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## Bis(*O*-methyldithiocarbonato)mercury(II)

BY EDWARD R. T. TIEKINK

*Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia 5001, Australia*

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**Abstract.** [Hg(S<sub>2</sub>COCH<sub>3</sub>)<sub>2</sub>], *M<sub>r</sub>* = 414.9, orthorhombic, *Pbca*, *a* = 10.605 (1), *b* = 8.003 (2), *c* = 23.478 (2) Å, *U* = 1993 (2) Å<sup>3</sup>, *D<sub>x</sub>* = 2.766 Mg m<sup>-3</sup>, *Z* = 8, Mo *K*α radiation, λ = 0.7107 Å, μ = 16.16 mm<sup>-1</sup>, *F*(000) = 1520, *T* = 295 (2) K, *R* = 0.037 for 1190 reflections with *I* ≥ 2.5σ(*I*). The immediate environment about the Hg atom is defined by two S atoms derived from two different xanthate ligands; Hg–S 2.365 (3) and 2.383 (3) Å, S–Hg–S 164.9 (1)°. One of the xanthate ligands also coordinates a neighbouring Hg atom, Hg–S 2.924 (3) Å, thereby generating a helical polymeric chain.

**Introduction.** The bis(xanthato) (–S<sub>2</sub>COR) complexes of the Zn triad elements are characterized by the formation of polymeric arrays and the presence of tetrahedrally coordinated metal centres. Thus far three structural prototypes have been discovered, all of which can be related to a 16-membered ring of four metal centres bridged by four xanthate ligands [see Watanabe (1981) for schematic representations of these structures]. An isolated tetrameric ring has been observed in Zn(S<sub>2</sub>CO<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>2</sub> (Ito, 1972) in which the two remaining tetrahedral sites on each Zn atom are occupied by a chelating xanthate ligand. In the structures of Zn(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (Ikeda & Hagihara, 1966), Cd(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (Iimura, Ito & Hagihara, 1972), Cd(S<sub>2</sub>CO<sup>n</sup>C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> (Rietveld & Maslen, 1965), and both polymorphs of Hg(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (Watanabe, 1977; Chieh & Moynihan, 1980) the tetrameric rings are linked *via* bridging xanthate ligands which results in the formation of infinite two-dimensional arrays; as a consequence each central atom is coordinated by four bridging xanthate ligands. A third structural type was

found for Hg(S<sub>2</sub>CO<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>2</sub> (Watanabe, 1981) in which there are two crystallographically unique Hg atoms; the coordination geometry of two of the Hg atoms constituting the 16-membered ring is completed by a chelating xanthate ligand [as for Zn(S<sub>2</sub>CO<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>2</sub> above] while the remaining two Hg atoms link neighbouring tetrameric units *via* bridging xanthate ligands as for example in Zn(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (Ikeda & Hagihara, 1966) so that the two-dimensional arrays of the tetramer are connected *via* helical chains. A recent X-ray study of the methylxanthates of the Group 15 elements (Snow & Tiekink, 1986) has shown that the polymeric structure found for Bi(S<sub>2</sub>CO<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> (Hoskins, Tiekink & Winter, 1985) no longer persists in the Bi(S<sub>2</sub>COCH<sub>3</sub>)<sub>3</sub> analogue. These studies have now been extended to include Hg(S<sub>2</sub>COCH<sub>3</sub>)<sub>2</sub> to examine what effect the presence of the –S<sub>2</sub>COCH<sub>3</sub> anion has on the polymeric structures adopted by the closely related derivatives described above.

**Experimental.** Hg(S<sub>2</sub>COCH<sub>3</sub>)<sub>2</sub> prepared as in literature (Chieh & Moynihan, 1980). Colourless needle 0.09 × 0.88 × 0.03 mm grown from acetone. Enraf–Nonius CAD-4F diffractometer controlled by a PDP8/A computer, graphite-monochromated Mo *K*α radiation; ω:2θ scan technique. Cell parameters from least-squares procedure (De Boer & Duisenberg, 1984) on 25 reflections (10 ≤ θ ≤ 15°). Analytical absorption correction: max./min. transmission factors 0.5385, 0.0902 (Sheldrick, 1976). Total of 3322 reflections (1 ≤ θ ≤ 25°) measured in the range –12 ≤ *h* ≤ 1, –9 ≤ *k* ≤ 1, –27 ≤ *l* ≤ 6. No significant variation in the intensities of three standards (336, 146, 2,3,12) monitored every 3600 s. 1742 unique reflections (*R*<sub>int</sub>

= 0.039), 1190 satisfied  $I \geq 2.5\sigma(I)$ . Structure solved from Patterson method, full-matrix least-squares refinement of 101 parameters based on  $F$  (Sheldrick, 1976). Anisotropic thermal parameters for non-H atoms and H atoms included in the model at their calculated positions (C-H 0.97 Å). At convergence  $R = 0.037$ ,  $wR = 0.039$ ,  $w = [\sigma^2(F) + 0.0088F^2]^{-1}$ ,  $S = 0.55$ ,  $(\Delta/\sigma)_{\max} \leq 0.001$ ,  $(\Delta\rho)_{\max} = 1.09$ ,  $(\Delta\rho)_{\min} = -1.89 \text{ e } \text{Å}^{-3}$ ; no extinction correction. Scattering factors for H, C, O and S given in *SHELX76* (Sheldrick, 1976) and those for neutral Hg corrected for  $f'$  and  $f''$  (Hamilton & Ibers, 1974). University of Adelaide's VAX11/785 computer system. Atomic parameters given in Table 1, bond distances and angles in Table 2.\* The Hg-atom environment and numbering scheme are shown in Fig. 1.

**Discussion.** The coordination geometry about the Hg atom in  $\text{Hg}(\text{S}_2\text{COCH}_3)_2$  consists, in part, of two S atoms derived from two different xanthate ligands at

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43458 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and  $B_{\text{eq}}$  values (Å<sup>2</sup>)

	$x$	$y$	$z$	$B_{\text{eq}}$
Hg	0.14876 (4)	0.08574 (5)	0.20681 (2)	2.57
S(1)	0.3035 (3)	0.1965 (4)	0.1449 (1)	2.81
S(2)	0.2667 (4)	0.3553 (5)	0.0327 (1)	4.44
C(1)	0.2070 (10)	0.2855 (12)	0.0922 (4)	2.28
O(1)	0.0886 (7)	0.2881 (10)	0.1067 (3)	3.48
C(2)	-0.0019 (12)	0.3712 (22)	0.0697 (6)	5.35
S(3)	-0.0270 (3)	-0.0583 (3)	0.2467 (1)	2.61
S(4)	-0.2228 (3)	-0.2528 (5)	0.1866 (1)	4.07
C(3)	-0.1048 (10)	-0.1213 (12)	0.1849 (4)	1.96
O(2)	-0.0588 (7)	-0.0479 (9)	0.1380 (3)	2.88
C(4)	-0.1082 (14)	-0.0939 (19)	0.0841 (5)	4.65

Table 2. Interatomic distances (Å) and bond angles (°)

Hg-S(1)	2.365 (3)	Hg-S(3)	2.383 (3)
Hg-S(3 <sup>i</sup> )	3.313 (3)	Hg-S(4 <sup>i</sup> )	2.924 (3)
S(1)-C(1)	1.76 (1)	S(3)-C(3)	1.74 (1)
S(2)-C(1)	1.63 (1)	S(4)-C(3)	1.64 (1)
C(1)-O(1)	1.30 (1)	C(3)-O(2)	1.34 (1)
O(1)-C(2)	1.46 (1)	O(2)-C(4)	1.42 (2)
S(1)-Hg-S(3)	164.9 (1)	S(1)-Hg-S(4 <sup>i</sup> )	100.0 (1)
S(3)-Hg-S(4 <sup>i</sup> )	95.0 (1)	Hg-S(4 <sup>i</sup> )-C(3 <sup>i</sup> )	95.7 (4)
Hg-S(1)-C(1)	100.4 (4)	Hg-S(3)-C(3)	100.6 (3)
S(1)-C(1)-S(2)	121.1 (7)	S(3)-C(3)-S(4)	121.8 (6)
S(1)-C(1)-O(1)	112.6 (7)	S(3)-C(3)-O(2)	112.6 (7)
S(2)-C(1)-O(1)	126.3 (8)	S(4)-C(3)-O(2)	125.5 (8)
C(1)-O(1)-C(2)	119.2 (9)	C(3)-O(2)-C(4)	119.1 (9)

Superscripted atoms (i) are related by the symmetry operation  $-x, \frac{1}{2}+y, \frac{1}{2}-z$ .

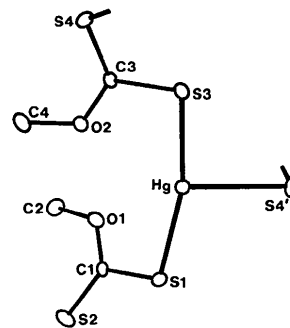


Fig. 1. The immediate environment about the Hg atom showing the numbering scheme employed (Johnson, 1971).

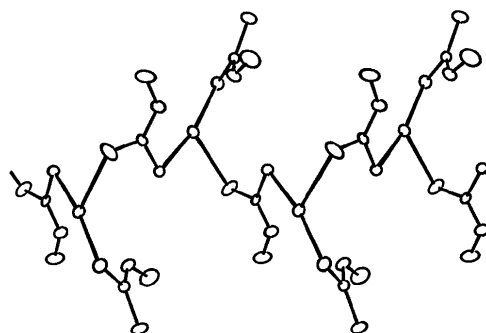


Fig. 2. A view of the helical chain along the  $b$  axis.

distances 2.365 (3) and 2.383 (3) Å respectively. The xanthate ligand S(1), S(2) functions as a monodentate ligand; the pendant S(2) atom does not participate in a significant intermolecular interaction. In contrast the S(4) atom of the second xanthate ligand bridges a neighbouring Hg<sup>i</sup> atom (symmetry operation  $-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ) at a distance of 2.924 (3) Å. This distance is less than the sum of the van der Waals radii of Hg and S of 3.3 Å (Bondi, 1964) and must therefore be considered a bonding interaction. It is noted that although S(3) approaches Hg<sup>i</sup> at a distance of 3.313 (3) Å this separation is not indicative of a substantial interaction between these atoms. The net result of the presence of the bridging xanthate ligands is the formation of helical polymeric chains generated by the twofold screw parallel to the  $b$  axis. A portion of the polymer thus generated is illustrated in Fig. 2.

There are no significant interchain interactions involving the Hg atom; the closest Hg...S contact between the helical chains involves S(1) and Hg<sup>ii</sup> (symmetry operation  $\frac{1}{2}-x, \frac{1}{2}+y, z$ ) at a distance of 3.474 (3) Å. As can be seen from Fig. 1, the xanthate ligands are orientated such that the O atoms are directed towards the Hg atom; however, the Hg-O(1) and Hg-O(2) distances of 2.926 (8) and 2.932 (8) Å respectively [*cf.* 3.0 Å for the sum of the van der Waals radii for Hg and O (Bondi, 1964)] are not indicative of

significant bonding interactions. The Hg-atom geometry is thus best described as being approximately T-shaped with S—Hg—S angles of 165, 100 and 95°.

The remaining xanthate ligand geometries are as expected. The C—S bond distances are not equivalent with the longer bonds being associated with the S atoms more strongly coordinated to the Hg atom.

The polymeric structure reported here for Hg(S<sub>2</sub>COCH<sub>3</sub>)<sub>2</sub> resembles those noted earlier for the related 1,1-dithiolate derivatives Hg[S<sub>2</sub>P(O<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>]<sub>2</sub> (Lawton, 1971) and Te(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)Br (Gable, Hoskins, Steen & Winter, 1983). In the Hg compound bridging dithiophosphate ligands lead to a zigzag chain, as in Hg(S<sub>2</sub>COCH<sub>3</sub>)<sub>2</sub>; however, the remaining dithiophosphate ligand chelates the Hg atom so that approximate tetrahedral coordination about the central atom is retained. In contrast, the backbone of the helical structure in Te(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)Br comprises Te and bridging Br atoms; the xanthates function as chelating ligands so that each Te atom in the polymer is four-coordinate.

Whereas in the previously reported Hg 1,1-dithiolates described above and in the closely related Hg[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> compounds (Iwasaki, 1973) the Hg atoms exist in distorted tetrahedral environments, the Hg atom in Hg(S<sub>2</sub>COCH<sub>3</sub>)<sub>2</sub> has been shown to be three-coordinate. A similar decrease in coordination number has also been recently noted for the tris(xanthates) of Bi<sup>III</sup>. In Bi(S<sub>2</sub>CO<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> (Hoskins, Tiekink & Winter, 1985) bridging xanthate ligands lead to a polymeric structure with seven-coordinate Bi; however, for the methyl analogue (Snow & Tiekink, 1986) two centrosymmetrically related molecules only loosely associate *via* weak Bi...S interactions of 3.405 (1) Å so that the Bi atoms must be considered

six-coordinate. It would seem that the presence of the -S<sub>2</sub>COCH<sub>3</sub> anion in the Hg(S<sub>2</sub>COCH<sub>3</sub>)<sub>2</sub> and Bi(S<sub>2</sub>COCH<sub>3</sub>)<sub>3</sub> compounds decreases the Lewis acidity of the central atoms. These observations may indicate a different coordinating ability of the methylxanthate anion compared with higher homologues.

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## Chloro(triphenylphosphine sulfide)gold(I)

BY M. SAKHAWAT HUSSAIN\*

*Department of Chemistry, University of Petroleum and Minerals, UPM Box 1830, Dhahran 31261, Saudi Arabia*

AND E. O. SCHLEMPER

*Department of Chemistry, University of Missouri, Columbia, Missouri 65211, USA*

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**Abstract.** [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PS}AuCl], *M<sub>r</sub>* = 526.8, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 12.286 (2), *b* = 9.447 (1), *c* = 14.814 (2) Å, β = 94.39 (2)°, *V* = 1714.4 (3) Å<sup>3</sup>, *Z*

= 4, *D<sub>m</sub>* = 2.025 (7), *D<sub>x</sub>* = 2.041 g cm<sup>-3</sup>, λ(Mo Kα) = 0.7107 Å, μ = 89.26 cm<sup>-1</sup>, *F*(000) = 1000, room temperature, *R* = 0.024, 3008 unique reflections. The structure consists of monomeric [(Ph<sub>3</sub>PS)AuCl] molecules with linear gold(I) having an S—Au—Cl angle

\* To whom correspondence should be addressed.