Isaacs and C.H.L. Kennard, J. Chem. Soc. (A), (1970) 1257.

53 T.J. Karol, J.P. Hutchinson, J.R. Hyde, H.G. Kuivila and J.A. Zubieta, Organometallics, 2 (1983) 106.

54 L. Coghi, C. Pelizzi and G. Pelizzi, Gazz. Chim. Ital., 104 (1974) 873.

55 L. Coghi, M. Nardelli, C. Pelizzi and G. Pelizzi, Gazz. Chim. Ital., 105 (1975) 1187.

56 C.A. Filgueiras, P.R. Holland, B.F.G. Johnson, P.R. Raithby, Acta Cryst. B, 29 (1982) 2684.

57 A. Mangia, C. Pelizzi and G. Pelizzi, J. Chem. Soc., Dalton Trans., (1973) 2557.

58 L. Coghi, C. Pelizzi and G. Pelizzi, J. Organomet. Chem., 114 (1976) 53.