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$\{Me_2NCH[(EtO)_2P{=}O]_2 \cdot Me_2SnCl_2\}$-dimer:

Crystal structure of a binuclear bis(chelate) complex of tin(IV) with *cis*-linked octahedra

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Abstract

Dimethyltin dichloride and the potentially tridentate ligand $Me_2NCH[(OEt)_2P{=}O]_2$ form a 1:1 complex I which crystallizes in the space group $I\bar{4}2m$ as dimers $\{Me_2NCH[(OEt)_2P{=}O]_2 \cdot Me_2SnCl_2\}_2$ in which the oxygen atoms of one phosphoryl ligand are bridging two tin atoms each having a distorted octahedral coordination sphere, the first example of this bridging mode in the coordination chemistry of dialkyltin dihalides. Molecular parameters are: Sn–C 2.16(2) and 2.11(2), Sn–Cl 2.481(5), Sn–O 2.48(2) Å; C–Sn–C 156.6(8), Cl–Sn–Cl 90.8(2), O–Sn–O 98.1(4), Cl–Sn–Cl 90.8(2), C(1)–Sn–Cl 99.4(6)°. The metal and ligand atoms form a twisted 12-membered ring in which the nitrogen atoms are clearly outside the coordination spheres of the metals. ^{119}Sn Mössbauer data are correlated with the observed deviation of 153° from an ideal 180° geometry for the C–Sn–C bond angle.

Introduction

Complexes of donor molecules and diorganotin dihalides can be readily made and many have been characterized by molecular spectroscopy [1]. Some of them serve as model substances for the investigation of the biological activity of metalorganic compounds [2]. From the many possible donor molecules we decided to study phosphoryl ligands because they are stronger donors than phosphanes and can coordinate through both available coordination sites to form mononuclear chelates [3], bridged (polymer) structures [4], or binuclear dimeric units. Crystal structures are known for the first two classes, but to our knowledge there has up to now been no structural evidence for binuclear complexes of the third type, although hydrogen-bridged species have been described recently [5]. By use of suitable polydentate ligands the coordination number at tin may be increased from 6 up to even 8 and this was the main reason for selecting the potentially tridentate

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phosphoryl ligand $Me_2NCH[(OEt)_2P{=}O]_2$: nitrogen and oxygen are both "hard" donor sites, and there can be competition between nitrogen and oxygen for the vacant octahedral sites at tin.

Results and discussion

Me_2SnCl_2 and $Me_2NCH[(OEt)_2P{=}O]_2$ yield a 1 : 1 adduct I, the crystal structure of which has been determined by single crystal X-ray diffraction methods. This results revealed that unexpectedly, it is a binuclear coordination compound, the first example of this kind in the chemistry of diorganotin dihalides. Two octahedrally coordinated tin atoms are linked via the oxygen atoms of one phosphoryl ligand in a *cis*-fashion, with the tin-bonded methyl groups mutually *trans* orientated. The metal and ligand atoms of the binuclear complex form a twisted 12-membered ring with the nitrogen atoms outside the bonding range of the tin atoms, as shown by the long tin–nitrogen distance. The two tin octahedra are distorted and are twisted towards each other (Fig. 1); the 12-membered ring, which is easy to recognize in the stereoplot depicted in Fig. 2, adopts a boat conformation. The molecule has two mirror planes, perpendicular to each other.

Important molecular parameters in I, e.g. Sn–C, Sn–Cl and Sn–O bond distances with Sn–C 2.16(2) and 2.11(2), Sn–Cl 2.481(5) and Sn–O 2.48(2) Å are within normal ranges and comparable with those for related species listed in Table 1; the P=O bond distances of 1.49(3) and 1.51(2) Å are in the range found for P–O-single

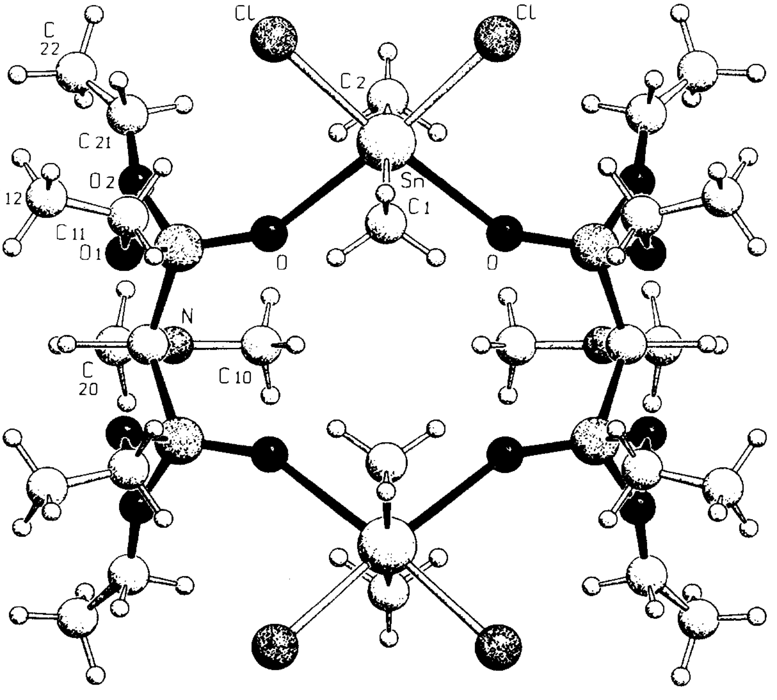

Fig. 1. SCHAKAL [11] plot of one molecule of the dimer I in [0 0 1] direction; labelling of atoms shown only in one asymmetric unit.

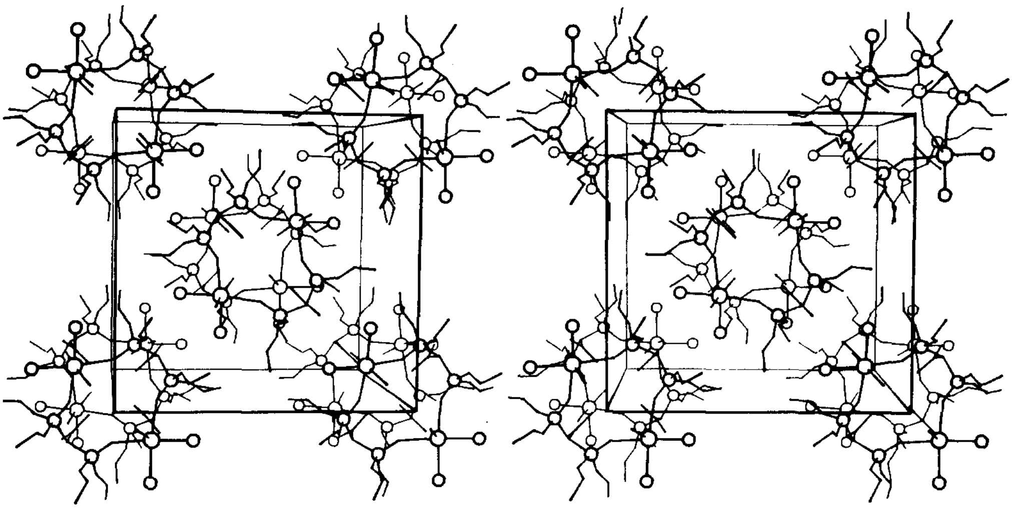

Fig. 2. SCHAKAL [11] stereo plot of the unit cell of compound I.

bonds in other phosphoryl compounds, indicating a considerable lengthening of the P=O bond by (P–O → Sn) coordination.

More interesting is a comparison of bond angles in I with those in related molecules (Table 1): the C–Sn–C angle in I is 156.6(8)°, showing the extent of distortion of the tin octahedra, which is similar to that in $Bu_2SnCl_2 \cdot$ *cis*-$[O{=}PPh_2CH_2{-}]_2$ [3] and almost as large as that in crystalline Me_2SnCl_2 (142°) (it is noteworthy that Me_2SnCl_2 is tetrahedral in the gas phase [6]).

A literature survey [7] revealed a correlation between C–Sn–C bond angles and the quadrupole splitting $\delta\{^{119}Sn\}$ in ^{119}Sn Mössbauer spectra: for a C–Sn–C angle in the region of 180° δ ^{119}Sn is 4.4 mm sec^{-1}, and the smaller this bond angle the

Table 1

Comparison of some bond distances (Å) and bond angles (°) in I and related species

	$Bu_2SnCl_2 \cdot$ *cis*-$[Ph_2P(O)CH_2{-}]_2$ [3]	Me_2SnCl_2 [6]	I this work
Distances			
Sn–C	2.12(9)	2.21(8)	2.16(2)
	2.11(8)		2.11(2)
Sn–Cl	2.48(2)	2.40(4)	2.48(5)
	2.46(3)		
Sn–O	2.38(7)	–	2.48(2)
	2.64(7)		
Angles			
C–Sn–C	154.3(3)	141.9	156.6(8)
Cl–Sn–Cl	90.1(1)	95.0	90.8(2)
O1–Sn–O2	93.6(2)	–	98.1(4)
C1–Sn–Cl	90.1(1)	123(4)	99.4(6)
C2–Sn–Cl	98.2(2)	109(4)	96.9(6)
Structure	distorted octahedron	distorted tetrahedron	distorted octahedron

Table 2

Selected bond lengths (Å) and bond angles (°) in I

Sn–Cl	2.482(4)	Sn–O	2.466(13)
Sn–C1	2.08(2)	Sn–C2	2.15(2)
P–O	1.424(13)	P–O1	1.52(2)
P–O2	1.48(2)	P–C	1.83(2)
O1–C11	1.38(2)	O2–C21	1.25(3)
N–C	1.50(2)	N–C10	1.37(3)
N–C20	1.38(3)	C11–C12	1.36(3)
C21–C22	1.34(4)		
Cl–Sn–O	85.5(3)	O–P–O2	113.0(8)
Cl–Sn–C1	99.3(5)	O–P–C	118.7(7)
Cl–Sn–C2	98.6(5)	O1–P–O2	106.0(1)
Cl–Sn–Cl[b]	90.7(2)	O1–P–C	102.3(8)
Cl–Sn–O[b]	176.2(3)	O2–P–C	101.5(9)
O–Sn–C1	81.9(6)	Sn–O–P	150.1(7)
O–Sn–C2	81.5(6)	P–O1–C11	141(1)
O–Sn–Cl[b]	176.2(3)	P–O2–C21	156(2)
O–Sn–O[b]	98.3(4)	C–N–C10	125(2)
C1–Sn–C2	154.5(7)	C–N–C20	115(2)
C1–Sn–Cl[b]	99.3(5)	C10–N–C20	121(2)
C1–Sn–O[b]	81.9(6)	P–C–N	109(1)
C2–Sn–Cl[b]	98.6(5)	P–C–P[a]	113(1)
C2–Sn–O[b]	81.5(6)	N–C–P[a]	109(1)
Cl[b]–Sn–O[b]	85.5(3)	O1–C11–C12	114(2)
O–P–O1	113.6(8)	O2–C21–C22	141(2)

[a] Symmetry code: $1-y$, $1-x$, z. [b] Symmetry code: y, x, z.

Table 3

Atomic parameters and equivalent isotropic temperature factors for non-H-atoms $U_{eq} = 1/3\{\Sigma_i \Sigma_j U_{ij} a_i^{\star} a_j^{\star} (\mathbf{a}_i \cdot \mathbf{a}_j)$

Atom	x	y	z	U_{eq}
Sn	0.36805(6)	0.36805(6)	0.30007(8)	0.0438(4)
Cl	0.3746(3)	0.2301(2)	0.3411(2)	0.069(2)
P	0.5709(3)	0.3043(3)	0.2500(3)	0.049(2)
O	0.5047(7)	0.3522(6)	0.2607(7)	0.075(4)
O1	0.6048(7)	0.275(1)	0.3290(9)	0.179(6)
O2	0.5549(9)	0.235(1)	0.200(1)	0.215(6)
N	0.634(1)	0.366(1)	0.1143(9)	0.153(6)
C	0.6556(7)	0.3444(7)	0.199(1)	0.037(5)[a]
C1	0.418(1)	0.418(1)	0.402(1)	0.055(5)
C2	0.352(1)	0.352(1)	0.172(1)	0.085(6)
C10	0.579(1)	0.421(1)	0.095(1)	0.080(6)
C11	0.583(1)	0.256(1)	0.4067(9)	0.092(6)
C12	0.615(2)	0.188(2)	0.434(1)	0.207(7)
C20	0.673(1)	0.327(1)	0.055(1)	0.084(6)
C21	0.515(1)	0.180(1)	0.172(1)	0.121(7)
C22	0.520(1)	0.121(2)	0.120(2)	0.224(8)

[a] Refined isotropically.

smaller the quadrupole splitting. This correlation is confirmed by our data for I, for which the value of the C–Sn–C angle of 156.6° is associated with a quadrupole splitting δ of 4.05 mm sec^{-1}.

Examination of the packing of the molecules I in the unit cell reveals a possible reason for the twisting of the tin octahedra namely the space demanding *cis*-chlorine atoms which are close to the nearest molecules of the next cell unit force the planes defined by atoms Cl(1), Cl(2), O(1), (O2) and Sn from positions parallel to each other into the observed skew positions; the shortest distances between chlorine atoms Cl(1) and Cl(2) and the nearest carbon atoms are 3.47(9) and 3.50(7) Å, respectively.

Structure determination

Compound I crystallizes in the space group $I\bar{4}2m$ with $Z = 4$ dimers and lattice constants $a = 1729.6(2)$, $c = 1649.3(2)$ pm, $d_c = 1.479$ g cm^{-3}, $V = 4934.1(9)$ $Å^3$. The crystal size was about 0.5 × 0.5 × 0.2 mm. On a four circle diffractometer (CAD4, Enraf–Nonius, Mo-K_α-radiation, graphite monochromator, $T = 190$ K) a total of 2373 reflections were obtained in the range $\theta = 1$–$35°$ by ω-scans over $(1.0 + 0.35\ \mathrm{tg}\theta)°$ and additional 25% before and after each reflection for background determination. After an empirical correction for absorption ($\mu = 14.1$ cm^{-1}, ψ-scan) the structure was solved by Patterson and Fourier methods and refined with anisotropic temperature factors for all atoms except hydrogen and carbon atom C with full matrix [8,9]. Hydrogens were kept in fixed positions and refined with isotropic temperature factors. Using weights $w = 1/\sigma^2(F_o)$ for 1202 independent reflections $F_o > 3\sigma(F_o)$ resulted $R = 0.074$ or $R_w = 0.042$.

A test for correct polarity was performed by refining Rogers η-parameter (which implies the imaginary components of atomic scattering factors) in SHELXTL [9]. Refinement to the value of +1 indicated that we had assumed the correct polarity.

Details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, with quotation of the deposit number CSD-55201, the name of the authors, and the journal citation.

Experimental

The ligand [10] (15 ml) and 1.2 g (5 mmol) of Me_2SnCl_2 were dissolved in ca. 15 ml of hot n-hexane (or pentane) and the solution was kept for 2 days at −6°C in the refrigerator to allow I to crystallize. Filtration and washing of the precipitate with small amounts of cold n-pentane gave white crystals of I, m.p. 40–42°C (uncorr.), 3.2 g (82.9% of theory).

Elemental analyses: Found: C, 28,39; H, 5.96; N, 2.43. $C_{22}H_{54}N_4O_4P_4 \cdot 2Me_2SnCl_2$ calc.: C, 28.31; H, 5.99; N, 2.54%.

Spectra

The ^{119}Sn Mössbauer spectrum was obtained by courtesy of Prof. V.I. Gol'danski, Moscow State University: δ IS = 1.60 mm sec^{-1}; δ QS = 4.05 mm sec^{-1}.

NMR spectra: The ^{119}Sn-NMR spectrum was uninformative owing to rapid exchange processes at room temperature and down to −45 °C. The ^{1}H and ^{13}C NMR data correspond to those of the free ligand [10] and Me_2SnCl_2; the ^{31}P signal appears at δ −17.8 ppm.

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