

Preliminary communication

CRYSTAL STRUCTURE OF A 1,2-PHENYLENEDIMERCURY
 DIXANTHATE

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Summary

The X-ray structure of $C_6H_4[HgS_2COMe]_2$ is reported in which two HgS_2COMe units are bridged by a C_6H_4 moiety in a *cis* configuration. The xanthate ligands function in the monodentate mode.

Crystallographic studies on organometallic xanthate (S_2COR) complexes have shown that the xanthate ligand may adopt a variety of different coordination modes. Bidentate coordination, as is observed for many transition metal complexes [1], was found in the structure of $Me_2Tl(S_2COMe)$ [2] whereas a monodentate coordination mode has been noted for the xanthate ligands in $MeHg(S_2COMe)$ [3] and $Me_2Te(S_2COMe)_2$ [4]. In $Ph_2Bi(S_2CO^iPr)$ [4] a polymeric structure arises as a result of weak intermolecular $-Bi-S-C-S-Bi-$ bridging. More interesting however, are the asymmetric or intermediate modes of coordination found in the structures of $Me_2Sn(S_2COEt)_2$ [6], $Ph_2Sn(S_2CO^iPr)Cl$ [7], $MeSb(S_2COEt)_2$ [8], and $PhBi(S_2COMe)_2$ [9]. As a part of a continuing study designed to determine the factor(s) responsible for the different modes of coordination of the xanthate ligand, the 1/1 reaction of $PhHgCl$ (CH_2Cl_2 , 20 ml) and the potassium salt of S_2COMe (H_2O , 10 ml) was investigated. The unexpected product, $C_6H_4[HgS_2COMe]_2$, was isolated, as its dichloromethane solvate, and characterized by X-ray diffraction methods.

Intensity data for 2444 reflections were measured on an Enraf-Nonius CAD4-F diffractometer with the use of $Mo-K\alpha$ radiation [10]. The data were corrected for intensity variation, Lorentz and polarization effects, and for absorption [10]. Of the reflections measured, 1565 were unique, and 1486 satisfied the $I \geq 2.5\sigma(I)$ criterion.

Crystal data: $C_{11}H_{12}Cl_2O_2S_4Hg_2$, M 776.5, triclinic, space group $P\bar{1}$ (C_1^1 ,

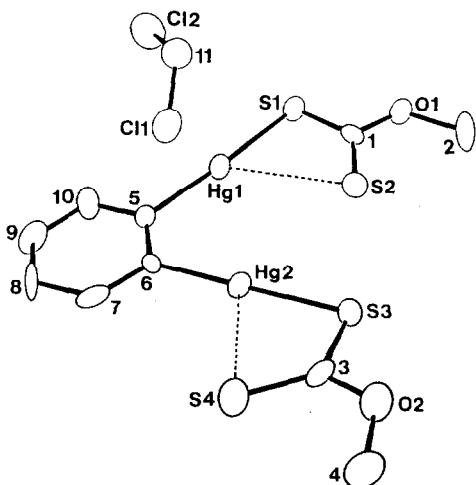


Fig. 1. The molecular structure of $C_6H_4[HgS_2COMe]_2$. Important interatomic parameters: Hg(1)—S(1) 2.379(5), Hg(2)—S(3) 2.401(4), Hg(1)—S(2) 3.151(5), Hg(2)—S(4) 3.015(5), Hg(1)—C(5) 2.07(2), Hg(2)—C(6) 2.05(2), S(1)—C(1) 1.68(2), S(2)—C(1) 1.65(2), S(3)—C(3) 1.73(2), S(4)—C(3) 1.65(2), C(1)—O(1) 1.34(2), C(3)—O(2) 1.32(2) Å; S(1)—Hg(1)—C(5) 175.5(5), S(3)—Hg(2)—C(6) 179.5(4), S(1)—Hg(1)—S(2) 63.8(1), S(3)—Hg(2)—S(4) 66.0(1), S(2)—Hg(1)—C(5) 120.6(5), S(4)—Hg(2)—C(6) 114.0(5), S(1)—C(1)—S(2) 128.5(11), S(3)—C(3)—S(4) 124.9(10), Hg(1)—C(5)—C(6) 120.7(11), Hg(2)—C(6)—C(5) 123.8(11), Hg(1)—C(5)—C(10) 116.3(13), Hg(2)—C(6)—C(7) 118.3(13), C(5)—C(6)—C(7) 117.9(14), C(6)—C(5)—C(10) 123.0(16)°.

No 2), a 10.637(2), b 12.022(2), c 7.692(1) Å, α 101.60(1), β 98.75(1), γ 89.96(1)°, V 951.9 Å³, D_x 2.709 g cm⁻³, Z = 2, $F(000)$ 704, Mo- K_α (graphite monochromator) λ 0.71073 Å, $1 \leq \theta \leq 22.5^\circ$, $\mu(\text{Mo-}K_\alpha)$ 167.6 cm⁻¹, absorption correction applied: max/min transmission factors 0.3363 and 0.0466.

The structure was solved from the Patterson and refined by a full-matrix least-squares method [10]. Anisotropic thermal parameters were introduced for all non-H atoms and a weighting scheme included. H atoms were not included in the model; at the convergence of the refinement R = 0.042, R_w = 0.044 for $w = 2.15/[\sigma^2(F) + 0.001|F|^2]$. Selected interatomic parameters are listed with Fig. 1*.

The crystal structure is comprised of molecules of $C_6H_4[HgS_2COMe]_2$ and CH_2Cl_2 ; the only significant intermolecular contact between the complex and the solvent molecule occurs between Hg(1) and Cl(1) of 3.485(8) Å. All remaining intermolecular contacts in the lattice are those expected from normal Van der Waals contacts.

The complex consists of two HgS_2COMe units bridged by a *cis*-substituted benzene ring. The two HgS_2COMe moieties are essentially planar and form dihedral angles of 1.89 and 5.59° respectively with the C_6H_4 ring. The xanthate ligands function in the monodentate mode so that each Hg atom is linearly coordinated. The deviation of the C—Hg—S angles from 180° may be due, in part, to additional weak Hg...S interactions, of approximately 3.1 Å, between the non-coordinating S atoms and the Hg atoms. Further weak intra-

*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

molecular interactions are noted. As can be seen from Fig. 1, whereas S(4) is directed away from Hg(1), the orientation of S(2) is such that this atom approaches Hg(2) at a distance of 3.504(5) Å and the S(2) . . S(3) separation is approximately 3.49 Å.

The linear coordination geometries about each of the Hg atoms in $C_6H_4[HgS_2COMe]_2$ is in essential agreement to that found in the related xanthate [3] and dithiocarbamate [11] complexes with the MeHg moiety and, within the limits of experimental accuracy, there are no significant differences in their Hg-atom coordination geometries.

A number of crystal structures [12–14] are now available which feature the 1,2- $C_6H_4Hg_2$ core described above. In each of the previously reported examples however, the two Hg atoms are further bridged by either $C_6H_4-Hg-C_6H_4$ as in $[Hg(C_6H_4)]_4$ [12,13] or Cl as in $[C_6H_4(HgCl)_2]_2Cl$ [14]. Similar $C_6F_4-Hg-C_6F_4$ bridging has been found in the perfluoro derivative $[Hg(C_6F_4)]_3$ [15]. On the basis of their crystallographic results it has been suggested by Brown, Massey and Wickens [12] that 1.72 Å is the more realistic estimate (cf. 1.50 Å [16]) for the Van der Waals radii for Hg. The Hg(1) . . Hg(2) separation of 3.571(1) Å in $C_6H_4[HgS_2COMe]_2$ provides further support for the larger value.

The mode of formation of $C_6H_4[HgS_2COMe]_2$ from the reaction of PhHgCl and potassium xanthate remains unclear. The integrity of PhHgCl was confirmed by a mass spectral analysis and further studies are in progress to investigate this system.

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