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Methylmercury Xanthates

EDWARD R. T. TIEKINK

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, S.A., 5001, Australia

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Structural studies of xanthate complexes of the zinc triad elements, $M(S_2COR)_2$ (where $R = CH_3$, CH_2CH_3, ${}^iC_3H_7$, and ${}^nC_4H_9$), have shown that these complexes invariably adopt polymeric structures in the solid state which arise as a result of intermolecular bridging by either one or both of the xanthate ligands [1]. The addition of pyridine and 1,10-phenanthroline to the bis ethylxanthates of Zn and Cd results in monomeric five [2] and six [3] coordinate structures respectively in which dissimilar M–S bond distances are formed by the chelating xanthate ligands. In the anion, $Cd(S_2COCH_2CH_3)_3^-$, a monodentate and two bidentate ligands define a tetragonal pyramidal environment about the Cd atom [4]. As a part of a study of the coordination chemistry (in particular asymmetric coordination of xanthate and related 1,1-dithiolate ligands of the non-transition metal elements, the methylmercury xanthates ($R = CH_3$, CH_2CH_3, and ${}^iC_3H_7$) have been prepared and the crystal structure of a representative compound, $CH_3Hg(S_2COCH_3)$, determined.

$CH_3Hg(S_2COR)$ was prepared from the facile 1:1 reaction of CH_3HgCl (Ventron-Alfa Inorganics, 0.4 g, 25 ml CH_2Cl_2) and $K^+\ {}^-S_2COR$ (10 ml water). The mixture was stirred for 30 min, separated, and the non-aqueous layer dried over anhydrous Na_2SO_4. Petroleum spirit (40–60 °C) was added and the solution allowed to stand until pale-yellow crystals were deposited. In the infrared spectrum characteristic absorptions were observed in the C–O, C–S and Hg–C regions; $R = CH_3$: 1220, 1050 and 545 cm^{-1}, respectively; $R = CH_2CH_3$: 1218, 1041 and 548 cm^{-1}; $R = {}^iC_3H_7$: 1227, 1030 and 548 cm^{-1}.

Intensity data for a well-defined crystal of $CH_3Hg(S_2COCH_3)$ were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using the $\omega{:}2\theta$ scan technique and Mo K$\bar{\alpha}$ radiation. A total of 837 reflections were measured in the range $1° \leqslant \theta \leqslant 25°$ which included a set of high-angle Friedel pairs. A satisfactory solution was found in the *Pnma* space group for which 583 reflections satisfied the $I \geqslant 2.5\sigma(I)$ criterion. The intensity data were corrected for Lorentz, polarization and absorption effects using the programs REDUCT [5a] and SUSCAD [5b].

TABLE I. Fractional Atomic Coordinates for $CH_3Hg(S_2COCH_3)$

Atom	*x/a*	*y/b*	*z/c*
Hg	0.1140(1)	0.25	0.0674(1)
C(1)	0.2177(30)	0.25	0.1963(16)
S(1)	0.0138(7)	0.25	−0.0879(4)
S(2)	−0.3303(7)	0.25	0.0310(4)
C(2)	−0.2257(26)	0.25	−0.0678(11)
O(1)	−0.3171(18)	0.25	−0.1493(9)
C(3)	−0.5245(23)	0.25	−0.1476(14)

TABLE II. Interatomic Bond Distances (Å) and Angles (°) for $CH_3Hg(S_2COCH_3)$

Atoms	Distance	Atoms	Angle
Hg–C(1)	2.04(2)	C(1)–Hg–S(1)	176.1(7)
Hg–S(1)	2.396(6)	C(1)–Hg–S(2)	120.8(7)
Hg–S(2)	3.201(6)	S(1)–Hg–S(2)	63.1(1)
S(1)–C(2)	1.73(2)	Hg–S(1)–C(2)	97.4(6)
S(2)–C(2)	1.64(2)	Hg–S(2)–C(2)	72.6(7)
C(2)–O(1)	1.37(2)	S(1)–C(2)–S(2)	127(1)
O(1)–C(3)	1.47(2)	S(1)–C(2)–O(1)	109(1)
S(1)•••S(2)	3.01(1)	S(2)–C(2)–O(1)	125(1)
		C(2)–O(1)–C(3)	117(1)

Crystal Data

$CH_3Hg(S_2COCH_3)$, $C_3H_6OS_2Hg$, $M = 322.8$, orthorhombic, *Pnma* ($D_{2h}{}^{16}$, No. 62), $a = 7.102(1)$, $b = 6.875(3)$, $c = 14.739(2)$ Å, $U = 719.7$ Å^3, $D_c = 2.979$ Mg m^{-3}, $Z = 4$, $F(000) = 608$ electrons, Mo K$\bar{\alpha}$ radiation (graphite monochromator) $\lambda = 0.71073$ Å, $\mu = 21.82$ mm^{-1}, number parameters/number variables = 14.

The structure was initially solved in both the *Pnma* and $Pn2_1a$ space groups and refined using a least-squares procedure [6]. Anisotropic thermal parameters and a weighing scheme, $[\sigma^2(F) + 0.008F^2]^{-1}$, were introduced for both models. Severe correlation effects inhibited convergence for $Pn2_1a$ however it is noted that there were no significant differences between chemically equivalent parameters for both space groups. Hydrogen atoms were not included in the models. The *Pnma* model converged with conventional values for R and R_w of 0.054 and 0.058 respectively.

Crystallographic results are listed in Tables I and II and the numbering scheme used is shown in Fig. 1 [7]. A full listing of the anisotropic thermal parameters and the observed and calculated structure factors have been deposited with the Editor-in-Chief.

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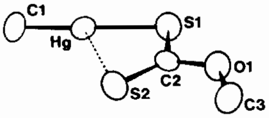

Fig. 1. The numbering scheme used for $CH_3Hg(S_2COCH_3)$; note that all atoms shown lie on a crystallographic mirror plane.

The crystals are composed of discrete molecules of $CH_3Hg(S_2COCH_3)$ which sit on a crystallographic mirror plane. The immediate environment of the Hg atom consists of the methyl substituent and one of the S atoms of the xanthate ligand. The Hg–C bond distance of 2.04(2) Å lies in the range expected for Hg–C bonds and similarly the Hg–S(1) distance of 2.396(6) Å lies in the narrow range (2.32–2.42 Å) found for Hg–S bond distances in two-coordinate Hg compounds [8]. The C(1)–Hg–S(1) angle of 176.1(7)° is close to that expected for a linear system. The second S atom of the xanthate group forms a weak interaction with the Hg atom at a distance of 3.201(6) Å which is within the sum of the van der Waals radii for these atoms of 3.35 Å [9]. The S(2)–C(2) bond distances of 1.64(2) Å is slightly longer than the value expected for a formal C–S double bond [10]; an observation which suggests that the xanthate ligand is functioning as a monodentate ligand. The remaining xanthate geometry is normal.

The crystal structure of the related dithiocarbamate complex, $CH_3Hg[S_2CN(CH_2CH_3)_2]$, has been reported to adopt a similar structure with a Hg–S bond distance of 2.418(7) Å [11]. The second S atom, however, is only 2.964(7) Å from the Hg atom and forms an additional contact with a centrosymmetrically related Hg atom at 3.147(7) Å so that the crystal structure is composed of loosely associated dimers. The closest intermolecular contact involving Hg and S atoms in $CH_3Hg(S_2COCH_3)$ is formed between Hg and S(1′), where S(1′) is related by a centre of symmetry, of 3.567(6) Å.

A number of xanthate complexes of non-transition metal elements in which an organo-substituent has been incorporated into the environment of the central atom have been structurally characterised. Both symmetric (Tl(III) [12]) and asymmetric (Sn(IV) [13, 14], Sb(III) [15], Bi(III) [16, 17]) coordination of the xanthate ligand has been found in these complexes. The structure of $CH_3Hg(S_2COCH_3)$ provides a further example of a xanthate complex in which asymmetric coordination of the xanthate ligand is not associated with any obvious lone-pair effect on the central atom.

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