Dibutyldichlorobis{2-[(phenylethylimino)-methyl]phenol-*O*}tin(IV)

Guan-Yeow Yeap and Nobuo Ishizawa

*Structures and Materials Laboratory, Tokyo Institute of
Technology, 4259 Nagatsuta, Midori, Yokohama 226, Japan.
E-mail: nishizaw@n.cc.titech.ac.jp*

Abstract

A crystal of the title compound, $[SnCl_2(C_4H_9)_2$-$(C_{15}H_{15}NO)_2]$, was prepared and its structure determined as the 1:2 tin–Schiff base adduct with space group $P\bar{1}$. The planes of the two phenyl rings of each Schiff base ligand were found to be almost perpendicular to each other and the ligand is coordinated to the Sn atom *via* the phenolic O atom. The ligand adopts a zwitterionic structure in which the H atom from the hydroxy group is strongly attached to the imine N atom, forming an N—H···O intramolecular hydrogen bond.

Comment

A considerable number of reports on the adducts derived from organotin(IV) halides and pseudohalides with aromatic Schiff bases have appeared over the past few decades (Ruddick & Sams, 1973; Srivastava & Chauhan, 1977; Kamwaya & Khoo, 1985; Dwivedi *et al.*, 1986; Fun, Teo, Teoh & Yeap, 1991; Fun, Teo, Teoh, Yeap & Yeoh, 1991; Teoh *et al.*, 1992, 1993, 1995; Yeap *et al.*, 1996).

Generally, the Schiff bases each consist of two aromatic rings linked by an imine C=N bond, which hinders the rotation of the rings. As such, the ability of Schiff bases to avoid steric hindrance within the coordination sphere is limited to a certain degree, especially when the substituent on the aromatic ring is in close proximity to the C=N bond. It has been reported that the reaction of diphenyltin(IV) dichloride with *ortho*-substituted 2-hydroxy-1-naphthylideneaniline formed a 1:1 adduct wherein the methyl substituent points towards the central Sn atom (Fun, Teo, Teoh & Yeap, 1991). Similarly, our recent study on dichlorodiphenyl{6-methoxy-2-[(4-cyanophenylimino)-methyl]phenol}tin(IV) has shown that the introduction of the OCH_3 substituent at position 6 of the aldehyde fragment in the Schiff base leads to the formation of a five-coordinate 1:1 diorganotin adduct with the ligand (Yeap & Ishizawa, 1998).

In this paper, we report the crystal structure of an adduct derived from dibutyltin(IV) dichloride and 2-[(phenylethylimino)methyl]phenol. This ligand con-

sists of two aromatic rings bridged by an exocyclic C=N—C—C chain, thus allowing rotation about the C—C single-bond axis. The ultimate 1:2 six-coordinate adduct thus obtained, (I), was characterized by single-crystal structure diffraction analysis.

(I)
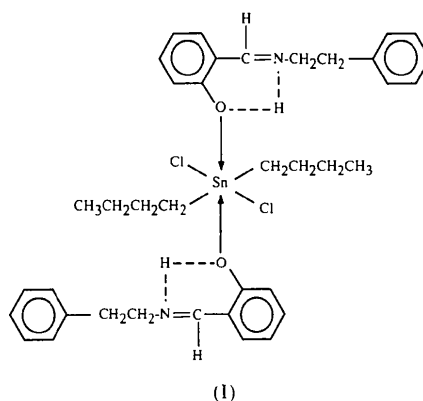
The Sn atom in the title compound is coordinated in an octahedral configuration with two equivalent Sn—O bonds. The Sn—O bond length [2.236 (2) Å] is slightly greater than the corresponding bond lengths in the six-coordinate adducts dichlorodiphenylbis{1-(4-methoxyphenylimino)methyl]-2-naphthol}tin(IV) [2.228 (3) Å; Fun, Teo, Teoh, Yeap & Yeoh, 1991] and diisothiocyanatodimethylbis{2-[(4-methylphenylimino)methyl]-phenol}tin(IV) [2.208 (2) Å; Yeap *et al.*, 1996]. This can be ascribed to the stronger electron-donating properties of the butyl group compared with phenyl and methyl groups. As such, the Lewis acidity of the central Sn atom decreases, leading to the weakening of the Sn—O bond.

One of the noteworthy features is that the proton H6 of the hydroxy group of the ligand molecule has migrated to the exocyclic imine N atom. As a result, the Schiff base acts as a zwitterion, coordinating to the Sn atom *via* the phenolic O atom, as reported elsewhere in the literature (Kamwaya & Khoo, 1985; Fun, Teo, Teoh & Yeap, 1991; Fun, Teo, Teoh, Yeap & Yeoh, 1991; Teoh *et al.*, 1992, 1993, 1995; Yeap *et al.*, 1996). The existence of the zwitterion can be explained by the charges of the atoms of interest calculated by the Hirshfeld (1977) method; the charges are 0.20 (9), −0.19 (4) and 0.09 (4) for Sn, O and N, respectively.

There is a difference in the planarity of the aromatic rings of the ligand molecules between the title compound and the adduct containing a C=N bond as the bridging group (Teoh *et al.*, 1991, 1992). From Fig. 1, it can clearly be seen that the planes of the two phenyl rings of each ligand molecule are almost perpendicular to each other. This conformation is found to be different from that observed in other aromatic Schiff bases in which the planes of the phenyl rings are almost coplanar owing to limited rotation about the C=N bond (Fun,
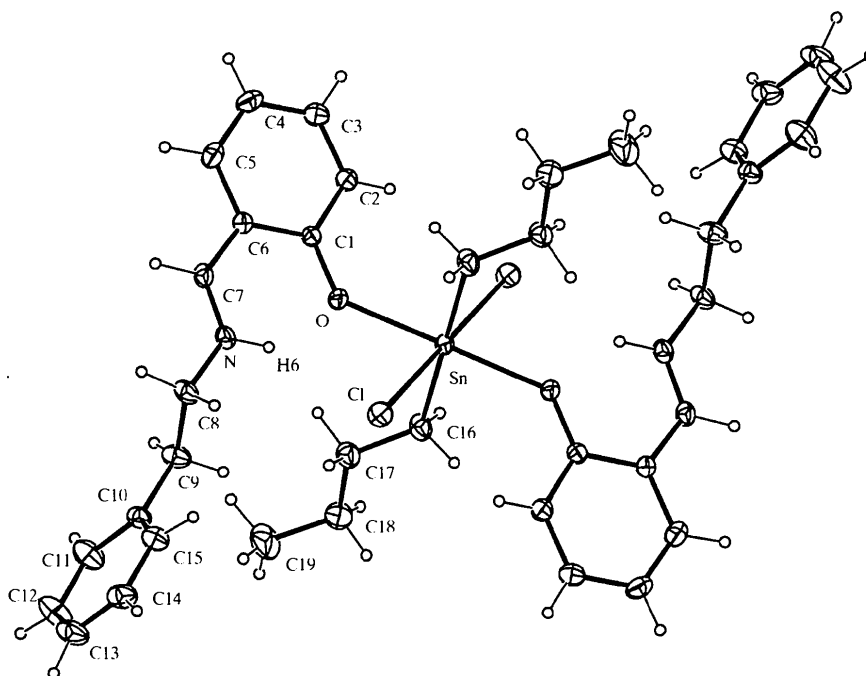
Fig. 1. The molecular structure of (I) showing 20% probability displacement ellipsoids (except for H atoms).

Teo, Teoh & Yeap, 1991; Fun, Teo, Teoh, Yeap & Yeoh, 1991; Teoh *et al.*, 1992, 1993, 1995; Yeap *et al.*, 1996; Yeap & Ishizawa, 1998).

Experimental

The Schiff base 2-[(phenylethylimino)methyl]phenol was prepared by condensation between equimolar 2-phenylethylamine and salicylaldehyde in 95% ethanol. The adduct was synthesized by adding a solution of dibutyltin(IV) dichloride (0.91 g, 3 mmol) in dichloromethane to a solution of the ligand (4.53 g, 6 mmol) in the same solvent.

Crystal data

[SnCl₂(C₄H₉)₂(C₁₅H₁₅NO)₂]

[SnCl$_2$(C$_4$H$_9$)$_2$(C$_{15}$H$_{15}$NO)$_2$]
M_r = 754.55
Triclinic
$P\bar{1}$
a = 9.889 (2) Å
b = 10.208 (3) Å
c = 9.466 (6) Å
α = 85.81 (4)°
β = 79.79 (3)°
γ = 79.14 (2)°
V = 922.8 (7) Å^3
Z = 1
D_x = 1.358 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 20 reflections
θ = 11–16°
μ = 0.87 mm^{-1}
T = 293 K
Plate
0.27 × 0.27 × 0.11 mm
Yellow

Data collection

Rigaku AFC-5 diffractometer

3926 reflections with
$F > 3\sigma(F)$

$\theta/2\theta$ scans
Absorption correction:
analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.804, T_{max} = 0.912
11 121 measured reflections
5382 independent reflections

R_{int} = 0.021
θ_{max} = 30°
h = −13 → 13
k = −14 → 14
l = −13 → 13
6 standard reflections
every 200 reflections
intensity decay: <1%

Refinement

Refinement on F
R = 0.029
wR = 0.020
S = 1.587
3924 reflections
301 parameters
All H atoms refined
$w = 1/\sigma(|F|)$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Sn—O	2.2356 (15)	N—H6	0.89 (2)
Sn—Cl	2.6340 (12)	C1—C6	1.427 (3)
Sn—C16	2.138 (3)	C1—C2	1.410 (3)
O—C1	1.301 (3)	C6—C7	1.418 (3)
O···H6	1.919 (19)	C6—C5	1.411 (4)
N—C7	1.286 (3)	C10—C9	1.515 (4)
N—C8	1.464 (3)		
O—Sn—Cl	97.05 (5)	N—C7—C6	124.7 (2)
O—Sn—C16	90.15 (8)	N—C8—C9	110.9 (2)
Sn—O—C1	136.84 (12)	Sn—C16—C17	119.6 (2)
C7—N—C8	125.7 (2)	C10—C9—C8	114.7 (3)
O—C1—C6	119.84 (18)	O···H6—N	134.8 (18)
O—C1—C2	123.29 (19)		

Data collection: Rigaku AFC-5 diffractometer system. Cell refinement: Rigaku AFC-5 diffractometer system. Data reduction: *Xtal*3.4 (Hall *et al.*, 1995). Program(s) used to solve

structure: *Xtal*3.4. Program(s) used to refine structure: *Xtal*3.4. Molecular graphics: *Xtal*3.4. Software used to prepare material for publication: *Xtal*3.4.

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A Star-Shaped Heptanuclear Tetramine Cadmium(II) Complex

PETER KLÜFERS AND PETER MAYER

Institut für Anorganische Chemie der Universität, Engesserstraße, Gebäude 30.45, D-76128 Karlsruhe, Germany. E-mail: kluefers@achibm2.chemie.uni-karlsruhe.de

Abstract

Colourless rhombohedral crystals of dodecakis[tris(2-aminoethyl)amine]heptacadmium(II) tetradecaperchlorate, [Cd$_7$(tren)$_{12}$](ClO$_4$)$_{14}$ (tren = C$_6$H$_{18}$N$_4$), form from

aqueous solutions of the cellulose solvent 'Cd–tren' on addition of perchloric acid. The heptanuclear cations are flat star-shaped disks and are composed of Cd(tren) moieties that are linked by further tren ligands, which exhibit the unusual $\mu^3,\kappa^3 N,N',N''$ mode of coordination.

Comment

Crystals of the perchlorate of the cation dodecakis[tris(2-aminoethyl)amine]heptacadmium(II) have been grown from aqueous solutions of cadmium oxide and tris(2-aminoethyl)amine (tren) in a molar ratio of about 1:1.2 on addition of perchloric acid. The rhombohedral crystals are composed of perchlorate anions and heptanuclear [Cd$_7$(tren)$_{12}$]$^{14+}$ cations, (I).

$$\bullet\!\!-\!\!\bullet = N_{1/3}-CH_2-CH_2-NH_2$$

(I)
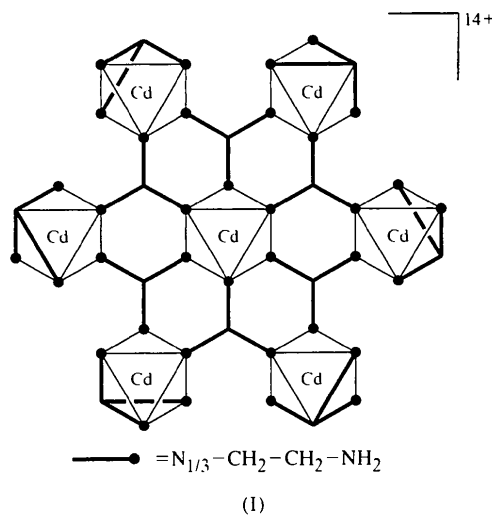
The star-shaped cations (Fig. 1) exhibit $\bar{3}$ symmetry and may be regarded as having an octahedrally coordinated Cd atom as a nucleus, surrounded by six monohapto-bonded tren ligands with two pendant primary amino functions each. The latter assemble as six Cd(tren) moieties, the free coordination sites of which exactly match the number of available NH$_2$ functions. Thus, of the 12 tren molecules, six are each bound to an equal number of Cd atoms (Cd2) in the usual tetradentate mode of coordination towards a single central atom. The other six tetramine entities, however, coordinate through the primary amine functions exclusively, in the unusual tridentate $\mu^3,\kappa^3 N,N',N''$ mode, thus giving rise to the star-shaped heptanuclear tetradecacationic structure. The molecular stars themselves are flat; their height is only about one third of their diameter. Accordingly, the crystal structure resembles a disk packing of cations, which may be regarded as a heavily [111]-compressed cubic closest packing of spheres. The anions are acceptors of hydrogen bonds, with the N—H functions of the cations acting as donors.

The bond distances are normal and narrowly distributed within the undisordered perchlorate anions and the tren ligands [mean value ± s.u. of the mean, mean