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Tris(ethylmaltolato)bismuth(III)

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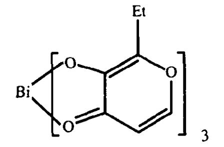
Abstract

The coordination around the Bi atom of the title compound, tris(2-ethyl-3-hydroxy-4*H*-pyran-4-onato-O^3,O^4)bismuth(III), $[Bi(C_7H_7O_3)_3]$, can be described as a distorted pentagonal bipyramid with five of the six coordinated O atoms approximately in the equatorial plane and the axial positions occupied by the sixth coordinated O atom and a stereoactive lone pair. This is a rare example of a six-coordinate Bi^{III} compound with a stereoactive lone pair.

Comment

The valence-shell electron-pair repulsion theory, VSEPR (Sidgwick & Powell, 1940; Gillespie & Nyholm, 1957), has proved an excellent guide to the stereochemistry of the *sp*-block elements towards the top of the Periodic Table and, indeed, for the halogens down to and including iodine. In this area non-bonding electron pairs are almost universally stereoactive. However, for the compounds and complexes of tin(II), antimony(III), bismuth(III) and tellurium(IV) the lone pair is commonly non-stereoactive (Wells, 1984). Examples of the relatively few bismuth(III) compounds with stereoactive lone pairs include Rb[Bi(SCN)$_4$] (Gałdecki, Główka & Goliński, 1976) and $Bi(S_2COCH_3)_3$ (Snow & Tiekink, 1987).

Tris(ethylmaltolato)bismuth(III), (1), was prepared by the addition of an acidic solution of bismuth(III) chloride to a methanolic solution of ethylmaltol (2-ethyl-3-hydroxy-4*H*-pyran-4-one) with the pH adjusted to be weakly alkaline. It provides a further example of a bismuth(III) stereoactive lone pair.



(1)

In the approximately pentagonal bipyramidal structure, five of the six coordinated O atoms occupying the equatorial sites are almost coplanar, with bond angles at the Bi atom in the range 69.6 (2)–73.3 (3)°. The Bi atom is displaced 0.35 Å out of the equatorial plane of the coordinated O atoms and away from the axial atom O(21), such that all six coordinated O atoms lie on one side of the Bi atom (Fig. 1). As a consequence of the displacement of the Bi atom from the plane, the angles between the equatorial O atoms and the axial O atom at Bi are all less than 90°. The molecule adopts pseudo-*m* symmetry, not imposed by crystallographic constraints, similar to that found in $M(S_2COCH_3)_3$ (M = Bi, Sb) (Snow & Tiekink, 1987). The maltolato group with axially coordinated atom O(21) occupies the pseudo mirror plane through the molecule with the terminal ethyl C atom C(21) the only atom not in the plane. Similarly, the terminal atoms C(1) and C(11) of the equatorial maltolato groups are not symmetrically sited in the otherwise

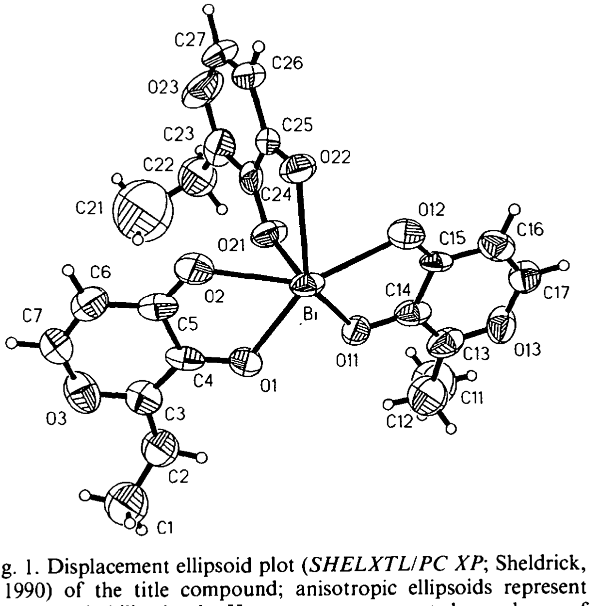


Fig. 1. Displacement ellipsoid plot (*SHELXTL/PC XP*; Sheldrick, 1990) of the title compound; anisotropic ellipsoids represent 50% probability levels, H atoms are represented as spheres of arbitrary radii.

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approximately mirrored ligands. All terminal C atoms have high displacement parameters.

Comparison of the ligand geometry for the Bi^{III} complex (Fig. 1) with those of the octahedral tris(maltolato) complexes of Fe^{III} (Ahmet, Frampton & Silver, 1988) and Al^{III} (Finnegan, Rettig & Orvig, 1986), and the bis(phenyl)maltolato complex of B^{III} (Orvig, Rettig & Trotter, 1987), shows the expected trends consistent with increasing radius of the metal ion. The O(1)—*M*—O(2) bond angles decrease as the *M*—O bond lengths and the O(1)···O(2) ligand bite size increase with the ionic radius of the metal. The Bi—O bond lengths show significant differences between those involving the hydroxyl O atoms (2.124–2.250 Å) and the weaker keto O-atom bonds (2.469–2.518 Å). The shortest Bi—O hydroxyl O-atom distance of 2.124 Å is that to the unique axial O atom O(21).

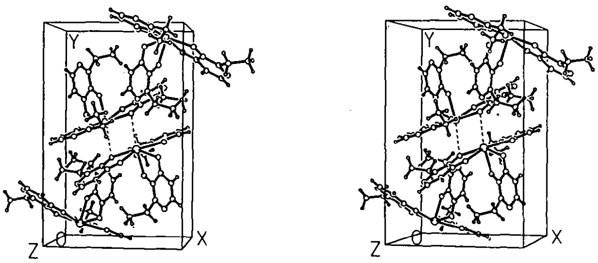

Fig. 2. Packing diagram (*SHELXTL/PC XP*; Sheldrick, 1990) viewed approximately along the *z* axis. The dashed lines represent short intermolecular Bi···O(1) contacts between centrosymmetrically related molecules.

The complexes of Bi^{III} and Sb^{III} with a stereoactive lone pair commonly associate in dimeric pairs through weak intermolecular bonds. Molecules of $M(S_2COCH_3)_3$ (*M* = Bi, Sb) (Snow & Tiekink, 1987) associate through weak *M*···S interactions (3.405 and 3.520 Å) and the K^+ and NH_4^+ salts of $[Sb(C_2O_4)_3]^{3-}$ (Poore & Russell, 1971) have an *M*···O contact of 3.420 Å. In compound (1), the Bi···O contact distance between pairs of centrosymmetrically related molecules is much shorter (Fig. 2), at 3.126 Å between Bi and O(1), with a second contact of 3.395 Å between Bi and O(11).

Experimental

Crystal data

$[Bi(C_7H_7O_3)_3]$
$M_r = 626.4$
Monoclinic
$P2_1/n$
$a = 10.647\ (2)$ Å
$b = 17.004\ (3)$ Å
$c = 11.623\ (2)$ Å
$\beta = 92.61\ (3)°$
$V = 2102.1\ (7)$ Å^3
$Z = 4$
$D_x = 1.98$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71069$ Å
Cell parameters from 30 reflections
$\theta = 5.2–10.9°$
$\mu = 8.56$ mm^{-1}
$T = 293$ K
Block
0.34 × 0.30 × 0.27 mm
Pale yellow

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical
$T_{min} = 0.05$, $T_{max} = 0.23$
5796 measured reflections
4028 independent reflections
2883 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0215$
$\theta_{max} = 28.1°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 22$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 100 reflections intensity variation: <5%

Refinement

Refinement on *F*
$R = 0.0466$
$wR = 0.0469$
2883 reflections
250 parameters
H-atom parameters not refined

$w = 1.6622/[\sigma^2(F) + 0.00067F^2]$
$(\Delta/\sigma)_{max} = 0.048$
$\Delta\rho_{max} = 1.19$ e Å^{-3}
$\Delta\rho_{min} = -0.78$ e Å^{-3}
Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1990)

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

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

	x	*y*	*z*	U_{eq}
Bi	0.12453 (4)	0.06436 (2)	0.07423 (3)	0.0642 (1)
O(1)	−0.0715 (7)	0.1044 (5)	0.0230 (6)	0.070 (3)
O(2)	0.0238 (7)	0.1239 (5)	0.2404 (6)	0.082 (3)
O(3)	−0.3073 (8)	0.2235 (5)	0.1509 (7)	0.089 (3)
O(11)	0.1083 (7)	0.0672 (4)	−0.1180 (6)	0.074 (3)
O(12)	0.3238 (7)	0.0282 (5)	−0.0031 (6)	0.079 (3)
O(13)	0.3008 (8)	−0.0021 (5)	−0.3447 (6)	0.084 (3)
O(21)	0.1754 (7)	0.1841 (4)	0.0536 (6)	0.074 (3)
O(22)	0.2983 (8)	0.0970 (5)	0.2206 (7)	0.080 (3)
O(23)	0.3488 (10)	0.3305 (5)	0.2121 (9)	0.104 (4)
C(1)	−0.4533 (14)	0.1666 (9)	−0.0389 (14)	0.121 (5)
C(2)	−0.3181 (12)	0.1772 (8)	−0.0389 (11)	0.093 (4)
C(3)	−0.2465 (11)	0.1793 (7)	0.0741 (9)	0.076 (4)
C(4)	−0.1325 (10)	0.1452 (7)	0.0986 (10)	0.069 (4)
C(5)	−0.0787 (10)	0.1549 (7)	0.2141 (9)	0.068 (4)
C(6)	−0.1474 (11)	0.2011 (7)	0.2912 (10)	0.077 (4)
C(7)	−0.2563 (12)	0.2330 (8)	0.2566 (11)	0.088 (5)
C(11)	0.1227 (17)	0.0975 (11)	−0.4635 (15)	0.136 (6)
C(12)	0.0912 (14)	0.0443 (8)	−0.3692 (13)	0.102 (4)
C(13)	0.2005 (13)	0.0278 (7)	−0.2903 (10)	0.080 (4)
C(14)	0.2064 (11)	0.0392 (6)	−0.1745 (9)	0.068 (4)
C(15)	0.3187 (9)	0.0207 (6)	−0.1109 (8)	0.061 (3)
C(16)	0.4188 (11)	−0.0083 (7)	−0.1723 (10)	0.078 (4)
C(17)	0.4063 (11)	−0.0194 (7)	−0.2845 (10)	0.077 (4)
C(21)	0.087 (2)	0.3764 (16)	0.097 (2)	0.228 (12)
C(22)	0.2021 (14)	0.3530 (9)	0.0591 (12)	0.103 (4)
C(23)	0.2688 (12)	0.2947 (7)	0.1364 (10)	0.081 (4)
C(24)	0.2515 (10)	0.2173 (6)	0.1318 (9)	0.066 (4)
C(25)	0.3176 (10)	0.1689 (7)	0.2163 (9)	0.067 (4)
C(26)	0.4004 (11)	0.2102 (9)	0.2947 (11)	0.090 (5)
C(27)	0.4127 (13)	0.2856 (9)	0.2896 (13)	0.097 (6)

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

O(1)—Bi	2.250 (7)	C(13)—O(13)	1.364 (15)
O(2)—Bi	2.469 (8)	C(17)—O(13)	1.328 (13)
O(11)—Bi	2.233 (7)	C(12)—C(11)	1.47 (2)
O(12)—Bi	2.420 (8)	C(13)—C(12)	1.475 (17)
O(21)—Bi	2.124 (7)	C(14)—C(13)	1.358 (15)
O(22)—Bi	2.518 (7)	C(15)—C(14)	1.412 (13)

C(4)—O(1)	1.314 (13)	C(16)—C(15)	1.400 (15)
C(5)—O(2)	1.238 (12)	C(17)—C(16)	1.319 (15)
C(3)—O(3)	1.354 (14)	C(24)—O(21)	1.317 (11)
C(7)—O(3)	1.331 (14)	C(25)—O(22)	1.240 (12)
C(2)—C(1)	1.450 (18)	C(23)—O(23)	1.342 (14)
C(3)—C(2)	1.489 (16)	C(27)—O(23)	1.341 (16)
C(4)—C(3)	1.363 (15)	C(22)—C(21)	1.38 (3)
C(5)—C(4)	1.445 (14)	C(23)—C(22)	1.495 (17)
C(6)—C(5)	1.420 (16)	C(24)—C(23)	1.330 (14)
C(7)—C(6)	1.326 (16)	C(25)—C(24)	1.440 (14)
C(14)—O(11)	1.346 (14)	C(26)—C(25)	1.424 (14)
C(15)—O(12)	1.258 (11)	C(27)—C(26)	1.290 (19)
Bi···Bi$^{\rm i}$	3.792 (2)	Bi···O(1$^{\rm i}$)	3.126 (7)
O(2)—Bi—O(1)	69.6 (2)	C(4)—O(1)—Bi	117.6 (6)
O(11)—Bi—O(1)	72.6 (3)	C(5)—O(2)—Bi	113.0 (7)
O(11)—Bi—O(2)	139.2 (2)	C(7)—O(3)—C(3)	119.3 (9)
O(12)—Bi—O(1)	142.8 (3)	C(3)—C(2)—C(1)	118.1 (13)
O(12)—Bi—O(2)	144.5 (2)	C(2)—C(3)—O(3)	110.7 (10)
O(12)—Bi—O(11)	70.3 (2)	C(4)—C(3)—C(2)	126.1 (12)
O(21)—Bi—O(1)	85.3 (3)	C(6)—C(5)—O(2)	123.6 (10)
O(21)—Bi—O(2)	79.4 (3)	C(13)—C(12)—C(11)	112.3 (13)
O(21)—Bi—O(11)	82.8 (3)	C(12)—C(13)—O(13)	113.3 (11)
O(21)—Bi—O(12)	88.3 (3)	C(14)—C(13)—C(12)	126.0 (13)
O(22)—Bi—O(1)	139.1 (3)	C(23)—C(22)—C(21)	113.8 (16)
O(22)—Bi—O(2)	73.3 (3)	C(22)—C(23)—O(23)	111.3 (11)
O(22)—Bi—O(11)	133.8 (3)	C(24)—C(23)—C(22)	124.8 (12)
O(22)—Bi—O(12)	71.2 (3)	C(26)—C(25)—O(22)	124.0 (11)
O(22)—Bi—O(21)	71.4 (3)	C(26)—C(25)—C(24)	115.0 (11)

Symmetry code: (i) $-x, -y, -z$.

Data collection and cell refinement: *XSCANS* (Fait, 1991). Data reduction and structure solution: *SHELXTL/PC* (Sheldrick, 1990). Refinement: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *SHELXTL/PC XP*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diaquadiphenylbis(p-toluenesulfonato)lead–Water (1/1)

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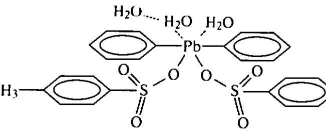
Abstract

The polyhedron around the Pb atom in $[Pb(C_7H_7SO_3)_2(C_6H_5)_2(H_2O)_2].H_2O$ is a slightly distorted pentagonal bipyramid, with two C(phenyl) atoms in the apical positions and three sulfonate O atoms and two O atoms of the coordinated water molecules forming the pentagonal plane. One sulfonate ligand is monodentate, the second is bidentate and links a neighbouring molecule to form a chain {*i.e. catena*-poly[diaquadiphenyl(p-toluenesulfonato-*O*)lead-μ-(p-toluenesulfonato)-*O*:*O*′]}. The chains are linked by the non-coordinated water molecules to form a two-dimensional network.

Comment

The present work continues structural studies on organometal organosulfonates (Huber, Westhof & Preut, 1987; Preut, Rüther & Huber, 1986; Rüther, Huber & Preut, 1985, 1986, 1988) and in this paper we present the first structure determination of an organolead organosulfonate, diaquadiphenylbis(p-toluenesulfonato)lead–water (1/1), (I), by single-crystal X-ray diffraction.



(I)

The coordination polyhedron around Pb is a slightly distorted pentagonal bipyramid (Fig. 1). The central atom is surrounded by two C(phenyl) atoms in apical positions with three sulfonate O atoms and two water O atoms forming the pentagonal plane. One of the sulfonate ligands is monodentately bonded to Pb, the distance Pb(1)—O(8) [2.447 (6) Å] being the shortest Pb—O distance observed in the molecule. The distance between Pb and O of the bidentate sulfonate [Pb(1)—O(1) 2.478 (6) Å] is consistently longer. A similar distance is found between Pb and O of one of the coordinated water molecules [Pb(1)—O(22) 2.494 (5) Å], while the distance to the second coor-

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