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Bis(2-methoxycarbonyl-ethyl)bis(quinolin-8-olato-*N,O*)tin

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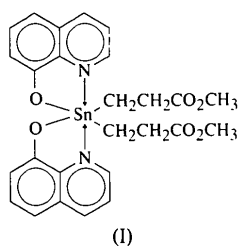
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Abstract

The Sn atom in the title complex, [Sn(C₉H₆NO)₂(C₄H₇O₂)₂], is six-coordinate in a distorted *cis*-octahedral environment.

Comment

Six-coordinate dialkyltin structures preferentially show *trans*-octahedral coordination at the Sn atom (Smith, 1981) as the *cis*-octahedral arrangement is sterically less favourable. Spectroscopic measurements on bis(2-methoxycarbonyl-ethyl)bis(quinolin-8-olato)tin, (I), indicate *cis*-octahedral geometry at the Sn atom (Kumar Das, Ng & Smith, 1981), a geometry that has been documented for dimethyl(quinolin-8-olato)tin (Schlemper, 1967). The assignment is confirmed in the present study, but the crystal structure shows a weak Sn...O interaction involving one of the two carbonyl O atoms at



a distance of 3.413(2) Å, which is less than the sum of the van der Waals radii for Sn and O. The interaction distorts the geometry towards *cis*-pentagonal bipyramidal, and if the O2 atom is regarded as being in the coordination sphere of the Sn atom, the equatorial plane is virtually flat [sum of angles subtended at the Sn atom = 365.6(4)°]. The Sn atom is displaced out of this plane by 0.849(1) Å. The two quinolin-8-olato chelating groups are flat and are tilted by 85.53(5)° with respect to each other. A similarly weak interaction in dibutyltin di-2-bromobenzoate [Sn...O = 3.451(5) Å] links two adjacent molecules to form a dimer, and the geome-

try is distorted towards *trans*-pentagonal bipyramidal (Ng, Kumar Das, Yip, Wang & Mak, 1990). For the more Lewis acidic bis(2-methoxycarbonyl-ethyl)chloro-(quinolin-8-olato)tin, the carbonyl O atom of one of the two alkyl groups bonds intramolecularly to the Sn atom [Sn—O = 2.847(4) Å] (Ng, Chen, Kumar Das, Charland & Smith, 1989).

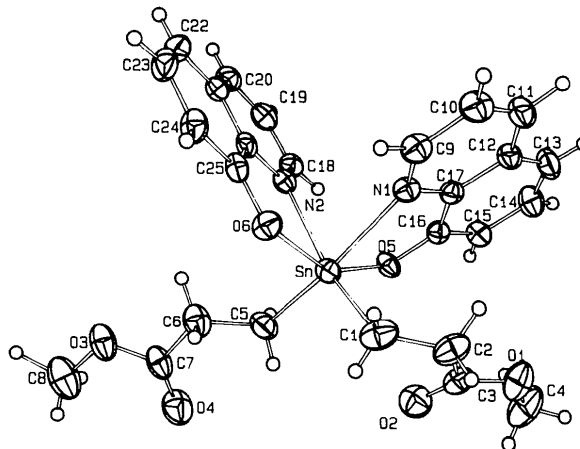


Fig. 1. Atomic labelling scheme for bis(2-methoxycarbonyl-ethyl)bis(quinolin-8-olato)tin. Ellipsoids are drawn at the 30% probability level.

Experimental

The compound was synthesized from bis(2-methoxycarbonyl-ethyl)tin dichloride and 8-hydroxyquinoline (Kumar Das, Ng & Smith, 1981) and was recrystallized from ethanol.

Crystal data

[Sn(C₉H₆NO)₂(C₄H₇O₂)₂]
 $M_r = 581.18$
 Triclinic
 $P\bar{1}$
 $a = 10.6502(9) \text{ \AA}$
 $b = 11.0148(4) \text{ \AA}$
 $c = 12.0539(11) \text{ \AA}$
 $\alpha = 97.511(6)^\circ$
 $\beta = 112.647(7)^\circ$
 $\gamma = 102.092(5)^\circ$
 $V = 1240.6(2) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.556 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 14.5\text{--}15.0^\circ$
 $\mu = 1.074 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Irregular strip
 $0.58 \times 0.29 \times 0.14 \text{ mm}$
 Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
 $T_{\min} = 0.907$, $T_{\max} = 1.000$
 5963 measured reflections
 5690 independent reflections

4918 observed reflections
 $[I > 2\sigma(I)]$
 $R_{\text{int}} = 0.014$
 $\theta_{\max} = 27.47^\circ$
 $h = -13 \rightarrow 12$
 $k = -14 \rightarrow 14$
 $l = 0 \rightarrow 15$
 3 standard reflections
 frequency: 60 min
 intensity decay: 1.4%

Refinement

Refinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.031$$

$$wR(F^2) = 0.074$$

$$S = 1.089$$

5690 reflections

316 parameters

H atoms were located and refined with $U = 0.1 \text{ \AA}^2$

$$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.0051P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.867 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\min} = -0.274 \text{ e \AA}^{-3}$$

Extinction correction: none

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

N2—C18	1.322 (3)	C23—C24	1.402 (5)
N2—C26	1.357 (3)	C24—C25	1.385 (4)
C1—C2	1.510 (5)	C25—C26	1.433 (4)
C2—C3	1.505 (4)		
C1—Sn—C5	109.7 (2)	O2—C3—C2	124.7 (3)
C1—Sn—N1	85.5 (1)	C5—C6—C7	114.2 (3)
C1—Sn—N2	158.1 (1)	O3—C7—O4	123.3 (3)
C1—Sn···O2	55.4 (1)	O3—C7—C6	110.3 (3)
C1—Sn—O5	105.7 (1)	O4—C7—C6	126.4 (3)
C1—Sn—O6	90.6 (1)	N1—C9—C10	122.0 (3)
C5—Sn—N1	162.0 (1)	C9—C10—C11	119.9 (3)
C5—Sn—N2	89.1 (1)	C10—C11—C12	120.7 (3)
C5—Sn···O2	78.1 (1)	C11—C12—C13	125.3 (3)
C5—Sn—O5	92.5 (1)	C11—C12—C17	115.8 (3)
C5—Sn—O6	104.0 (1)	C13—C12—C17	118.9 (3)
N1—Sn—N2	78.37 (7)	C12—C13—C14	119.8 (3)
N1—Sn···O2	104.34 (7)	C13—C14—C15	121.3 (3)
N1—Sn—O5	73.48 (7)	C14—C15—C16	121.1 (3)
N1—Sn—O6	84.95 (8)	O5—C16—C15	123.0 (2)
N2—Sn···O2	143.20 (7)	O5—C16—C17	119.1 (2)
N2—Sn—O5	83.90 (7)	C15—C16—C17	117.9 (2)
N2—Sn—O6	73.52 (7)	C12—C17—C16	120.9 (2)
O2···Sn—O5	62.71 (7)	N1—C17—C12	122.6 (2)
O2···Sn—O6	142.91 (7)	N1—C17—C16	116.5 (2)
O5—Sn—O6	151.53 (8)	N2—C18—C19	122.4 (3)
Sn—C1—C2	116.9 (2)	C18—C19—C20	119.3 (3)
Sn—C5—C6	116.8 (2)	C19—C20—C21	120.3 (3)
Sn—N1—C9	130.2 (2)	C20—C21—C22	125.1 (3)
Sn—N1—C17	110.1 (2)	C20—C21—C26	116.4 (3)
Sn—N2—C18	129.0 (2)	C22—C21—C26	118.5 (3)
Sn—N2—C26	111.8 (2)	C21—C22—C23	119.4 (3)
Sn—O5—C16	119.5 (2)	C22—C23—C24	122.6 (3)
Sn—O6—C25	119.4 (2)	C23—C24—C25	120.6 (3)
C3—O1—C4	115.2 (3)	O6—C25—C24	123.6 (3)
C7—O3—C8	116.0 (3)	O6—C25—C26	119.5 (2)
C9—N1—C17	119.0 (2)	C24—C25—C26	116.9 (3)
C18—N2—C26	119.2 (2)	C21—C26—C25	121.9 (2)
C1—C2—C3	113.2 (3)	N2—C26—C21	122.4 (2)
O1—C3—O2	123.8 (3)	N2—C26—C25	115.7 (2)
O1—C3—C2	111.5 (3)		

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	U_{eq}
Sn	0.91165 (2)	0.35666 (2)	0.21288 (2)	0.04178 (7)
O1	0.4421 (3)	0.2000 (3)	-0.0726 (2)	0.0844 (8)
O2	0.5782 (3)	0.3845 (3)	0.0610 (2)	0.0732 (6)
O3	1.1995 (3)	0.8374 (2)	0.4932 (2)	0.0746 (7)
O4	0.9790 (3)	0.8214 (2)	0.3625 (3)	0.0854 (8)
O5	0.8385 (2)	0.3463 (2)	0.0233 (2)	0.0441 (4)
O6	1.0480 (2)	0.3203 (2)	0.3777 (2)	0.0509 (4)
N1	0.8994 (2)	0.1488 (2)	0.1194 (2)	0.0416 (5)
N2	1.1341 (2)	0.3899 (2)	0.2088 (2)	0.0409 (5)
C1	0.7289 (3)	0.2634 (4)	0.2389 (3)	0.0681 (9)
C2	0.5974 (3)	0.1894 (4)	0.1238 (3)	0.0674 (9)
C3	0.5408 (3)	0.2709 (4)	0.0363 (3)	0.0572 (7)
C4	0.3802 (4)	0.2707 (5)	-0.1620 (4)	0.104 (2)
C5	0.9476 (4)	0.5607 (3)	0.2561 (3)	0.0645 (8)
C6	1.0607 (4)	0.6326 (3)	0.3780 (3)	0.0673 (9)
C7	1.0715 (4)	0.7727 (3)	0.4073 (3)	0.0603 (8)
C8	1.2216 (6)	0.9720 (4)	0.5347 (4)	0.103 (2)
C9	0.9287 (3)	0.0521 (3)	0.1695 (3)	0.0526 (7)
C10	0.8930 (3)	-0.0703 (3)	0.0979 (4)	0.0622 (8)
C11	0.8257 (3)	-0.0935 (3)	-0.0264 (3)	0.0615 (8)
C12	0.7915 (3)	0.0056 (2)	-0.0852 (3)	0.0485 (6)
C13	0.7223 (4)	-0.0081 (3)	-0.2129 (3)	0.0640 (8)
C14	0.6951 (4)	0.0960 (3)	-0.2592 (3)	0.0638 (8)
C15	0.7347 (3)	0.2163 (3)	-0.1807 (2)	0.0516 (6)
C16	0.8024 (3)	0.2346 (2)	-0.0543 (2)	0.0396 (5)
C17	0.8320 (3)	0.1275 (2)	-0.0056 (2)	0.0392 (5)
C18	1.1743 (3)	0.4295 (2)	0.1255 (3)	0.0483 (6)
C19	1.3126 (3)	0.4469 (3)	0.1371 (3)	0.0529 (7)
C20	1.4096 (3)	0.4198 (3)	0.2356 (3)	0.0543 (7)
C21	1.3706 (3)	0.3748 (2)	0.3261 (3)	0.0473 (6)
C22	1.4619 (3)	0.3421 (3)	0.4312 (3)	0.0580 (7)
C23	1.4131 (3)	0.3045 (3)	0.5131 (3)	0.0612 (8)
C24	1.2743 (3)	0.2966 (3)	0.4986 (3)	0.0548 (7)
C25	1.1794 (3)	0.3262 (2)	0.3969 (2)	0.0445 (6)
C26	1.2300 (3)	0.3641 (2)	0.3089 (2)	0.0399 (5)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Sn—C1	2.158 (3)	C5—C6	1.474 (4)
Sn—C5	2.156 (3)	C6—C7	1.507 (4)
Sn—N1	2.369 (2)	C9—C10	1.392 (4)
Sn—N2	2.341 (2)	C10—C11	1.349 (5)
Sn···O2	3.413 (2)	C11—C12	1.412 (4)
Sn—O5	2.090 (2)	C12—C13	1.398 (4)
Sn—O6	2.109 (2)	C12—C17	1.419 (3)
O1—C3	1.328 (4)	C13—C14	1.376 (5)
O1—C4	1.445 (5)	C14—C15	1.400 (4)
O2—C3	1.190 (4)	C15—C16	1.376 (4)
O3—C7	1.323 (4)	C16—C17	1.425 (3)
O3—C8	1.439 (4)	C18—C19	1.394 (4)
O4—C7	1.198 (4)	C19—C20	1.358 (4)
O5—C16	1.326 (3)	C20—C21	1.419 (4)
O6—C25	1.314 (3)	C21—C22	1.413 (4)
N1—C9	1.326 (3)	C21—C26	1.406 (4)
N1—C17	1.358 (3)	C22—C23	1.353 (5)

Data collection: *CAD-4 VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 VAX/PC*. Data reduction: *Xtal3.0* (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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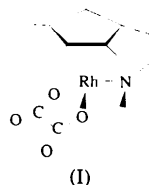
Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1055). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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ordination site. While for the diiodorhodium complex Cp[#]RhI₂, the intramolecular coordination mode of the side chain was indicated by NMR data and proved by an X-ray diffraction study, only NMR data were available for the analogous oxalate compound, (I). In addition, determination of the structure of (I) is interesting because no structures of cyclopentadienyl–oxalate complexes with Group 9 elements have been reported previously.



The structure determination of (I) shows that the dimethylamino group coordinates intramolecularly to the Rh atom. The Rh–N distance of 2.188 (6) Å is in good agreement with the metal–nitrogen distances observed in isostructural complexes containing the Cp[#] ligand (Jutzi, Kristen, Dahlhaus, Neumann & Stammler, 1993; Jutzi, Kristen, Neumann & Stammler, 1994). In addition, the Rh atom is not exactly centred below the cyclopentadienyl ring, but is shifted towards atom C5 to a small extent. Due to the intramolecular coordination of the side chain, the methylene C10 atom is bent towards the Rh atom; the C10–C5 vector intersects the Cp[#] ring plane at an angle of 10.7°. The Rh–C_{ring} distances are in the range expected for half-sandwich transition metal cyclopentadienyl complexes [2.092 (7)–2.191 (8) Å]. It

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Intramolecular Coordination of the Dimethylamino Group in a Rhodium–Oxalate Complex with the 1-[2-(Dimethylamino)-ethyl]-2,3,4,5-tetramethylcyclopentadienyl Ligand

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Abstract

The title compound, { η^5 -1-[2-(dimethylamino- κ N)ethyl]-2,3,4,5-tetramethylcyclopentadienyl}(oxalato- κ^2 O,O'')-rhodium, [Rh(C₂O₄)(C₁₃H₂₂N)], is the first rhodium–oxalate complex incorporating a cyclopentadienyl ligand. In this complex, the dimethylamino group of the hemilabile 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand is coordinated to the Rh atom in an intramolecular manner.

Comment

In the course of our work with transition metal complexes of the hemilabile 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand (Cp[#]) (Jutzi & Dahlhaus, 1993), we have examined several rhodium complexes (Jutzi, Kristen, Neumann & Stammler, 1994). Complexes of this type deserve special attention because the dimethylamino group can coordinate intramolecularly to the metal centre. Thus, they can act as an intramolecular protecting group and block a vacant co-

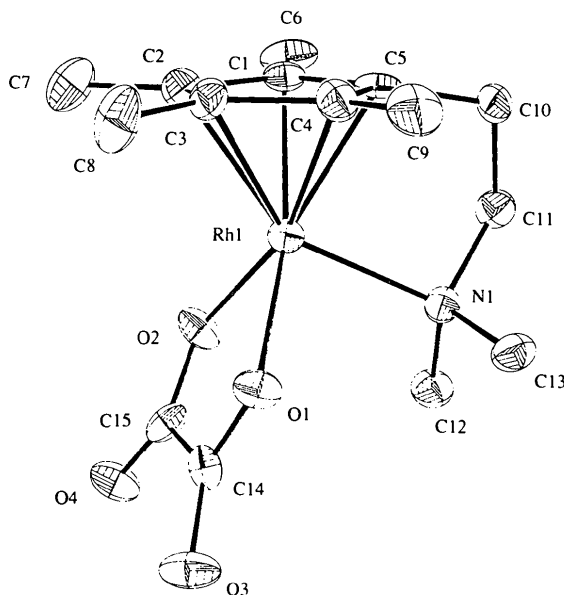


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.