C(2)—C(3)—C(2^{i})	111.9 (5)	O(3)—C(4)—O(4)	124.0 (4)
O(3)—C(4)—C(5)	123.0 (4)	O(4)—C(4)—C(5)	113.0 (4)
C(4)—C(5)—C(6)	116.1 (4)	C(5)—C(6)—C(5^{ii})	111.5 (5)
O(5)—C(7)—O(6)	123.2 (4)	O(5)—C(7)—C(8)	121.8 (4)
O(6)—C(7)—C(8)	115.0 (4)	C(7)—C(8)—C(9)	115.3 (4)
C(8)—C(9)—C(8^{i})	111.8 (5)		

Symmetry codes: (i) $x, -y, z$; (ii) $x, 1-y, z$.

The structure of caesium hydrogen carbonate could not be solved by Patterson techniques nor by conventional direct methods, despite exhaustive trials. The structure was elucidated using the symbolic addition procedure *LSAM* (Germain & Woolfson, 1968) programmed into the *MITHRIL* (Gilmore & Brown, 1988) package. Other calculations were made with the *GX* (Mallinson & Muir, 1985) package. The figures were drawn with the aid of the *MOG* (SciTech Software, 1992) program on a Commodore Amiga Computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and Cs···O distances have been deposited with the IUCr (Reference: MU1051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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New Crystal Data for $[Hg(SC_2H_5)_2]$

KELLY A. FRASER AND WILLIAM CLEGG

Department of Chemistry, The University of Newcastle upon Tyne, Newcastle NE1 7RU, England

DONALD C. CRAIG, MARCIA L. SCUDDER AND IAN G. DANCE

School of Chemistry, The University of New South Wales, Kensington, NSW 2033, Australia

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Abstract

A new precise determination of the crystal structure of bis(ethanethiolato)mercury reveals a cell [a = 7.342 (2), b = 4.702 (2), c = 23.131 (6) Å, β = 101.83 (1)°] and structure slightly different from that reported previously [Bradley & Kunchur (1965). *Can. J. Chem.* **43**, 2786–2792]. The Hg and S atoms lie in planes normal to the crystallographic c^* axis, separated by the alkyl chains. Weak van der Waals interactions between the alkyl chains give rise to perfect cleavage along the *ab* plane. The primary coordination of Hg is linear [Hg—S = 2.343 (1) Å, S—Hg—S = 176.48 (6)°]. Each Hg atom also takes part in four secondary interactions with S atoms of neighbouring molecules, two at 3.285 (1) Å and two at 3.386 (1) Å. The total coordination of Hg can be regarded as octahedral with severe tetragonal compression.

Comment

The majority of bis(thiolato)mercury(II) complexes reported in the literature have essentially linear twofold primary coordination of Hg, with Hg—S bond lengths in the range 2.3–2.4 Å, and weak secondary interactions between monomer units with Hg···S distances in the range 3.0–3.8 Å. These additional long-range interactions are often characteristic of the coordination of Hg with thiolate (and other) ligands.

Of the linearly coordinated compounds reported previously, the structure of $[Hg(SC_2H_5)_2]$, (I), (Bradley & Kunchur, 1965) stood out as being anomalous, with Hg—S bond lengths of 2.45 Å, S—C bond lengths of 1.65 Å and C—C bond lengths of 1.54 and 1.84 Å. The Hg—S bond thus appeared too long, the S—C bond length too short and one C—C distance very long. The cell reported by these authors was monoclinic with a = 7.54 (2), b = 4.87 (1), c = 23.80 (4) Å, β = 85°, and the space group was reported to be Cc.

As it is our intention to use the dimensions of these compounds in a study of the coordination geometry exhibited by homoleptic mercury thiolate compounds, we decided to redetermine the structure of this compound in order to obtain more precise data. The structure we report is slightly different to that reported by Bradley & Kunchur (1965).

The crystal structure contains discrete $Hg(SC_2H_5)_2$ molecules in which the primary coordination of Hg is linear [Hg—S = 2.343 (1) Å, S—Hg—S = 176.48 (6)°], with the Hg atoms lying on the twofold axis. The Hg atoms are approximately hexagonally arranged in a plane normal to c^* at $z = \frac{1}{4}$. On either side is a plane composed of S atoms. Separating these S—Hg—S layers and almost perpendicular to them are the alkyl chains. The S—Hg—S segments are parallel to each other and inclined at 51° to the normal to the Hg plane, with the S atoms 1.47 Å out of this plane. Each Hg atom participates in additional secondary interactions with four S atoms from neighbouring molecules in an approximately square-planar arrangement, two of which are at 3.285 (1) Å and two of which are at 3.386 (1) Å. The short Hg—S bonds are perpendicular

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to this plane; thus the overall coordination geometry at Hg can be regarded as octahedral with severe tetragonal compression.

We are puzzled by the small but unambiguous difference between the crystal structure we report here and that of Bradley & Kunchur (1965). The layered motif, with a central S—Hg—S sandwich and ethyl groups protruding almost normal to the layer, is very similar in both structures. Despite numerous attempts we have been unable to produce any crystals with the cell reported previously, and all the X-ray powder diffraction patterns we recorded during crystallizations of the title compound confirmed the cell we report here. Disagreement between the observed X-ray powder diffraction data and those calculated from the previous crystallographic data has also been reported by others (Wright, Natan, MacDonnell, Ralston & O'Halloran, 1990). It seems unlikely that the compound would crystallize with two very similar but different structures. The structure we report here has high precision.

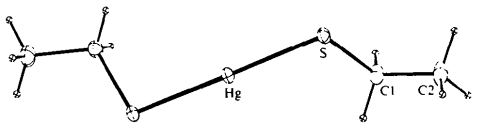

Fig. 1. A view of the title compound showing the atom-numbering scheme. Displacement ellipsoids are shown at the 10% probability level.

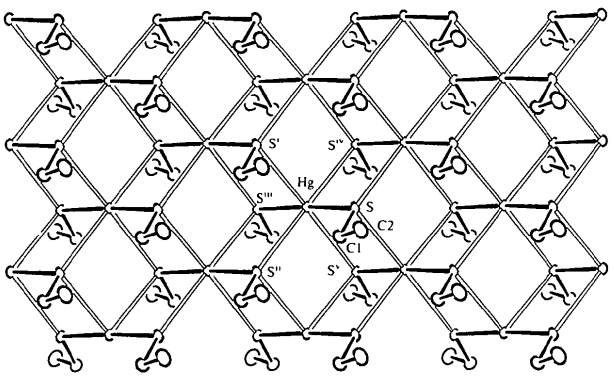

Fig. 2. A single layer of $[Hg(SC_2H_5)_2]$ viewed down c^*. The a axis is horizontal. Symmetry codes are given in Table 2.

Experimental

The title compound was precipitated as a fine white powder from an ethanolic solution of mercury(II) cyanide on addition of a slight excess of ethanethiol (Wertheim, 1929), and recrystallized from ethanol to produce very thin flaky plates. A good quality single crystal was obtained by very slow evaporation of a saturated ethanolic solution at room temperature.

Crystal data

$[Hg(C_2H_5S)_2]$
M_r = 322.8
Monoclinic
$C2/c$
a = 7.342 (2) Å
b = 4.702 (2) Å
c = 23.131 (6) Å
β = 101.83 (1)°
V = 781.5 (3) Å^3
Z = 4
D_x = 2.74 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 18 reflections
θ = 10–13°
μ = 20.09 mm^{-1}
T = 294 (1) K
Diamond-shaped tabular
0.2 × 0.19 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.036, T_{max} = 0.216
1359 measured reflections
1132 independent reflections
1029 observed reflections [$I \geq 3\sigma(I)$]
R_{int} = 0.017
θ_{max} = 30°
$h = 0 \rightarrow 10$
$k = -6 \rightarrow 0$
$l = -32 \rightarrow 32$
1 standard reflection frequency: 33.33 min intensity decay: from 1.00 to 0.80

Refinement

Refinement on F
R = 0.017
wR = 0.031
S = 1.22
1029 reflections
33 parameters
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ = 0.98
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −2.28 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
Hg	1/2	0.4589 (1)	1/4	0.0458 (1)
S	0.7899 (2)	0.4436 (3)	0.3151 (1)	0.0484 (4)
C1	0.7505 (8)	0.2223 (14)	0.3766 (2)	0.0614 (17)
C2	0.8921 (11)	0.2764 (23)	0.4313 (3)	0.0912 (28)

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

Hg—S	2.343 (1)	S—C1	1.832 (6)
Hg···S^{i}	3.285 (1)	C1—C2	1.486 (8)
Hg···S^{ii}	3.386 (1)		
S—Hg—S^{iii}	176.48 (6)	S—Hg···S^{v}	80.05 (4)
Hg—S—C1	104.4 (2)	S^{iv}···Hg···S^{ii}	178.25 (3)
S—C1—C2	111.7 (5)	S^{i}···Hg···S^{iv}	92.15 (4)
S—Hg···S^{i}	100.18 (4)	S^{ii}···Hg···S^{v}	88.64 (5)
S—Hg···S^{iv}	82.29 (4)	S^{iv}···Hg···S^{v}	89.61 (3)
S—Hg···S^{ii}	97.41 (4)		

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (ii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $1-x, y, \frac{1}{2}-z$; (iv) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$.

The data were corrected for the decrease in intensity observed during data collection. The structure was solved by Patterson methods. H atoms were included in calculated positions. The structure was refined using *BLOCKLS*, a local version of

ORFLS (Busing, Martin & Levy, 1962). All calculations were performed on an IBM 3090 computer. *ORTEP*II (Johnson, 1976) running on a Macintosh IIcx was used for the structural diagrams.

This research was supported by the Science and Engineering Research Council and the Australian Research Council. KAF would like to thank the SERC for a research studentship and also the Sir Robert Menzies Centre for Australian Studies for the award of a Northcote Visiting Scholarship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: OH1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(*N*,*N*-diethyldithiocarbamato-*S*,*S*')phenyltin

ELEONÓRA KELLÖ, VIKTOR VRÁBEL AND IVAN SKAČÁNI

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia

JAROSLAV HOLEČEK

Department of General and Inorganic Chemistry, Institute of Chemical Technology, 532 10 Pardubice, Czech Republic

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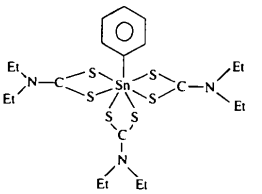
Abstract

The title structure, $[Sn(C_5H_{10}NS_2)_3(C_6H_5)]$, consists of monomeric molecular chelate complexes in which the Sn atom has distorted pentagonal bipyramidal coordination with five S atoms in equatorial sites. One of the dithiocarbamate ligands has a short [2.570 (2) Å] and a long [2.766 (2) Å] Sn—S distance, a second dithiocarbamate ligand has almost equal Sn—S distances [2.676 (2) and 2.602 (2) Å] and the axial–equatorial dithiocarbamate ligand has a long equatorial Sn—S distance [2.757 (2) Å] and a short axial Sn—S distance [2.458 (2) Å]. The axial Sn—C distance is 2.113 (3) Å. Distortion from the idealized pentagonal bipyramid has been attributed to the steric requirements of the four-membered MS_2C ring and to the limited bite angle of the dithiocarbamate ligand.

Comment

Organotin dithiocarbamate complexes have been the subject of numerous spectroscopic and structural studies because of their industrial importance (Evans & Karpel, 1985) and their antifungal and insecticidal properties (Kumar Das, Chen & Sinn, 1985). Although extensive biological and structural studies have been conducted on the five-coordinate Sn^{IV}–dtc (dtc = dithiocarbamate) complexes, there is less information available with regard to crystal structure determinations of seven-coordinate Sn^{IV} complexes. Morris & Schlemper (1978, 1979) investigated the crystal structures of $MeSn(Et_2dtc)_3$ and $^nBuSn(Et_2dtc)_3$ which each exhibit distorted pentagonal bipyramidal geometry around the Sn atom with an S atom and methyl/ethyl group in axial positions. The metal environment in the title compound differs from that of $MeSn(Et_2dtc)_3$ and $^nBuSn(Et_2dtc)_3$ in that the alkyl group is replaced by the bulkier phenyl group. This change was the reason for determining the structure of the title compound, (I).



(I)

The molecular structure and atom-numbering scheme are shown in Fig. 1. The structure of the title compound consists of monomeric chelate molecules. The Sn atom is pentagonal-bipyramidally coordinated with the phenyl C atom and the S atom of one of the three dtc ligands in apical positions. One equatorial bidentate dtc ligand shows two nearly equal Sn—S bond distances [Sn—S(5) 2.676 (2) and Sn—S(6) 2.602 (2) Å]; for the anisobidentate dtc ligand there is a significant difference in the Sn—S bond distances with Sn—S(3) and Sn—S(4) having

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