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Bis(*o*-methoxyphenyl)tin Dibromide

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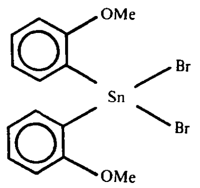
Abstract

The Sn atom in the title compound, $[SnBr_2(C_7H_7O)_2]$, has a distorted tetrahedral coordination geometry. There are indications of weak Sn···O intramolecular interactions.

Comment

A recent crystal structure determination of tris(*o*-methoxyphenyl)tin iodide (Howie, Ross, Wardell & Low, 1994) provided some evidence of weak Sn···O intramolecular coordination; the shortest Sn···O1 distance was 2.965 (7) Å with an I—Sn···O1 angle of 152.1 (1)°.

The crystal structure of the title compound, (I), has now been determined. The Sn···O intramolecular separations [2.90 (1) and 2.92 (1) Å] provide indications of weak tin–oxygen coordinations. The constraints of the *ortho*-disubstituted aryl system result in the four-membered chelate rings being highly strained. Of interest, there are significant differences between the valency angles Sn1—C1*A*—C2*A* and Sn1—C1*A*—C6*A* [114.2 (6) and 125.9 (6)°, respectively], and Sn1—C1*B*—C2*B* and Sn1—C1*B*—C6*B* [114.9 (6) and 124.9 (6)°, respectively]; these values allow the Sn atom to approach each of the two O atoms more closely. The differences in the exocyclic valency angles involving each of the O atoms and the aryl-ring C atoms are generally found in methoxyaryl compounds (Howie, Ross, Wardell & Low, 1994), and so cannot be used to confirm tin–oxygen interactions.



(I)

The Sn—Br bond lengths in the present study [2.480 (2) and 2.481 (2) Å], are much shorter than those found for the distorted octahedral bis(*C*,*N*)-chelate complex bis(8-dimethylamino-1-naphthyl)tin dibromide [2.610 (2) and 2.623 (2) Å; Jastrzebski, 1991]. The C—

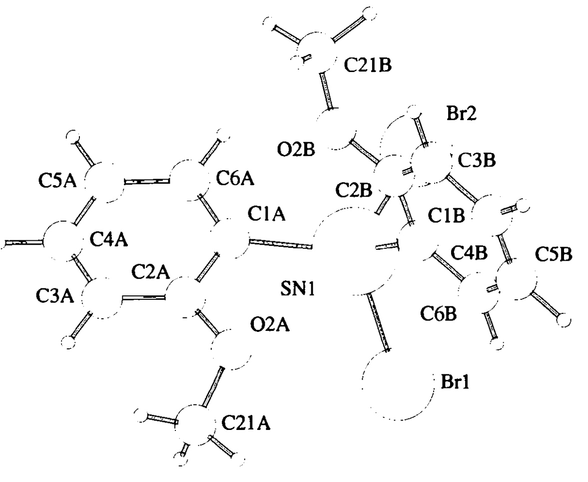


Fig. 1. Perspective view of the molecule.

Sn—C [124.7 (3)°] and Br—Sn—Br [103.9 (1)°] valency angles, and Sn—Br bond lengths in the title compound are more like those found for the essentially four-coordinate molecules [$SnBr_2(C_2H_5)_2$] [135.9 (10), 98.5 (1)° and 2.505 (4) Å, respectively (Alcock & Sawyer, 1977)] and [$SnBr_2(C_6H_{11})_2$] [133.8 (8)°, 98.3 (8)° and 2.492 (3)–2.516 (2) Å, respectively (Ganis, Valle, Furlani & Tabliavini, 1986)], than those of the six-coordinate complex bis(8-dimethylamino-1-naphthyl)tin dibromide (Jastrzebski, 1991).

In [$SnBr_2(C_2H_5)_2$], secondary and weak intermolecular interactions [Sn···Br 3.777 (4) Å and Br—Sn···Br 179.5 (5)°] were also reported. The shortest intermolecular Sn···Br contacts in [$SnBr_2(C_7H_7O)_2$] are, however, *ca* 5.5 Å.

Experimental

The title compound was prepared from [$Sn(C_7H_7O)_4$] and Br_2 in $CHCl_3$, and recrystallized from hexane–acetone (1:1); m.p. 416–417 K.

Crystal data

[$SnBr_2(C_7H_7O)_2$]
$M_r = 492.76$
Monoclinic
$P2_1/n$
$a = 14.0487$ (24) Å
$b = 7.5563$ (7) Å
$c = 16.9279$ (21) Å
$\beta = 113.409$ (9)°
$V = 1649.1$ (4) Å^3
$Z = 4$
$D_x = 1.985$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71067$ Å
Cell parameters from 25 reflections
$\theta = 14.05$–21.65°
$\mu = 6.32$ mm^{-1}
$T = 293$ K
Thin plate
0.417 × 0.375 × 0.069 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (ψ scan)
$T_{\min} = 0.304$, $T_{\max} = 0.999$
3688 measured reflections
3576 independent reflections
2131 observed reflections [$I > 2.5\sigma(I)$]

$R_{\rm int} = 0.017$
$\theta_{\max} = 26.88°$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 21$
3 standard reflections monitored every 60 reflections intensity variation: 2.5%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.050$
$S = 1.20$
2131 reflections
173 parameters
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.82$ e Å^{-3}
$\Delta\rho_{\min} = -0.72$ e Å^{-3}

Extinction correction: Larson (1970)
Extinction coefficient: 83 (12)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Sn1	0.78992 (5)	0.38233 (7)	0.01419 (4)	0.0433 (4)
Br1	0.87630 (9)	0.09407 (14)	0.01866 (7)	0.0735 (8)
Br2	0.93584 (9)	0.58836 (15)	0.08829 (7)	0.0760 (7)
C1*A*	0.7193 (6)	0.4690 (11)	−0.1144 (5)	0.042 (5)
C2*A*	0.6425 (7)	0.3571 (11)	−0.1678 (5)	0.045 (5)
O2*A*	0.6221 (5)	0.2146 (8)	−0.1264 (4)	0.059 (4)
C21*A*	0.5713 (12)	0.0656 (15)	−0.1784 (9)	0.095 (10)
C3*A*	0.5898 (7)	0.3947 (13)	−0.2542 (6)	0.056 (6)
C4*A*	0.6160 (8)	0.5426 (14)	−0.2870 (6)	0.060 (7)
C5*A*	0.6904 (8)	0.6571 (14)	−0.2360 (7)	0.065 (7)
C6*A*	0.7446 (7)	0.6215 (12)	−0.1478 (6)	0.056 (6)
C1*B*	0.7120 (7)	0.3498 (11)	0.0976 (5)	0.046 (5)
C2*B*	0.6453 (7)	0.4870 (11)	0.0957 (6)	0.048 (6)
O2*B*	0.6429 (6)	0.6207 (8)	0.0419 (4)	0.068 (5)
C21*B*	0.5913 (10)	0.7812 (14)	0.0458 (8)	0.088 (9)
C3*B*	0.5886 (8)	0.4802 (14)	0.1480 (7)	0.065 (7)
C4*B*	0.6026 (9)	0.3364 (16)	0.2012 (7)	0.067 (7)
C5*B*	0.6680 (9)	0.2008 (15)	0.2039 (7)	0.071 (8)
C6*B*	0.7235 (7)	0.2059 (12)	0.1512 (6)	0.055 (6)

Table 2. *Selected geometric parameters* (Å, °)

Sn1—Br1	2.4799 (11)	C4*A*—C5*A*	1.368 (16)
Sn1—Br2	2.4813 (12)	C5*A*—C6*A*	1.406 (14)
Sn1—C1*A*	2.106 (8)	C1*B*—C2*B*	1.390 (13)
Sn1—C1*B*	2.117 (9)	C1*B*—C6*B*	1.384 (12)
C1*A*—C2*A*	1.386 (12)	C2*B*—O2*B*	1.352 (11)
C1*A*—C6*A*	1.390 (13)	C2*B*—C3*B*	1.407 (14)
C2*A*—O2*A*	1.376 (10)	O2*B*—C21*B*	1.428 (12)
C2*A*—C3*A*	1.381 (12)	C3*B*—C4*B*	1.375 (16)
O2*A*—C21*A*	1.434 (13)	C4*B*—C5*B*	1.366 (17)
C3*A*—C4*A*	1.362 (15)	C5*B*—C6*B*	1.398 (15)
Br1—Sn1—Br2	103.87 (5)	C1*A*—C2*A*—O2*A*	114.2 (7)
Br1—Sn1—C1*A*	109.17 (23)	O2*A*—C2*A*—C3*A*	124.7 (8)
Br1—Sn1—C1*B*	104.72 (24)	C2*A*—O2*A*—C21*A*	117.0 (8)
Br2—Sn1—C1*A*	106.42 (23)	Sn1—C1*B*—C2*B*	114.9 (6)
Br2—Sn1—C1*B*	106.14 (22)	Sn1—C1*B*—C6*B*	124.9 (7)
C1*A*—Sn1—C1*B*	124.7 (3)	C2*B*—C1*B*—C6*B*	120.2 (8)
Sn1—C1*A*—C2*A*	114.2 (6)	C1*B*—C2*B*—O2*B*	114.2 (8)
Sn1—C1*A*—C6*A*	125.9 (6)	O2*B*—C2*B*—C3*B*	125.7 (8)
C2*A*—C1*A*—C6*A*	119.9 (8)	C2*B*—O2*B*—C21*B*	118.7 (8)

The structure was solved by the heavy-atom method. H atoms were included as riding atoms in calculated positions, the C—H distance being fixed at 0.95 Å. Data collection was performed with *CAD*-4 *Software*; *CELDIM* was used for cell refinement (Enraf–Nonius, 1989). Data reduction, structure solution, structure refinement, molecular graphics and preparation of material for publication were performed using the *NRCVAX* set of programs (Gabe, Le Page, Charland, Lee & White, 1989).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HA1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chlorobis{2-[(dimethylamino)methyl]-phenyl-C^1,N}(pyridine)vanadium(III)

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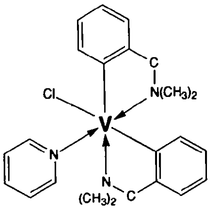
Abstract

The octahedral coordination of the tervalent bis-aryl vanadium complex [$VCl(C_5H_5N)(C_9H_{12}N)_2$] is completed by one pyridine and one Cl ligand with a V—Cl distance of 2.395 (2) Å.

Comment

Divalent and tervalent vanadium ions play a significant role in biological systems (Robson *et al.*, 1986). Nitrogen fixation and reduction (Denisov, Efimov, Shuvalova, Shilova & Shilov, 1970; Shilov *et al.*, 1971) is an important phenomenon with regard to the activity of V^{II} and V^{III} and has been studied by a number of research groups. The presence of either alkoxo or alkyl groups in the coordination sphere of the V atom may account for this particular type of activity of the transition metal. In a previous report, we described the formation of a V^{II} dinitrogen complex (Edema, Gambarotta & Meetsma, 1989) bearing *ortho*-dimethylaminomethylphenyl ligands (o-$Me_2NCH_2C_6H_4$). The highly reductive power of this complex was investigated by oxidation chemistry. We found that the dinitrogen species [{V(o-$Me_2CH_2C_6H_4)_2$(py)}$_2$(μ-N_2)] reacted smoothly with one equivalent of CuCl to release dinitrogen and concomittantly form the tervalent title compound (I), [VCl(o-$Me_2CH_2C_6H_4)_2$(py)], as a deep-red crystalline solid.



(I)

The geometry of the present V^{III} chlorine complex (Fig. 1) resembles closely that of its V^{II} dinitrogen precursor. However, comparable V—C bonds are now significantly shorter, *e.g.* the bond *trans* to Cl is 2.125 (5) Å compared to 2.204 (4) Å for the bond *trans* to dinitrogen.

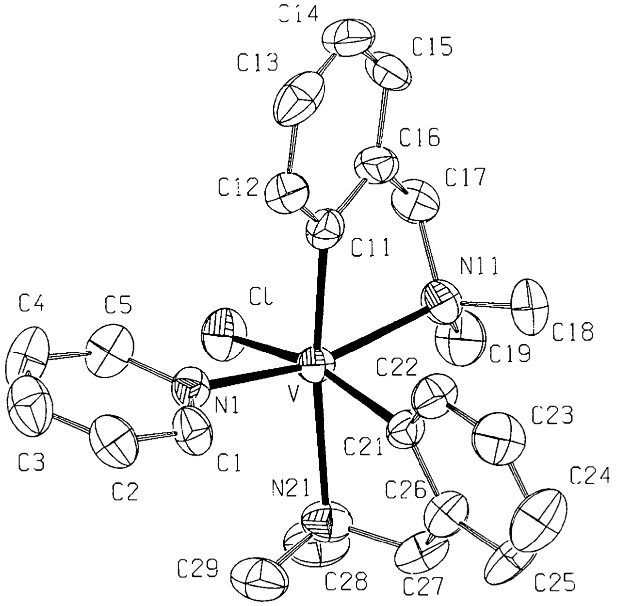


Fig. 1. View of the title complex with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted.