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Synthesis and structure of diethyltindichloride methylenediphosphinato complex: $Et_2SnCl_2 \cdot [Me(^iPrO)P(O)]_2CH_2$ *

Jörg Lorberth, Sigrid Wocadlo and Werner Massa
Fachbereich Chemie, Philipps-University, W-35032 Marburg / Lahn (Germany)

Natalia S. Yashina, Evgenii V. Grigor'ev and Valery S. Petrosyan
Moscow Lomonosov State University, 119899 Moscow (Russian Federation)

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Abstract

In the title complex the disphosphinato ligand coordinates in a chelate mode to give a distorted octahedral environment at tin with the ethyl groups in a *trans* position.

Key words: Tin; Crystal structure; Diethyltin Cpd.; Phosphinato-complex; X-ray diffraction

1. Introduction

In the past 30 years or so, organotin compounds and their complexes with electron-donor molecules have been much studied by various physicochemical methods. Much of the interest in such complexes arises from their biological and catalytical activity and, in these contexts, coordination involving organotin substrates and ligands of various types is of importance [1].

Examination of the literature on biologically active organotin compounds shows that the activity in the case of diorganotin coordination species is commonly associated with chelated octahedral structures containing O–Sn coordination bonds, and so the complex described in the present report can be regarded as a potentially biologically active species [2].

Our previous work on the synthesis and structural characterization of adducts of monoorganotin(IV) and diorganotin(IV) halides with tetraalkyl methylenediphosphonates [3] revealed the versatile behavior of the latter species towards organotin(IV) halides. In particular, the adduct $\{Me_2SnCl_2 \cdot [(EtO)_2P(O)\}_2CHNMe\}_2$ was found to have a dinuclear dimeric structure with bidentate ligands bridging two organotin moieties [4], whereas in adducts of methylenediphosphonates with Ph_2SnCl_2 or monoorganotin(IV) trihalides the diphosphoryl groups act as bidentate chelating ligands [5,6].

In order to provide information on the effect of the nature of the organophosphorous ligand on the molecular structure of the coordination complexes and particularly on the tin–ligand interaction we decided to use methylenediphosphinate $[Me(^iPrO)P(O)]_2CH_2$ as a diphosphoryl ligand. In this paper we report on the synthesis and X-ray diffraction analysis of the adduct of Et_2SnCl_2 with this ligand.

2. Experimental section

The ligand [7] (5 mmol) and Et_2SnCl_2 (5 mmol) were dissolved in about 15 ml of hot *n*-hexane (or pentane). The solution was kept for 2 days at 5–10°C to allow the complex to separate. The solid was filtered off and washed with several small amounts of cold *n*-pentane. The product was obtained as colourless crystals (m.p., 87°C; yield, about 90%).

Elemental anal. Found: C, 31.23; H, 6.22. $C_{13}H_{32}Cl_2O_4P_2Sn$ calc.: C, 31.01; H, 6.36%.

Correspondence to: Professor J. Lorberth or Dr. N.S. Yashina.

* In memory of Prof. I.F. Lutsenko, Moscow.

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TABLE 1. Experimental data for the crystal structure determination of $C_{13}H_{30}Cl_2O_4P_2Sn$

Crystal data	
Formula	$C_{13}H_{30}Cl_2O_4P_2Sn$
Absorption μ	15.5 cm^{-1}, numerical correction
Minimum transmission; maximum transmission	0.80; 0.92
Space group	$P2_1/c$, $Z = 4$
Lattice constants	
a	14.518(5) Å
b	9.125(2) Å
c	16.921(4) Å
β	98.15(3)°
Temperature	293 K
Density d_c	1.502 g cm^{-3}
Data collection	
Diffractometer	Four-circle, CAD4 (Enraf–Nonius)
Radiation	Mo Kα, graphite monochromator
Scan type	ω scan
Scan width	$(1.0 + 0.35 \tan \theta)$° and 25% on the left and right-hand side of a reflection for background determination
Measuring range θ	2–23°, $+h, +k, \pm l$
Reflections	3439, 3023 unique, 1936 > $3\sigma(F_o)$
Computing	
Program	SHELXTL-PLUS [8]
Solution	Patterson methods
Atomic scattering factors	For neutral atoms [9]
Refinement	Full matrix least squares, 212 parameters $\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$ minimized, $w = 1/\sigma^2(F)$; hydrogen atoms riding with fixed isotropic U; anisotropic U for other atoms except disordered atoms
Residuals	
R	0.065
wR	0.041
Goodness of fit	1.89
Maximum parameter shift	0.001 estimated standard deviation
$\Delta\rho_{max}$; $\Delta\rho_{min}$	0.65 electrons Å^{-3}; −0.80 electrons Å^{-3}

3. Crystal structure determination

Data for a crystal of **I** were collected on a four-circle diffractometer. Crystal data and details of data collection and refinement are given in Table 1. The structure was solved by Patterson methods and refined with anisotropic temperature factors for all non-hydrogen atoms except the C(9), C(91), C(51) and C(61) atoms of the disordered isopropyl groups (Fig. 1). The hydrogen atoms were placed in calculated positions (C–H distance, 0.96 Å) with fixed isotropic temperature factors. The resulting atomic coordinates are listed in Table 2, and the bond lengths and bond angles in Table 3.

Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, with quotation of the deposit number CSD-400455, the names of the authors, and the journal citation.

4. Discussion

The complex has a monomeric chelate structure with a distorted octahedral environment at tin and the ethyl groups in a *trans* position. The two Sn–O bond lengths differ by 0.08 Å, but the two Sn–C bonds are almost identical, as are the two Sn–Cl bonds. The fact that structure **I** is asymmetrical can be attributed to steric effects of the methyl substituents on the phosphoryl groups. The bond lengths and angles are within normal ranges and comparable with those for the related species listed in Table 4. The Sn–O bond distances are similar to those in adducts with methylenediphosphonates [1,2], but longer than those in

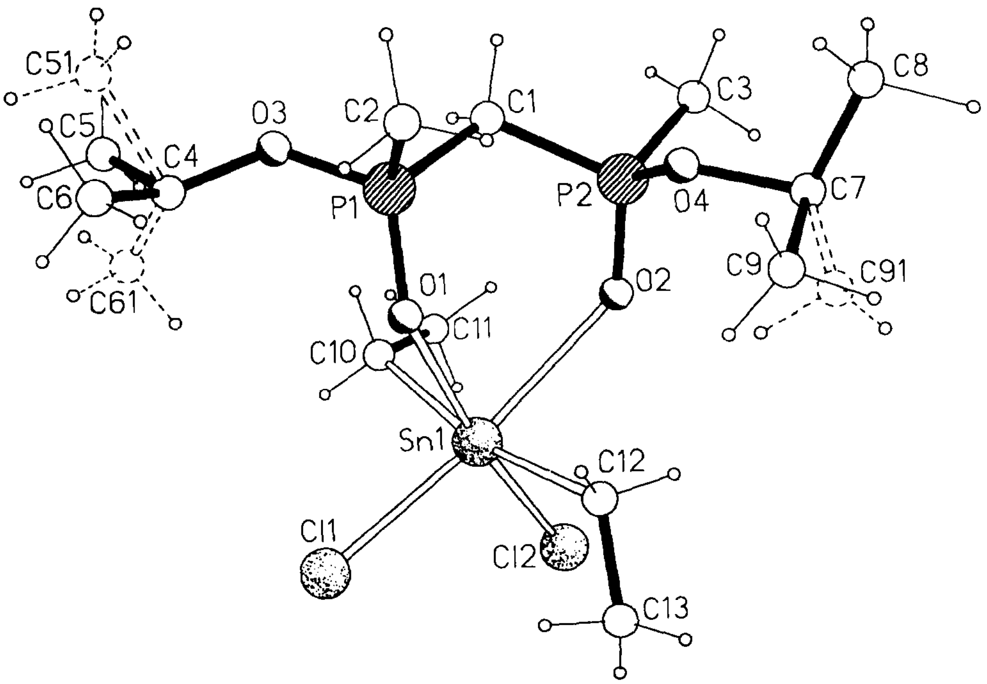

Fig. 1. Structure of I.

TABLE 2. Atomic fractional coordinates and equivalent isotropic temperature factors for $Et_2SnCl_2 \cdot [Me(^iPrO)P(O)]_2CH_2$

Atom	x	y	z	U_{eq} (Å^2)
Sn(1)	0.76665(7)	0.2331(1)	0.58514(5)	0.055(1)
Cl(1)	0.6385(3)	0.3898(4)	0.6162(2)	0.091(2)
Cl(2)	0.8908(3)	0.4228(4)	0.6077(2)	0.084(2)
P(1)	0.6607(3)	−0.1298(4)	0.5713(2)	0.057(2)
P(2)	0.8567(3)	−0.1236(4)	0.5288(2)	0.058(2)
O(1)	0.6591(5)	0.0319(8)	0.5552(4)	0.063(3)
O(2)	0.8709(5)	0.0373(7)	0.5450(4)	0.062(3)
O(3)	0.6277(6)	−0.1712(9)	0.6522(5)	0.068(4)
O(4)	0.8118(6)	−0.1616(8)	0.4412(5)	0.068(4)
C(1)	0.7770(7)	−0.204(1)	0.5858(6)	0.047(4)
C(2)	0.5930(8)	−0.230(1)	0.4950(6)	0.092(6)
C(3)	0.9647(7)	−0.218(1)	0.5506(6)	0.068(5)
C(4)	0.553(2)	−0.119(3)	0.681(2)	0.143(15)
C(5)[a]	0.574(2)	−0.151(4)	0.774(1)	0.191(22)
C(51)[b]	0.499(5)	−0.271(6)	0.694(4)	0.161(24)[e]
C(6)[a]	0.465(2)	−0.128(5)	0.657(2)	0.171(21)
C(61)[b]	0.544(4)	−0.018(6)	0.717(4)	0.139(30)[e]
C(7)	0.862(1)	−0.135(2)	0.3731(8)	0.089(7)
C(8)	0.867(1)	−0.277(2)	0.3333(8)	0.141(10)
C(9)[c]	0.754(2)	−0.067(3)	0.310(2)	0.047(12)[e]
C(91)[d]	0.825(2)	−0.028(3)	0.323(1)	0.099(8)[e]
C(10)	0.787(1)	0.148(1)	0.7036(7)	0.085(7)
C(11)	0.888(1)	0.138(2)	0.7397(9)	0.155(10)
C(12)	0.7515(9)	0.266(1)	0.4596(6)	0.081(6)
C(13)	0.737(1)	0.411(1)	0.4284(8)	0.167(11)

[a] Occupation factor, 0.667. [b] Occupation factor, 0.333. [c] Occupation factor, 0.36. [d] Occupation factor, 0.64. [e] Isotropic temperature factors refined.

TABLE 3. Bond lengths (Å) and bond angles (°), with disordered groups not included

Bond lengths			
Sn(1)–Cl(1)	2.462(4)	Sn(1)–Cl(2)	2.489(4)
Sn(1)–O(1)	2.417(7)	Sn(1)–O(2)	2.497(7)
Sn(1)–C(10)	2.132(12)	Sn(1)–C(12)	2.125(10)
P(1)–O(1)	1.500(8)	P(1)–O(3)	1.560(9)
P(1)–C(1)	1.802(11)	P(1)–C(2)	1.766(12)
P(2)–O(2)	1.502(8)	P(2)–O(4)	1.572(9)
P(2)–C(1)	1.766(11)	P(2)–C(3)	1.783(11)
O(3)–C(4)	1.34(3)	O(4)–C(7)	1.47(2)
Bond angles			
Cl(1)–Sn(1)–Cl(2)	96.7(1)	Cl(1)–Sn(1)–O(1)	90.0(2)
Cl(1)–Sn(1)–O(2)	168.3(2)	Cl(1)–Sn(1)–C(10)	91.1(4)
Cl(1)–Sn(1)–C(12)	99.1(4)	Cl(2)–Sn(1)–O(1)	173.1(2)
Cl(2)–Sn(1)–O(2)	94.9(2)	Cl(2)–Sn(1)–C(10)	96.3(4)
Cl(2)–Sn(1)–C(12)	91.5(4)	O(1)–Sn(1)–O(2)	78.4(3)
O(1)–Sn(1)–C(10)	85.3(4)	O(1)–Sn(1)–C(12)	85.7(4)
O(2)–Sn(1)–C(10)	89.2(4)	O(2)–Sn(1)–C(12)	79.0(4)
C(10)–Sn(1)–C(12)	166.4(5)	O(1)–P(1)–O(3)	113.5(5)
O(1)–P(1)–C(1)	112.6(5)	O(1)–P(1)–C(2)	112.7(5)
O(3)–P(1)–C(1)	100.9(5)	O(3)–P(1)–C(2)	107.9(5)
C(1)–P(1)–C(2)	108.5(5)	O(2)–P(2)–O(4)	114.5(4)
O(2)–P(2)–C(1)	112.9(5)	O(2)–P(2)–C(3)	110.0(5)
O(4)–P(2)–C(1)	102.0(5)	O(4)–P(2)–C(3)	108.8(5)
C(1)–P(2)–C(3)	108.1(5)	Sn(1)–O(1)–P(1)	135.7(5)
Sn(1)–O(2)–P(2)	132.5(5)	P(1)–O(3)–C(4)	127.0(1)
P(2)–O(4)–C(7)	121.3(8)	P(1)–C(1)–P(2)	116.3(6)

TABLE 4. Comparison of some bond distances (Å) and bond angles (°) in I and related species: $Et_2SnCl_2[Me(^iPrO)P(O)]_2CH_2$ (I), $Ph_2SnCl_2[(EtO)_2P(O)]_2CH_2$ (II), $Bu_2SnCl_2 \cdot$(cdppoet) (III) and $Pr_2SnCl_2 \cdot$(cdppoet) (IV)

Structure	I	II	III	IV
	This work	[2]	[10]	[10]
	distorted chelate	Chelate	Chelate	Strongly distorted chelate
Distances				
Sn–O	2.417(7)	2.427(5)	2.29(1)	2.24(1)
	2.497(7)	2.400(5)	2.27(1)	2.58(1)
Sn–C	2.132(12)	2.140(7)	2.14(2)	2.14(1)
	2.125(10)	2.138(7)	2.12(2)	2.15(1)
Sn–Cl	2.462(4)	2.449(3)	2.529(5)	2.436(3)
	2.489(4)	2.434(2)	2.509(5)	2.563(4)
P–O	1.500(8)	1.475(5)	1.48(1)	1.48(1)
	1.502(8)	1.470(5)	1.50(1)	1.50(1)
Angles				
C–Sn–C	166.4(5)	162.2(3)	169.4(8)	156.6(6)
O–Sn–O	78.4(3)	82.1(2)	77.4(4)	74.8(4)
Cl–Sn–Cl	96.7(1)	98.8(8)	99.0(2)	94.5(1)
Sn–O–P	135.7(5)	137.3(3)	150.1(7)	155.7(6)
	132.5(5)	133.9(3)	148.7(7)	143.1(6)

complexes involving *cis*-$[Ph_2P(O)CH]_2$ (cdppoet) [10], indicating the weaker donor ability of phosphinate groups than of phosphinoxides. The bond angles C–Sn–C, O–Sn–O, Cl–Sn–Cl and Sn–O–P (see Table 3) are typical of octahedral chelate complexes with six-membered rings, such as adducts of Ph_2SnCl_2 with methylenediphosphonates.

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