

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *CSD* (Akselrud *et al.*, 1993). Program(s) used to refine structure: *CSD*. Molecular graphics: *CrystalDesigner* (Crystal Structure Design, 1997) and *ORTEP3* (Farrugia, 1997). Software used to prepare material for publication: *CSD*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1011). Services for accessing these data are described at the back of the journal.

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Di- μ -chloro-bis[chlorodimethyl(3-methyl-4-nitropyridine *N*-oxide-*O*)tin]

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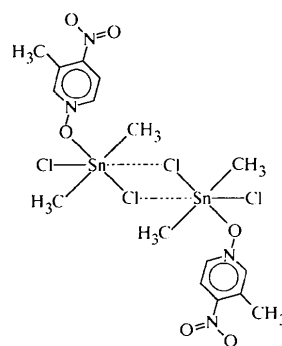
Abstract

The title compound, $[\text{Sn}_2\text{Cl}_4(\text{CH}_3)_4(\text{C}_6\text{H}_6\text{N}_2\text{O}_3)_2]$, crystallizes as a six-coordinate *trans*- C_2SnOCl_3 octahedral chlorine-bridged centrosymmetric dimer; some geometric details are Sn—O 2.399 (2), Sn—Cl 2.3583 (7) and 2.4774 (7), Sn—Cl_{bridge} 3.9341 (8) Å and C—Sn—C 137.7 (2)°.

Comment

3-Methyl-4-nitropyridine *N*-oxide (POM), a material for non-linear optics (Sigelle *et al.*, 1982), forms complexes

with a number of inorganic salts. These complexes exhibit strong second harmonic generation (SHG) effects, as exemplified by $\text{CdBr}_2 \cdot 2\text{POM}$, the SHG of which is 18 times that of potassium dihydrogen phosphate (Li *et al.*, 1992; Hu *et al.*, 1994). This SHG property implies that the complexes must be non-centrosymmetric (Dougherty & Kurtz, 1976). On the other hand, POM is an O-donor ligand that should yield complexes with Lewis basic dimethyltin dichloride, which forms 1:2 complexes with pyridine *N*-oxide (Blom *et al.*, 1969) and quinoline *N*-oxide (Ng, 1994), but a 1:1 complex with 2,6-dimethylpyridine *N*-oxide (Ng *et al.*, 1983). The dimethyltin dichloride–POM adduct was expected to crystallize in a non-centrosymmetric space group, but the crystal structure determination shows that the adduct, (I), packs across a center of inversion as a chlorine-bridged $[\text{Sn}—\text{Cl} \ 3.9341(8) \text{ \AA}]$ six-coordinate dimeric compound.



(I)

The Sn—Cl bridge is much weaker than that [3.399 (1) Å] in the 2,6-dimethylpyridine *N*-oxide complex, as well as that [3.561 (1) Å] in the 1,2-diphenylcyclopropanone complex (Ng *et al.*, 1982). With only one possible exception, that of the dimethyl sulfoxide complex (Ng & Rheingold, 1989), the 1:1 adducts of dimethyltin dichloride show sixfold coordination at tin in the solid state (Ng & Zuckerman, 1982). The bridging distance is also longer than that [3.54 (5) Å] found in the parent Lewis base, the sixfold-coordinated geometry of which is supported by Mössbauer measurements (Davies *et al.*, 1970).

The Sn atom in the complex shows distorted C_2SnOCl_3 octahedral coordination geometry [C—Sn—C 137.7 (2) Å]. The C—Sn—C angle has been opened somewhat by the long chlorine bridge. The complex adopts five-coordinate geometry in solution, as suggested by the magnitudes of the coupling constants in the NMR spectra. Bond distances involving the POM moiety are similar to those found in POM itself (Shiro *et al.*, 1977; Baert *et al.*, 1988). However, the nitro plane is twisted out of the pyridyl plane by 24.7 (2)° in the complex, whereas in POM, the twist is only 16.7° (Shiro *et al.*, 1977).

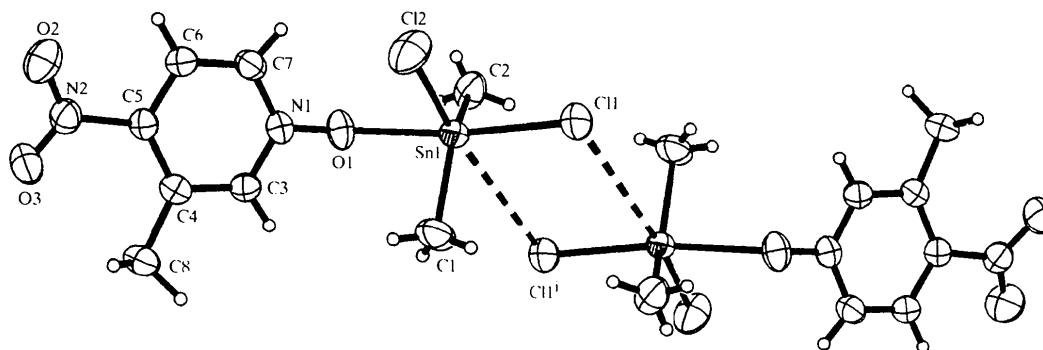


Fig. 1. ORTEP (Johnson, 1976) plot of (I) at the 50% probability level. The intramolecular Sn—Cl bridging interactions are shown as solid dashed lines. H atoms are drawn as spheres of arbitrary radii.

Experimental

Dimethyltin dichloride and 3-methyl-4-nitropyridine *N*-oxide in a 1:1 molar ratio were dissolved in a small volume of warm ethanol; the title complex separated as large crystals on cooling the filtered solution. The formulation of the adduct was established from satisfactory ¹H NMR spectral integration in CDCl₃. ¹³C NMR (chemical shifts in p.p.m.): Sn—CH₃ = 8.36, aryl CH₃ = 18.14, aryl C = 121.97, 133.03, 138.27, 142.23, 144.78. ¹J(¹¹⁹Sn—¹³C) = 548.1 Hz.

Crystal data

[Sn₂Cl₄(CH₃)₄(C₆H₆N₂O₃)₂] Mo K α radiation
M_r = 747.57 λ = 0.71073 Å
 Monoclinic Cell parameters from 25 reflections
*P*₂/n θ = 12.0–13.0°
a = 9.9216 (6) Å μ = 2.356 mm⁻¹
b = 11.2148 (6) Å *T* = 298 (2) K
c = 12.1991 (7) Å Irregular block
 β = 105.558 (5)° 0.36 × 0.32 × 0.28 mm
V = 1307.6 (1) Å³ Yellow
Z = 2
D_x = 1.899 Mg m⁻³
D_m not measured

Data collection

Enraf–Nonius CAD-4 3056 reflections with
 diffractometer $I > 2\sigma(I)$
 ω scan *R*_{int} = 0.023
 Absorption correction: θ_{\max} = 29.97°
 ψ scans (North *et al.*, $h = -13 \rightarrow 13$
 1968) $k = 0 \rightarrow 15$
 $T_{\min} = 0.349$, $T_{\max} = 0.502$ $l = -17 \rightarrow 17$
 7991 measured reflections 3 standard reflections
 3800 independent reflections frequency: 60 min
 intensity decay: 20%

Refinement

Refinement on *F*² $(\Delta/\sigma)_{\max} = -0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.026$ $\Delta\rho_{\max} = 0.404 \text{ e \AA}^{-3}$
 $wR(F^2) = 0.063$ $\Delta\rho_{\min} = -0.722 \text{ e \AA}^{-3}$
 $S = 1.009$ Extinction correction: none

3800 reflections

193 parameters

H atoms located and refined

$w = 1/[\sigma^2(F_o^2) + (0.0340P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Sn1—C1	2.105 (3)	Sn1—Cl1	2.4774 (7)
Sn1—C2	2.088 (3)	Sn1—Cl1'	3.9341 (8)
Sn1—O1	2.399 (2)	Sn1—Cl2	2.3583 (7)
C1—Sn1—C2	137.7 (2)	C2—Sn1—Cl2	113.4 (1)
C1—Sn1—O1	90.0 (1)	O1—Sn1—Cl1	172.27 (5)
C1—Sn1—Cl1	97.7 (1)	O1—Sn1—Cl1'	103.36 (5)
C1—Sn1—Cl1'	74.3 (1)	O1—Sn1—Cl2	84.52 (5)
C1—Sn1—Cl2	106.1 (1)	Cl1—Sn1—Cl2	92.50 (3)
C2—Sn1—O1	79.6 (1)	Cl1—Sn1—Cl1'	79.68 (2)
C2—Sn1—Cl1	95.2 (1)	Cl1'—Sn1—Cl2	172.12 (2)
C2—Sn1—Cl1'	68.6 (1)		

Symmetry code: (i) $-x, -y, -z$.

Data collection: *CAD-4/PC* (Kretschmar, 1994). Cell refinement: *CELDIM* in *CAD-4 VAX/PC* (Enraf–Nonius, 1988). Data reduction: *XCAD4* (Harms, 1997). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1174). Services for accessing these data are described at the back of the journal.

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Mixed-Halide Complex *trans*-Tetrahalobis-(triphenylphosphine oxide)rhenium(IV)

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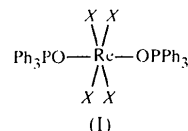
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Abstract

The molecule of the red title compound, *trans*-tetra-(chloro/bromo)bis(triphenylphosphine oxide)-rhenium(IV), $[\text{ReBr}_{2.5}\text{Cl}_{1.5}\{\text{OP}(\text{C}_6\text{H}_5)_3\}_2]$, lies on a crystallographic centre of symmetry. Coordination of rhenium by the four halides is square planar, capped by two mutually-*trans* triphenylphosphine oxide groups.

Comment

In the course of our work investigating the binding of rhenium by hydroxyimino-2,2'-dipropionic acid, we isolated the title compound, (I), which lies on a crystallographic centre of symmetry. The rhenium is coordinated by four halides, which are square planar, and two mutually-*trans* OPPh_3 molecules. Trial site-occupancy and displacement-parameter refinements with various constraints suggested that the halogen Br:Cl stoichiometry is 5:3, *i.e.* an overall composition of $[\text{ReBr}_{2.5}\text{Cl}_{1.5}(\text{OP}\{\text{C}_6\text{H}_5\}_3)_2]$. This result is consistent with the elemental analysis.



X = Cl/Br (stoichiometry 1.5:2.5)

The Re—O1 bond distance, 2.030 (7) Å, compares with those of 2.063 (9) and 2.053 (7) Å in $[\text{ReOCl}_3\text{-(PEt}_2\text{Ph)}(\text{OPEt}_2\text{Ph})]$ and $[\text{ReOBr}_3(\text{PEt}_2\text{Ph)}(\text{OPEt}_2\text{Ph})]$, respectively (Sergienko *et al.*, 1982). A search of the Cambridge Structural Database (Allen & Kennard, 1993) reveals very few structurally-characterized rhenium complexes with four halide ligands and a phosphine oxide group, making the structure of $[\text{ReBr}_{2.5}\text{Cl}_{1.5}(\text{OPPh}_3)_2]$ unusual. The Re^{IV} complex $[\text{ReCl}_4\text{-(dppom-}P,O)]$ [dppom = $\text{Ph}_2\text{PCH}_2\text{P(=O)Ph}_2$] has been reported (Rossi *et al.*, 1993) from the reaction of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ and dppm (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) under aerobic conditions. The crystal structure showed that the complex forms with a Cl atom *trans* to the O atom. The Re—O [2.087 (7) Å] and P—O [1.523 (8) Å] distances were slightly longer, and the Re—O—P angle far smaller [$130.1(1)^\circ$] than are observed for $[\text{ReBr}_{2.5}\text{Cl}_{1.5}(\text{OPPh}_3)_2]$. Rossi *et al.* (1993) also reported the synthesis of the Re^{V} compound $[\text{AsPh}_4]\text{-}[\text{ReCl}_4\{\text{N}(\text{OPPh}_2)(\text{PPh}_2)\text{-}O,P\}]$, also with a Cl atom *trans* to the O atom; the Re—O [2.054 (3) Å] and P—O [1.543 (3) Å] distances are slightly longer, and the Re—O—P angle far smaller [$128.2(3)^\circ$] than were observed for $[\text{ReBr}_{2.5}\text{Cl}_{1.5}(\text{OPPh}_3)_2]$. However, the small Re—O—P angles observed for these two complexes are probably due to the bidentate nature of the dppom and $\text{N}(\text{OPPh}_2)\text{PPh}_2$ ligands. Comparison with monodentate OPPh_3 -containing rhenium complexes $[\text{ReCl}_3(\text{NO})(\text{NPPh}_3)(\text{OPPh}_3)]$ [Re—O 2.092 (6), P—O 1.502 (7) Å and Re—O—P $148.7(4)^\circ$; Mronga *et al.*, 1983] and $[\text{ReOI}_2(\text{PPh}_3)(\text{OPPh}_3)(\text{OReO}_3)]$ [Re—O 2.075 (9), P—O 1.49 (1) Å and Re—O—P $151.5(6)^\circ$; Ciana *et al.*, 1986] shows that the Re—O—P angle [$158.1(5)^\circ$] for $[\text{ReBr}_{2.5}\text{Cl}_{1.5}(\text{OPPh}_3)_2]$ is not unusual. Comparisons of the Re—X bond lengths for these compounds with (I) show that, as expected, due to the mixed nature of the halogen atoms in (I), the bond lengths