METAL-ORGANIC COMPOUNDS

Dichlorobis(triphenylphosphine oxide)-tin(II)

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Abstract

The title compound, $[SnCl_2(C_{18}H_{15}OP)_2]$ or $SnCl_2$.2TPPO (TPPO is triphenylphosphine oxide), has been found to be a four-coordinate tin(II) complex by single-crystal X-ray diffraction analysis. The distorted axial arrangement of the two TPPO ligands and the equatorial disposition of the two chlorines around tin(II) are confirmed.

Comment

In contrast to the several structural investigations of tin(IV)–phosphine oxide complexes (Tudela *et al.*, 1993), no characterizations of the analogous tin(II) complexes have so far been carried out. However, the preparation of two series of complexes of TPPO, SnX_2.TPPO and SnX_2.2TPPO (X = Cl, Br), have been reported, together with their IR and Mossbauer data (Donaldson & Nicholson, 1970). In the present work, the structure of the title complex, (I), was determined by X-ray diffraction. Tin(II) adopts an unsymmetrical four-coordinate geometry involving two chlorine ligands and two TPPO groups. The geometry of the complex can be best described as a ψ-trigonal bipyramid. As expected, the bond pairs associated with the more electronegative O atoms prefer to be away from each other and so occupy axial positions.

(I)
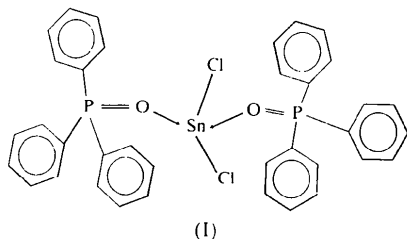
The IR spectrum of $SnCl_2$.2TPPO has prominent absorptions at 1145 and 1115 cm^{-1}, which are much lower than the ν_{P-O} absorption observed for TPPO itself (1195 cm^{-1}). However, the P—O bond lengths and P—O—metal angles are comparable to the corresponding values observed in TPPO and its metal complexes (Spek, 1987; Alfarhan, 1992; Bombieri *et al.*, 1983; Mazhar-Ul-Haque *et al.*, 1971; Nardelli *et al.*, 1978; Ng & Kumar Das, 1992; Eppley *et al.*, 1992; Burford *et al.*, 1990; Tudela *et al.*, 1993). The Cl—Sn—Cl [96.78 (5)°] and O—Sn—O [164.8 (1)°] angles are narrower than their ideal values of 120 and 180°, respectively, due to the presence of a lone pair of electrons on the Sn atom. The two Sn—O—P angles, 146.8 (2) and 167.2 (2)°, fall within the range of 140–180° observed for other phosphine oxide complexes.
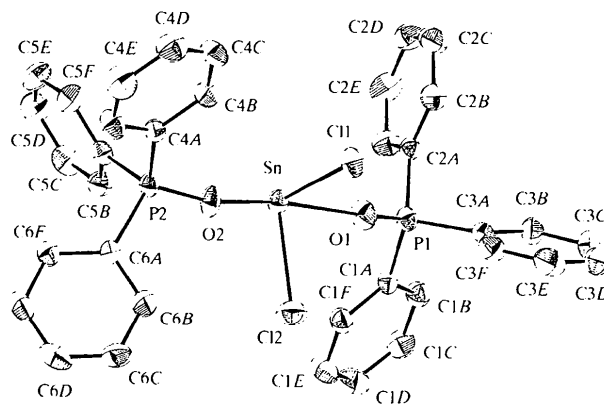

Fig. 1. The molecular structure and atom-numbering scheme for the title compound. Displacement ellipsoids are plotted at the 30% probability level.

Experimental

The title complex was prepared according to Donaldson & Nicholson (1970). Crystals suitable for X-ray diffraction analysis were obtained by slow cooling of a benzene solution containing a few drops of heptane.

Crystal data

$[SnCl_2(C_{18}H_{15}OP)_2]$	Mo $K\alpha$ radiation
$M_r = 746.13$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 14.354 (5)$ Å	$\theta = 2–22°$
$b = 13.594 (4)$ Å	$\mu = 1.029$ mm^{-1}
$c = 17.501 (3)$ Å	$T = 298 (2)$ K
$\beta = 91.29 (2)°$	Plate
$V = 3414.2 (17)$ Å^3	0.25 × 0.22 × 0.13 mm
$Z = 4$	Colourless
$D_x = 1.452$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
T_{min} = 0.779, T_{max} = 0.875
6020 measured reflections
5765 independent reflections

4410 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 25°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 16$
$l = -20 \rightarrow 20$
2 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.077$
$S = 1.218$
5765 reflections
388 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0120P)^2 + 4.1072P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.454$ e Å^{-3}
$\Delta\rho_{min} = -0.321$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Sn—O2	2.364 (3)	P1—C2A	1.795 (4)
Sn—O1	2.394 (3)	P1—C3A	1.796 (4)
Sn—Cl1	2.452 (1)	P1—C1A	1.804 (4)
Sn—Cl2	2.480 (1)	P2—C5A	1.797 (4)
O1—P1	1.489 (3)	P2—C6A	1.798 (4)
O2—P2	1.495 (3)	P2—C4A	1.799 (4)
O2—Sn—O1	164.78 (11)	O1—P1—C3A	111.2 (2)
O2—Sn—Cl1	85.22 (8)	O1—P1—C1A	111.0 (2)
O1—Sn—Cl1	84.35 (9)	O2—P2—C5A	111.8 (2)
O2—Sn—Cl2	84.83 (9)	O2—P2—C6A	110.9 (2)
O1—Sn—Cl2	85.44 (9)	O2—P2—C4A	110.1 (2)
Cl1—Sn—Cl2	96.78 (5)	C2F—C2A—C2B	118.4 (4)
P1—O1—Sn	167.2 (2)	C4B—C4A—C4F	118.2 (4)
P2—O2—Sn	146.8 (2)	C5D—C5E—C5F	121.2 (5)
O1—P1—C2A	112.3 (2)		

The title structure was solved by conventional Patterson and Fourier methods. The H atoms were located from a difference Fourier map. In the final refinement, their positions and isotropic displacement parameters (0.05 Å^2) were fixed.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1080). Services for accessing these data are described at the back of the journal.

References

Alfarhan, K. A. (1992). *J. Crystallogr. Spectrosc. Res.* **22**, 687–689.
Bombieri, G., Benetollo, F., Bagnall, K. W., Plews, M. J. & Brown, D. (1983). *J. Chem. Soc. Dalton Trans.* pp. 343–348.
Burford, N., Royan, B. W., Spence, R. E. V. H. & Rogers, R. D. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1521–1528.
Donaldson, J. D. & Nicholson, D. G. (1970). *J. Chem. Soc. A.* pp. 145–150.
Enraf–Nonius (1989). *CAD-4 Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Eppley, H. J., Ealy, J. L., Yoder, C. H., Spencer, J. N. & Rheingold, A. L. (1992). *J. Organomet. Chem.* **431**, 133–141.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Mazhar-Ul-Haque, Caughlan, C. N., Hart, F. A. & VanNice, R. (1971). *Inorg. Chem.* **10**, 115–132.
Nardelli, M., Pelizzi, C. & Pelizzi, G. (1978). *J. Chem. Soc. Dalton Trans.* pp. 131–133.
Ng, S. W. & Kumar Das, V. G. (1992). *Acta Cryst.* C**48**, 1839–1840.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1987). *Acta Cryst.* C**43**, 1233–1235.
Tudela, D., Tornero, J. D., Monge, A. & Sanchez-Herencia, A. J. (1993). *Inorg. Chem.* **32**, 3928–3930.
Zsolnai, L. (1997). *ZORTEP. Molecular Graphics Program.* University of Heidelberg, Germany.

Platinum Complexes of 1,4,7-Trithiacyclodecane

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Abstract

A neutral Pt^{II} complex, dichloro(1,4,7-trithiacyclodecane-S^1,S^7)platinum, [PtCl$_2$(C$_7$H$_{14}$S$_3$)], and a hydrated salt of a cationic Pt^{II} complex, bis(1,4,7-trithiacyclodecane-S^1,S^4)platinum dichloride heptahydrate, [Pt(C$_7$H$_{14}$S$_3$)$_2$]Cl$_2$.7H$_2$O, have been studied. The ten-membered heterocyclic ligand, 1,4,7-trithiacyclodecane (10S3), forms a six-membered chelate ring in the neutral complex, where the average Pt—S and Pt—Cl bond lengths are 2.255 (5) and 2.334 (4) Å, respectively, and the average weak axial Pt$\cdots$S interaction distance is 3.137 (5) Å. The same ligand in the cationic complex forms two five-membered chelate rings in which the average length of the four equatorial Pt—S bonds is 2.296 (2) Å and the lengths of the two weak axial Pt$\cdots$S bonds are 3.159 (2) Å.