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Diphenylbis(2-pyridinethiolato)tin(IV)

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Abstract

The polyhedron around tin in the title compound is a distorted trapezoidal bipyramid with the two C(phenyl) atoms in axial positions. The trapezoidal plane is formed by the two 2-pyridinethiolato residues which act as bidentate ligands with *cis* Sn—S and *cis* Sn—N bonds. Sn—N coordination is indicated by short intramolecular Sn—N distances [Sn—N(1) = 2.636 (4), Sn—N(2) = 2.698 (4) Å]. The axial C atoms are shifted towards the half-sphere occupied by two N atoms resulting in a C—Sn—C angle of 125.5 (1)°. No short intermolecular interactions are observed.

Comment

Predictions of the coordination number of tin in diorganotin complexes with S,N chelate ligands from ^{119}Sn NMR shift data are, in contrast to other types of organotin compounds, still unreliable since knowledge of the structure of such compounds is insufficient. To improve this situation we started to study the structures of various types of diorganotin compounds with S,N ligands, for instance, diorganobis(2-pyridinethiolato)tin(IV) compounds, both in solution and in the solid state. From IR and Mössbauer spectra, a distorted octahedral coordination polyhedron could be inferred, but a decision as to whether the chelate ligands are arranged *cis* or *trans* was only possible by single-crystal structure determination. We report here the structure of the title compound which was first prepared by Mullins (1979).

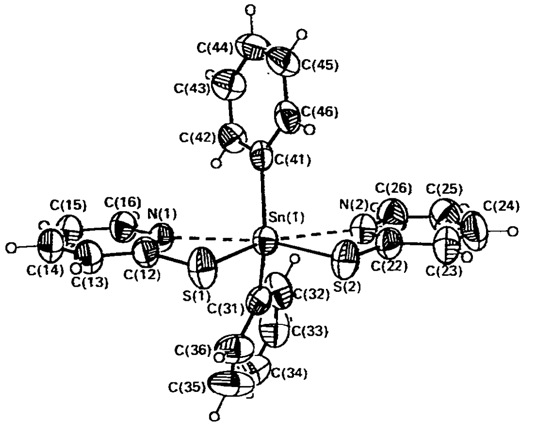

Fig. 1. The title molecule and numbering scheme.

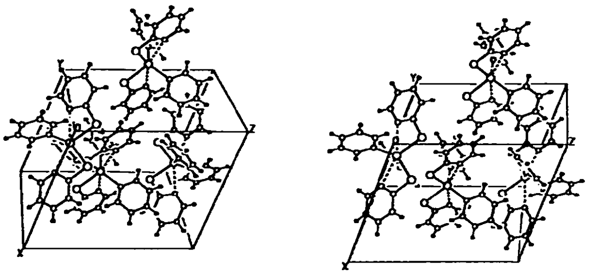

Fig. 2. Stereoscopic view of the unit cell.

The polyhedron around Sn in $Ph_2Sn(2\text{-}SPy)_2$ (2-SPy = 2-pyridinethiolate) corresponds to that found in $^n Bu_2Sn(2\text{-}SPy\text{-}5\text{-}NO_2)_2$ (Domazetis, James, Mackay & Magee, 1979). It is a distorted trapezoidal bipyramid with S(1), S(2), N(1) and N(2) in the trapezoidal plane, and the two C(phenyl) atoms in apical positions. The trapezoidal plane containing the two 2-SPy ligands and tin is nearly planar. The bond distances Sn—N(1) and Sn—N(2) [mean 2.667 (4) Å] are appreciably shorter than the sum of the appropriate van der Waals radii of 3.75 Å (Bondi, 1964) and indicate the bidentate chelating nature of the 2-SPy ligands. Similar distances exist in $^n Bu_2Sn(2\text{-}SPy\text{-}5\text{-}NO_2)_2$ [Sn—N = 2.77 (1) Å; Domazetis, James, Mackay & Magee, 1979] and shorter values are found in $Cl_2Sn(2\text{-}SPy)_2$ [Sn—N = 2.271 (9) and 2.256 (9) Å; Masaki, Matsunami & Ueda, 1978]. The Sn—S bond distances [Sn—S = 2.485 (1) and 2.476 (2) Å] are essentially the same as in $^n Bu_2Sn(2\text{-}SPy\text{-}5\text{-}NO_2)_2$ [Sn—S = 2.477 (3) Å; Domazetis, James, Mackay & Magee, 1979] or $Ph_2Sn(S_2COEt)_2$ [Sn—S = 2.482 (1) and 2.500 (1) Å; Donoghue & Tiekink, 1991]. The C—Sn—C axis is bent [125.5 (1)°] towards the coordinative Sn—N bonds. No intermolecular distances exist which are shorter than the sum of the van der Waals radii.

Experimental

Crystal data

$[Sn(C_5H_4NS)_2(C_6H_5)_2]$
M_r = 493.21
Monoclinic
$P2_1/c$
a = 9.990 (2) Å
b = 17.875 (4) Å
c = 12.743 (2) Å
β = 111.76 (1)°
V = 2113.4 (7) Å^3
Z = 4
D_x = 1.550 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 7.5-15.1°
μ = 1.41 mm^{-1}
T = 291 (1) K
Block
0.2 × 0.1 × 0.1 mm
Colourless

Data collection

Nicolet *R3m/V* diffractometer
ω-2θ scans (3.0-15.0° min^{-1} in θ)
Absorption correction: empirical (ψ scans)
T_{min} = 0.80, T_{max} = 1.00
7912 measured reflections
3665 independent reflections
3170 observed reflections [$F > 4.0\sigma(F)$]

R_{int} = 0.027
θ_{max} = 25°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 22$
$l = -16 \rightarrow 16$
6 standard reflections
frequency: 150 min
intensity variation: none

Refinement

Refinement on F
Final R = 0.031
wR = 0.042
S = 0.83
3170 reflections
221 parameters

Only H-atom U's refined
$w = 1.0/[\sigma^2F + (0.003751F^2)]$
$(\Delta/\sigma)_{max}$ = 0.03
$\Delta\rho_{max}$ = 0.4 e Å^{-3}
$\Delta\rho_{min}$ = −0.6 e Å^{-3}

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

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

	x	y	z	U_{eq}
Sn(1)	0.20888 (3)	0.18288 (1)	0.04679 (2)	0.0463
S(1)	0.3661 (1)	0.09393 (8)	0.1893 (1)	0.0641
N(1)	0.4478 (3)	0.1350 (2)	0.0268 (3)	0.0482
C(12)	0.4837 (4)	0.0899 (2)	0.1157 (3)	0.0488
C(13)	0.6067 (4)	0.0447 (3)	0.1498 (4)	0.0602
C(14)	0.6928 (5)	0.0482 (3)	0.0881 (5)	0.0685
C(15)	0.6600 (5)	0.0948 (3)	−0.0031 (4)	0.0686
C(16)	0.5342 (5)	0.1366 (3)	−0.0332 (4)	0.0594
S(2)	0.0452 (1)	0.17899 (7)	0.1526 (1)	0.0625
N(2)	−0.0333 (4)	0.2664 (2)	−0.0245 (3)	0.0580
C(22)	−0.0724 (4)	0.2433 (3)	0.0596 (4)	0.0554
C(23)	−0.1984 (5)	0.2683 (3)	0.0709 (5)	0.0703
C(24)	−0.2855 (6)	0.3166 (3)	−0.0071 (7)	0.0854
C(25)	−0.2467 (7)	0.3400 (4)	−0.0930 (5)	0.0863
C(26)	−0.1198 (6)	0.3141 (3)	−0.1002 (5)	0.0759
C(32)	0.2680 (3)	0.3435 (2)	−0.0138 (2)	0.0692
C(33)	0.3401 (3)	0.4119 (2)	0.0016 (2)	0.0843
C(34)	0.4627 (3)	0.4241 (2)	0.0982 (2)	0.0894
C(35)	0.5133 (3)	0.3680 (2)	0.1794 (2)	0.1022
C(36)	0.4412 (3)	0.2996 (2)	0.1640 (2)	0.0759
C(31)	0.3185 (3)	0.2874 (2)	0.0674 (2)	0.0492
C(42)	0.1537 (3)	0.1356 (2)	−0.1980 (2)	0.0531
C(43)	0.0889 (3)	0.0961 (2)	−0.2987 (2)	0.0672
C(44)	−0.0251 (3)	0.0475 (2)	−0.3109 (2)	0.0724
C(45)	−0.0743 (3)	0.0383 (2)	−0.2225 (2)	0.0724
C(46)	−0.0094 (3)	0.0778 (2)	−0.1219 (2)	0.0558
C(41)	0.1046 (3)	0.1265 (2)	−0.1097 (2)	0.0451

Table 2. *Geometric parameters* (Å, °)

Sn(1)—C(31)	2.132 (3)	C(14)—C(15)	1.367 (8)
Sn(1)—C(41)	2.130 (2)	C(15)—C(16)	1.389 (7)
Sn(1)—S(1)	2.485 (1)	C(12)—C(13)	1.399 (6)
Sn(1)—S(2)	2.476 (2)	S(2)—C(22)	1.752 (4)
Sn(1)—N(1)	2.636 (4)	N(2)—C(22)	1.335 (7)
Sn(1)—N(2)	2.698 (4)	N(2)—C(26)	1.336 (6)
S(1)—C(12)	1.756 (5)	C(22)—C(23)	1.393 (7)
N(1)—C(12)	1.326 (5)	C(23)—C(24)	1.360 (8)
N(1)—C(16)	1.348 (7)	C(24)—C(25)	1.36 (1)
C(13)—C(14)	1.365 (9)	C(25)—C(26)	1.38 (1)
C(31)—Sn(1)—S(1)	108.29 (9)	C(31)—Sn(1)—S(2)	111.74 (9)
C(31)—Sn(1)—N(1)	81.6 (1)	C(31)—Sn(1)—N(2)	85.0 (1)
C(41)—Sn(1)—S(1)	109.77 (8)	C(41)—Sn(1)—S(2)	107.68 (9)
C(41)—Sn(1)—N(1)	84.4 (1)	C(41)—Sn(1)—N(2)	83.1 (1)
N(1)—Sn(1)—N(2)	151.5 (1)	S(1)—Sn(1)—S(2)	87.15 (5)
N(1)—Sn(1)—S(2)	148.02 (8)	C(31)—Sn(1)—C(41)	125.5 (1)
N(1)—Sn(1)—S(1)	60.88 (8)	N(2)—Sn(1)—S(2)	60.52 (8)
Sn(1)—N(1)—C(12)	94.7 (3)	Sn(1)—N(2)—C(22)	92.9 (2)
Sn(1)—N(1)—C(16)	147.2 (3)	Sn(1)—N(2)—C(26)	148.7 (3)
Sn(1)—S(1)—C(12)	90.1 (1)	Sn(1)—S(2)—C(22)	91.5 (2)
S(1)—C(12)—N(1)	114.1 (3)	S(2)—C(22)—N(2)	115.1 (3)
C(12)—N(1)—C(16)	118.0 (4)	C(22)—N(2)—C(26)	118.3 (4)
N(1)—C(12)—C(13)	123.0 (4)	N(2)—C(22)—C(23)	121.8 (4)
S(1)—C(12)—C(13)	122.8 (3)	S(2)—C(22)—C(23)	123.1 (4)
C(12)—C(13)—C(14)	117.5 (4)	C(22)—C(23)—C(24)	119.1 (5)
C(13)—C(14)—C(15)	120.9 (5)	C(23)—C(24)—C(25)	119.3 (6)
C(14)—C(15)—C(16)	118.1 (5)	C(24)—C(25)—C(26)	119.5 (6)
N(1)—C(16)—C(15)	122.3 (4)	N(2)—C(26)—C(25)	121.9 (5)

Single crystals were obtained from chloroform after adding petroleum ether (b.p. 313-333 K). Diffractometer data were corrected for Lorentz-polarization effects. Systematic absences ($h0l$) $l = 2n + 1$ and ($0k0$) $k = 2n + 1$ conform to space group $P2_1/c$. The structure was solved *via* Patterson function, ΔF syntheses and full-matrix least squares with anisotropic displacement parameters for all non-H atoms and a common isotropic displacement parameter for H atoms, which were placed in geometrically calculated positions (C—H 0.96 Å). Atomic scattering factors for neutral atoms and real/imaginary dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Programs used: *PARST* (Nardelli, 1983), *SHELXTL-Plus* (Sheldrick, 1987), *SHELX76* (Sheldrick, 1976), *PCK83* (Williams, 1984), *PLATON* (Spek, 1982) and *MISSYM* (Le Page, 1987).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry, least-squares-planes data and dihedral angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71178 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1057]

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Structure of Dioxo[*N*,*N*,*N'*,*N'*-tetrakis-(2-pyridylmethyl)ethylenediamine]-vanadium(V) Chloride Monohydrate, [VO_2(tpen)]Cl.H_2O

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Abstract

In the complex cation of the title compound (1), with site symmetry C_2, the VO_2 group is coordinated by tpen *via* two ethylenediamine N atoms and two pyridyl N atoms. The VO_2 moiety shows *cis* configuration with an O(1)—V—O(1′) angle of 107.90 (2)° and short V—O distances of 1.615 (2) Å.

Comment

Recently the synthesis, magnetism and crystal structure of the first binuclear vanadyl–tpen [tpen = *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)ethylenediamine] complex, containing a *syn*-$V_2O_2(\mu\text{-}OH)_2^{2+}$ core, was reported (Neves, Wieghardt, Nuber & Weiss, 1988). Here we describe the molecular structure of an octahedral *cis*-dioxo vanadium(V) complex with tpen as tetradentate ligand. [VO_2(tpen)]$^+$ represents the first cationic species of this class of complexes in which the *cis*-VO_2 entity is bonded exclusively by N-donor atoms of a neutral ligand.

The title compound is built up by discrete mononuclear [VO_2(tpen)]$^+$ cations, uncoordinated Cl anions, and water molecules of crystallization. The vanadium(V) ion is in a pseudo-octahedral environment in which the VO_2 moiety is in the expected *cis* configuration and lies *trans* to the N atoms of the ethylenediamine backbone. The coordination sphere around the V atom is completed by two pyridyl N atoms, while two pendant pyridyl groups remain uncoordinated. The molecule has a crystallographically imposed twofold axis which passes through the V-atom centre and the midpoint of the C(3)—C(3′) bond (Fig. 1). The five-membered ring (VN_2C_2) formed by chelation of the ethylenediamine backbone has the usual skew conformation with a torsion angle N(1)—C(3)—C(3′)—N(1′) of 28.1°; the two atoms of the ethylene bridge are displaced by 0.35 (2) Å on opposite sides of the V–N(1)–N(1′) plane. The sum of the interior angles is 514.6°. This value is in excellent agreement with that observed for [VO_2(edta)]$^{3-}$ [515.0° (edta = ethylenediaminetetraacetate) (Scheidt, Countryman & Hoard, 1971)]. The two remaining five-membered rings are formed by the 2-pyridylmethyl groups. An analysis of the planarity of these rings (sum of the interior ring angles = 521.2°) shows the extent of puckering in the inner regions of these rings (Mandel & Douglas, 1989). Similar values have been observed for glycinato five-membered rings in [VO_2(edtaH_2)]$^-$ (Scheidt, Collins & Hoard, 1971) and [VO_2(edta)]$^{3-}$ (Scheidt, Countryman & Hoard, 1971).

The VO_2 entity in the *cis* configuration has an O—V—O obtuse angle of 107.90 (2)°, significantly deviated from the ideal angle of 90°. As expected, the opposite N(1)—V—N(1′) angle is acute, and has a value of 75.52 (1)°. The O—V—O angle of 107.90 (2)° is almost equal to those observed in [VO_2(edtaH_2)]$^-$ (107.1°) and [VO_2(edta)]$^{3-}$ (107.0°), and somewhat larger than in other octahedral *cis*-VO_2 complexes, which have values in the range 104–106° (Drew, Einstein & Gransden, 1974; Neves, Walz, Wieghardt, Nuber & Weiss, 1988).

The short V—O distances of 1.615 (2) Å in (1) indicate strong multiple-bond character as previously discussed by other authors (Scheidt, Tsai & Hoard, 1971). However, it is important to note that these V=O bonds are significantly shorter (by 0.025 Å) than the mean values reported in the above literature