

Dichlorodiethyl[2-(5-methyl-1,2,4-oxadiazol-3-yl)-1,10-phenanthroline]tin(IV)*

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Abstract. $C_{19}H_{20}Cl_2N_4OSn$, monoclinic, $P2_1/c$, $a = 7.848$ (3), $b = 21.124$ (1), $c = 12.777$ (1) Å, $\beta = 105.25$ (2)°, $Z = 4$, $D_x = 1.658$ Mg m⁻³. The final residual is $R_F = 0.03$ on 2364 observed reflections at room temperature (296 K). The coordination around the Sn atom is a pentagonal bipyramid, with the two ethyl groups in the axial positions and the two Cl atoms and the three N atoms of the 2-(5-methyl-1,2,4-oxadiazol-3-yl)-1,10-phenanthroline (phenmethoxa) ligand in the equatorial plane.

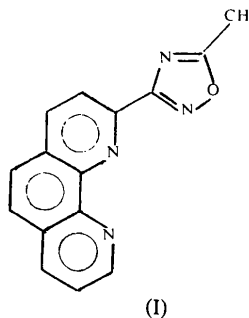
Introduction. In general, diorganotin dichlorides react with tridentate, α -diimine-type ligands (L) to give 2:1 complexes with the stoichiometry $[R_2SnCl_2]_2 \cdot L$. The complexes have the ionic structure $[LSnClR_2]^+ \cdot [R_2SnCl_3]^-$ with six-coordinate anions (Fergusson, Roper & Wilkins, 1965; Debye, Rosenberg & Zuckerman, 1968; Smith & Khoo, 1979). However, the corresponding isothiocyanates are 1:1 complexes and have seven-coordinate pentagonal-bipyramidal structures with *trans* organic groups (May & Curran, 1972; Naik & Scheidt, 1973).

Pelizzi & Pelizzi (1976) have reported that a series of planar tridentate chelating agents with mixed oxygen and nitrogen donor atoms form 1:1 complexes with organotin dihalides, with possible seven coordination around the Sn atom.

However, as yet, there has been no definite confirmation of a seven-coordinate organotin complex formed between a diorganotin dichloride and a planar tridentate chelating agent.

The ligand phenmethoxa (I), which bears a close structural relationship to 2,2':6',2''-terpyridyl, be-

haves as a planar tridentate chelating agent (Goodwin & Smith, 1974).



When it was discovered that (I) gave 1:1 complexes with diorganotin dihalides, it was considered worthwhile to perform a crystal-structure analysis on one of the complexes in order to study the coordination around the Sn atom.

Diethyltin dichloride was obtained commercially and 2-(5-methyl-1,2,4-oxadiazol-3-yl)-1,10-phenanthroline was prepared from 1,10-phenanthroline-2-carboxamide oxime as previously reported (Goodwin & Smith, 1974).

The title complex was obtained in good yield by mixing hot ethanolic solutions containing the stoichiometric quantities of diethyltin dichloride and the ligand. Buff crystals of the complex were obtained by recrystallization from ethanol. Microanalyses were carried out by the Australian Microanalytical Service, CSIRO, Melbourne, Australia. Found (%): C 44.41, H 4.15, N 10.98, Sn 23.5; calculated (%) for $C_{19}H_{20}Cl_2N_4OSn$: C 44.75, H 3.95, N 10.99, Sn 23.27.

The diffraction intensities of a $0.35 \times 0.35 \times 0.35$ mm crystal of the title compound were measured at room temperature. Graphite-monochromatized Mo $K\alpha$ radiation generated at 50 kV and 15 mA was used in a

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$\theta/2\theta$ scan with line-profile analysis (Grant & Gabe, 1978). A total of 4317 measurements were made up to 45° in 2θ giving 2679 unique reflections, of which 2364 had a net intensity larger than $3\sigma(I)$ based on counting statistics and were considered to be observed. From the systematic absences, the space group was determined as $P2_1/c$. The intensities were corrected for measured direct-beam polarization (Le Page, Gabe & Calvert, 1979). Absorption corrections were not calculated ($\mu = 1.53 \text{ mm}^{-1}$). The cell parameters were obtained by least-squares refinement of the setting angles of 54 reflections with 2θ greater than 40° [$\lambda(\text{Mo } K\alpha_1) = 0.70932 \text{ \AA}$].

Table 1. Atomic coordinates and equivalent isotropic thermal parameters

E.s.d.'s refer to the last digit printed.

	x	y	z	B_{eq}^* (Å ²)
Sn	0.21291 (5)	0.330344 (15)	0.29649 (3)	3.477 (13)
Cl(1)	0.13599 (19)	0.25557 (6)	0.14639 (10)	5.05 (6)
Cl(2)	0.41939 (19)	0.25031 (6)	0.39697 (11)	5.60 (7)
O	0.4733 (5)	0.43240 (16)	0.6697 (3)	6.28 (19)
N(1)	-0.0408 (5)	0.40450 (16)	0.1439 (3)	4.02 (18)
N(2)	0.1148 (5)	0.46435 (15)	0.3367 (3)	3.43 (17)
N(3)	0.3547 (5)	0.39526 (16)	0.5058 (3)	4.08 (18)
N(4)	0.3711 (6)	0.48153 (19)	0.6116 (3)	5.75 (22)
C(1)	0.0021 (6)	0.31778 (21)	0.3702 (4)	4.02 (23)
C(2)	-0.0900 (7)	0.25545 (24)	0.3501 (5)	5.9 (3)
C(3)	0.3930 (7)	0.39068 (23)	0.2440 (4)	5.0 (3)
C(4)	0.5186 (8)	0.3595 (3)	0.1932 (6)	7.8 (4)
C(5)	-0.1219 (7)	0.37772 (23)	0.0506 (4)	5.7 (3)
C(6)	-0.2423 (8)	0.4079 (3)	-0.0338 (4)	6.5 (3)
C(7)	-0.2774 (7)	0.4695 (3)	-0.0221 (4)	6.0 (3)
C(8)	-0.1958 (7)	0.49993 (22)	0.0741 (4)	4.69 (25)
C(9)	-0.2342 (7)	0.56542 (24)	0.0921 (4)	5.7 (3)
C(10)	-0.1571 (7)	0.59368 (23)	0.1848 (4)	6.0 (3)
C(11)	-0.0360 (6)	0.56154 (21)	0.2700 (4)	4.43 (25)
C(12)	0.0438 (7)	0.59002 (21)	0.3691 (4)	5.2 (3)
C(13)	0.1535 (7)	0.55787 (22)	0.4489 (4)	4.9 (3)
C(14)	0.1879 (6)	0.49362 (20)	0.4297 (4)	3.80 (22)
C(15)	0.0026 (6)	0.49699 (20)	0.2566 (4)	3.51 (21)
C(16)	-0.0791 (6)	0.46610 (20)	0.1570 (4)	3.59 (22)
C(17)	0.3053 (6)	0.45727 (21)	0.5159 (4)	3.87 (23)
C(18)	0.4559 (7)	0.38208 (23)	0.6019 (4)	4.8 (3)
C(19)	0.5527 (7)	0.32359 (24)	0.6451 (4)	6.4 (3)
H(C1)1	-0.073 (5)	0.3478 (16)	0.344 (3)	5.1 (11)
H(C1)2	0.093 (6)	0.3216 (20)	0.439 (3)	9.1 (14)
H(C2)1	-0.194 (6)	0.2538 (22)	0.388 (4)	10.3 (15)
H(C2)2	-0.016 (6)	0.2253 (19)	0.373 (3)	8.3 (13)
H(C2)3	-0.125 (5)	0.2538 (20)	0.269 (3)	8.2 (13)
H(C3)1	0.462 (6)	0.4047 (20)	0.308 (3)	9.0 (14)
H(C3)2	0.328 (6)	0.4101 (22)	0.184 (3)	10.3 (16)
H(C4)1	0.590 (8)	0.327 (3)	0.220 (4)	15.4 (21)
H(C4)2	0.439 (7)	0.360 (3)	0.138 (5)	15.3 (21)
H(C4)3	0.601 (7)	0.3939 (23)	0.166 (4)	12.6 (18)
H(5)	-0.106 (5)	0.3379 (17)	0.046 (3)	6.0 (11)
H(6)	-0.299 (5)	0.3848 (18)	-0.095 (3)	5.8 (11)
H(7)	-0.363 (5)	0.4923 (18)	-0.082 (3)	6.7 (12)
H(9)	-0.323 (5)	0.5851 (17)	0.025 (3)	7.0 (12)
H(10)	-0.183 (5)	0.6368 (20)	0.202 (3)	8.1 (13)
H(12)	0.019 (5)	0.6314 (18)	0.377 (3)	6.3 (12)
H(13)	0.211 (5)	0.5738 (17)	0.520 (3)	6.1 (11)
H(C19)1	0.641 (6)	0.3346 (21)	0.700 (4)	9.9 (15)
H(C19)2	0.483 (7)	0.3019 (24)	0.691 (4)	13.3 (19)
H(C19)3	0.541 (6)	0.2918 (21)	0.582 (3)	10.5 (15)

* B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

The Sn-atom position was found from a Patterson map and all the other non-H atoms were located in a heavy-atom-phased Fourier map. The structure was first refined to $R_F = 0.039$. At this stage, all the H atoms were located in a difference map. Their positional parameters were refined along with isotropic temperature factors, while all other atoms were refined anisotropically, by block-diagonal least squares. Weights based on counting statistics were used throughout. An extinction correction was included (Larson, 1970). The scattering curves for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The final residuals are $R_F = 0.030$ and $R_{wF} = 0.027$ for 2364 observed reflections and $R_F = 0.035$ and $R_{wF} = 0.027$ for a total of 2679 reflections. The atomic positional and equivalent isotropic temperature factors are listed in Table 1.* All calculations were performed using the NRC PDP8-e system of programs (Larson & Gabe, 1978).

Discussion. A stereoscopic view of the molecule is shown in Fig. 1 and the atom names, distances and angles are indicated in Fig. 2.

The configuration around the Sn atom can be described as a pentagonal bipyramid with the two ethyl groups in the axial positions. The two Cl atoms and the three N atoms of the phenmethoxa ligand are in the equatorial plane.

The two Sn—Cl distances, 2.457 (1) and 2.435 (1) Å, are within the range of Sn—Cl distances quoted in the literature (Harrison, King & Richards, 1974). The Sn—C(Et) distances of 2.125 (5) and 2.138 (5) Å compare well with the distances reported previously (Alcock & Sawyer, 1977; Sham & Bancroft, 1975).

However, the distances between the Sn atom and the three N atoms of the phenmethoxa ligand [2.860 (3), 3.013 (3) and 2.951 (3) Å] are much longer than any

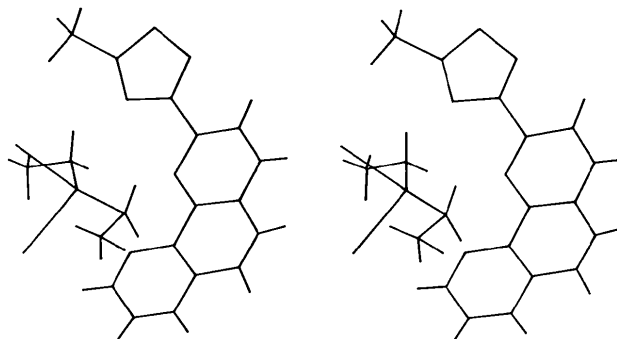


Fig. 1. Stereoscopic pair of the molecule seen along [100].

previously reported Sn—N distance [2.05 (3)–2.570 (4) Å; Harrison *et al.*, 1974]. This raises the question as to whether or not the phenmethoxa molecule is actually coordinated to the Sn atom. Since the three Sn—N distances are about the same, it would appear that either all three N atoms are coordinated, or none of them is coordinated to the Sn atom. In the latter instance, *i.e.* if the phenmethoxa molecule is considered as not bonded to the Sn atom, then the Sn-atom coordination should be considered tetrahedral. However, the measured bond angles are not in line with this interpretation, especially the Cl(1)—Sn—Cl(2) angle [87.6 (1)°] and the C(1)—Sn—C(3) angle [150.4 (2)°]. In fact, there is a large gap in the coordination sphere around the Sn

atom into which the ligand molecule fits. Furthermore, although the Sn—N distances are longer than those normally associated with Sn—N bonds, they are still substantially less than 3.75 Å, which is the sum of the van der Waals radii for N and Sn (Bondi, 1964). So we consider that the phenmethoxa molecule is bonded to the Sn atom by all three N atoms, and that the Sn may be regarded as seven-coordinate.

Table 2 gives the edge distances of the Sn coordination polyhedron. The distances N(1)—Cl(1), Cl(1)—Cl(2) and Cl(2)—N(3) are comparable while the short N(1)—N(2) and N(2)—N(3) distances are probably dictated by the steric requirements of the ligand. The distances between the axial C atoms and the atoms in the equatorial plane compare well with the distances quoted for the seven-coordinate Sn complex, diisothiocyanatodimethyl(terpyridyl)tin(IV) (Naik & Scheidt, 1973).

The relative weakness of the Sn—N bonds in the phenmethoxa complex may well be due to the presence of the five-membered oxadiazole ring instead of a six-membered ring as in terpyridine, which changes the orientation of the N atoms. The resulting tridentate ligand has a geometry slightly less favourable for coordination of the donor atoms than terpyridine itself. Such an effect has been observed previously in the bis(ligand)iron(II) complexes of 2,4-di(2-pyridyl)-1,3-thiazole (Goodwin & Sylva, 1968). Other instances of rather weak metal—donor interaction have also been reported. In Me₂SnCl₂ and Et₂SnCl₂, the Sn atoms are strongly distorted from tetrahedral arrangement. The C—Sn—C angle in Me₂SnCl₂ is 123.5 (5)° and the corresponding angle in Et₂SnCl₂ is 134.0 (6)°. The molecules in both structures are linked by weak intermolecular interactions, forming infinite chains in the crystal and the Sn coordination polyhedron can be considered as a distorted octahedron (Alcock & Sawyer, 1977).

The bond lengths and angles of the phenmethoxa moiety are all normal for a conjugated system. There are no short intermolecular contacts in the unit cell.

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Table 2. Edge distances of the Sn coordination polyhedron

The e.s.d.'s range from 0.005–0.006 Å.

Cl(1)—N(1)	3.435	C(1)—N(2)	3.279
N(1)—N(2)	2.753	C(1)—N(3)	3.289
N(2)—N(3)	2.864	C(3)—Cl(1)	3.528
N(3)—Cl(2)	3.455	C(3)—Cl(2)	3.527
Cl(2)—Cl(1)	3.386	C(3)—N(1)	3.320
C(1)—Cl(1)	3.549	C(3)—N(2)	3.154
C(1)—Cl(2)	3.505	C(3)—N(3)	3.437
C(1)—N(1)	3.364		

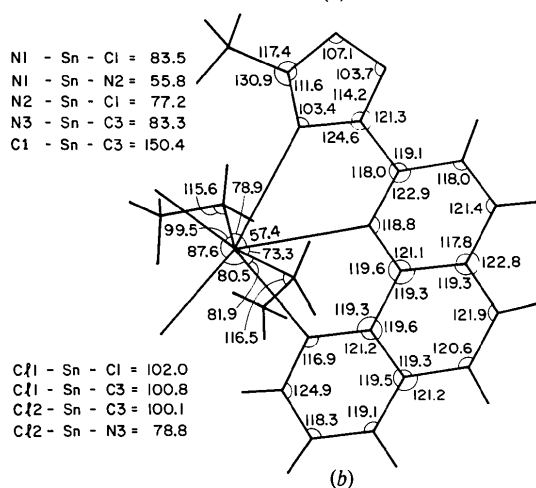
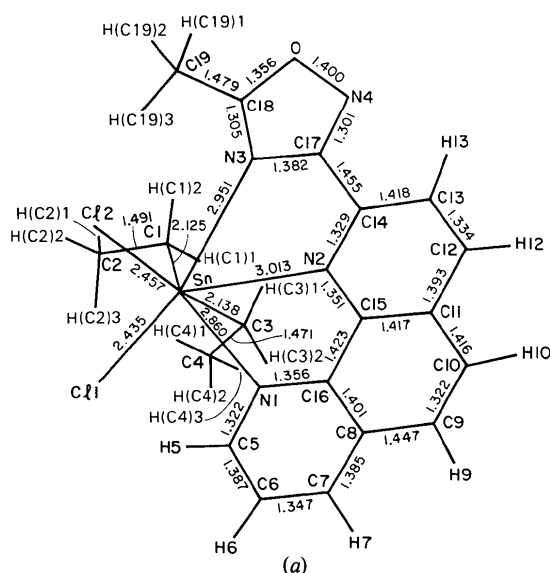


Fig. 2. (a) Atom names and bond distances (Å) (uncorrected for thermal motion). The e.s.d.'s on bond distances involving Sn range from 0.001 to 0.005 Å and the others range from 0.005–0.006 Å. (b) Angles (°). The e.s.d.'s on angles involving Sn are 0.1° and the others 0.4°.

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Structure of (+)₅₈₉-cis- α -[(2*S*,7*S*)-2,7-Di(2-pyridyl)-3,6-diazaoctane]oxalatocobalt(III) Perchlorate Monohydrate

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Abstract. [Co(C₁₆H₂₂N₄)(C₂O₄)]·ClO₄·H₂O, C₁₈H₂₂CoN₄O₄⁺·ClO₄⁻·H₂O, (+)₅₈₉-cis- α -[Co(ox)(*S,S*-peaen)]ClO₄·H₂O, *M_r* = 534.8, monoclinic, *P*2₁, *a* = 10.807 (1), *b* = 12.353 (2), *c* = 8.512 (1) Å, β = 91.20 (1)°, *V* = 1136.0 (3) Å³, *Z* = 2, *D_m* = 1.57, *D_x* = 1.56 Mg m⁻³, λ (Mo *K* α) = 0.7107 Å, μ (Mo *K* α) = 0.963 mm⁻¹. The structure was solved by Patterson–Fourier methods and refined to a final *R*(*F*) value of 0.029 for 1662 observed reflections. The quadridentate ligand *S,S*-peaen is linked to the Co atom in *A*-cis- α -($\delta\delta\delta$) coordination.

Introduction. A new type of optically active tetramine, NC₅H₄–*CH(CH₃)–NH–(CH₂)_{*n*}–NH–*CH(CH₃)–C₅H₄N (abbreviations for *n* = 2 and 3 being peaen and peatn, respectively) was derived from 1-(2-pyridyl)ethylamine (pea) in order to investigate the stereospecificity caused by terminal aromatic rings (Suzuki, Kimura & Fujita, 1980). The crystal structure of (–)₅₈₉-*A*-cis- β -[Co(ox)(*R,R*-peatn)]ClO₄ has already been reported (Ohba, Sato & Saito, 1981). The title compound involving the related quadridentate ligand, *S,S*-peaen, has been examined to obtain its conformational details and to establish the absolute

configuration of the complex ion. Crystals were kindly supplied by Dr T. M. Suzuki of Government Industrial Research Institute, Tohoku. A spherical crystal *ca* 0.4 mm in diameter was mounted on a Rigaku AFC-5 four-circle diffractometer equipped with a graphite monochromator. The cell parameters were refined by least squares on the basis of 26 *2* θ values (21 < *2* θ < 30°) measured with Mo *K* α radiation (λ = 0.7107 Å). 2142 reflections were measured by the θ -*2* θ scan technique up to a *2* θ value of 55°; 1662 with $|F_o| > 3\sigma(|F_o|)$ were considered observed and used in the analysis. Correction for absorption was ignored (μr = 0.19).

The structure was solved by Patterson–Fourier methods and refined by block-diagonal least squares with anisotropic thermal parameters for all non-H atoms. With *R*(*F*) (= $\sum |F_o| - |F_c| / \sum |F_o|$) = 0.042, all the H atoms were located from a difference synthesis except those of the water molecule. The final *R*(*F*) was 0.029 and *R_w*(*F*) [= $(\sum w|F_o| - |F_c|)^2 / \sum w|F_o|^2$]^{1/2} = 0.036 for 1662 reflections. The weights were assigned as $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. Complex neutral-atom scattering factors were taken from *International Tables for X-ray*