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Structure of Acetato(benzenethiolato)mercury(II)

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Abstract. $[\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_6\text{H}_5\text{S})]$, $M_r = 368.80$, monoclinic, $P2_1/n$, $a = 18.362(2)$, $b = 7.485(1)$, $c = 14.292(2)$ Å, $\beta = 104.72(1)^\circ$, $V = 1900.0(3)$ Å³, $Z = 8$, $D_x = 2.58$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 164$ cm⁻¹, $F(000) = 1344$, $T = 295$ K, $R = 0.034$ for 2326 unique observed reflections. The structure is built up of infinite —S—Hg—S— chains linked *via* acetate groups into sheets. The two independent Hg atoms, five- and six-coordinated, are in addition to the two thiolate groups also bonded to two and three acetate ligands, respectively.

Introduction. It has been known for a long time that Hg^{II} forms extremely stable, water insoluble compounds with organic sulfur ligands of the thioalcohol RSH ($R = \text{alkyl, aryl}$) type. Solid complexes between these thiols and Hg^{II} have been isolated with thiol/mercury (Th/Hg) ratios varying from 1 to 4. Many of these complexes have been the subject of intense spectroscopic investigations and the crystal structures of some of them have been determined. For Th/Hg ratios 3 or 4, thiophenols have mostly been used as ligands, *e.g.* by Christou, Foltling & Huffman (1984) and Choudhury, Dance, Guerny & Rae (1983). For structure determinations of the neutral compounds Hg(SR)₂ and for the 1:1 complexes Hg(SR)X, however, alkyl thiols have so far been preferred as ligands, *e.g.* by Wells (1937), Bradley & Kunchur (1963, 1964), Kunchur (1964), Taylor & Carty (1977), Perchard, Zuppiroli, Gouzerh, Jeannin & Robert (1981), Perchard, Baron & De Loze (1984), Barrera *et al.* (1982), Biscarini, Foresti & Pradella (1984), Canty, Raston & White (1978, 1979*a,b*), Johansson (1939) and Puff, Sievers & Elsner (1975). The crystal structures of the 1:1 complexes so far studied (Canty, Raston & White, 1979*a*) have been found to be dependent on the donicity of the anion X; the chloride, bromide and acetate anions have been used earlier. In

this study acetate and thiophenolate anions were chosen to allow a direct comparison with the previous work.

Experimental. Crystals grown from an acetonitrile solution of mercury acetate and mercury thiophenolate. Plate-shaped transparent crystal, $0.25 \times 0.20 \times 0.09$ mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, variable speed, ω - 2θ scans, width $(0.80 + 0.60 \tan \theta)^\circ$, max. recording time 150 s. Three standard reflections, no significant variations. Lattice parameters based on 40 diffractometer θ values. 3585 reflections, $\theta \leq 25^\circ$, $0 \leq h \leq 17$, $0 \leq k \leq 7$, $-13 \leq l \leq 13$, 2327 with $I > 3\sigma(I)$. Lp and absorption corrections, transmission factors 0.06–0.22. Structure solved by direct methods with MULTAN80 (Main *et al.*, 1980). Full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$, $w = [\sigma^2(F_o) + (0.030F_o)^2 + 2.5]^{-1}$, anisotropic temperature factors for non-C atoms and phenyl-H atoms included with fixed parameters in calculated positions [$d(\text{C—H}) = 1.00$ Å]. Final refinement with 2326 reflections, 138 variables, $R = 0.034$, $wR = 0.041$, $S = 1.0$. Corrections for secondary extinction (Zachariasen, 1967), $g = 0.19(2) \times 10^{-4}$. $(\Delta/\sigma)_{\text{max}} = 0.02$, final $\Delta\rho$ excursions $\leq |1.3| \text{ e } \text{Å}^{-3}$. Scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Program used: see Lundgren (1982).

Discussion. Final atomic coordinates and temperature factors are listed in Table 1† and selected interatomic distances and angles in Table 2. The present structure may be described as built up of endless (—Hg—SR—)_n chains running in the y direction, linked *via* the acetate

† Lists of structure factors, anisotropic thermal parameters and phenyl-H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43226 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates and isotropic temperature factors (\AA^2)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{iso}/U_{eq}
Hg(1)	0.22966 (2)	0.27218 (6)	0.78315 (3)	0.0372 (2)
Hg(2)	0.11076 (2)	0.03241 (6)	0.57394 (3)	0.0389 (2)
S(1)	0.10624 (15)	0.29901 (36)	0.67547 (19)	0.0359 (9)
S(2)	0.33096 (14)	0.23898 (37)	0.92707 (20)	0.0367 (9)
O(1)	0.3139 (5)	0.4126 (12)	0.6931 (6)	0.0563 (34)
O(2)	0.2847 (5)	0.1336 (11)	0.6562 (6)	0.0519 (31)
O(3)	0.0156 (4)	0.1238 (12)	0.4360 (6)	0.0532 (31)
O(4)	0.1273 (4)	0.1907 (13)	0.4226 (7)	0.0663 (37)
C(11)	0.0439 (6)	0.2476 (14)	0.7496 (7)	0.034 (2)
C(12)	0.0666 (7)	0.2466 (17)	0.8495 (10)	0.056 (3)
C(13)	0.0144 (8)	0.2185 (20)	0.9032 (11)	0.066 (4)
C(14)	-0.0595 (8)	0.1852 (19)	0.8572 (11)	0.063 (4)
C(15)	-0.0823 (7)	0.1892 (18)	0.7584 (10)	0.055 (3)
C(16)	-0.0316 (6)	0.2177 (16)	0.7040 (9)	0.044 (3)
C(21)	0.2818 (6)	0.2328 (14)	1.0194 (8)	0.035 (2)
C(22)	0.2435 (6)	0.3779 (16)	1.0444 (8)	0.045 (3)
C(23)	0.2038 (7)	0.3603 (19)	1.1138 (10)	0.059 (3)
C(24)	0.2045 (8)	0.1965 (20)	1.1613 (11)	0.065 (4)
C(25)	0.2428 (8)	0.0581 (19)	1.1383 (10)	0.061 (4)
C(26)	0.2809 (7)	0.0690 (17)	1.0671 (9)	0.050 (3)
C(31)	0.3182 (6)	0.2731 (14)	0.6461 (8)	0.035 (2)
C(32)	0.3663 (8)	0.2767 (18)	0.5736 (10)	0.060 (3)
C(41)	0.0572 (7)	0.1952 (17)	0.3883 (9)	0.051 (3)
C(42)	0.0232 (9)	0.2823 (21)	0.2913 (12)	0.076 (4)

groups to sheets parallel to [101]. Infinite chains with Hg diagonally coordinated by O or S atoms are the building elements of many Hg^{II} structures. The chains can be either planar or spiral, the latter being found in the trigonal forms of HgO and HgS . The planar chains are of two types, + - or overall *trans* chains as found in orthorhombic HgO (Aurivillius, 1965a) and ++ - - or alternating *cis-trans* chains originally found in $\text{Hg}(\text{OHg})_4\text{Br}_2$ (Aurivillius, 1965b) but later on also in $\text{Hg}_3\text{S}_2\text{Cl}_2$ (Aurivillius, 1967).

Previous studies of 1:1 mercury thiolate complexes of type RSHgX with $X = \text{acetate}$ have shown the presence of $(-\text{Hg}-\text{SR}-)_n$ chains (Canty, Raston & White, 1979a) often crosslinked by weakly bonded ($\text{Hg}-\text{O}$ 2.70–2.86 \AA) acetate groups (Puff, Sievers & Elsnér, 1975; Canty, Raston & White, 1979a). If the compounds with $R = \text{methyl}$ and ethyl are crystallized from pyridine, 1:1 adducts are obtained, containing isolated chains with pyridine and acetate coordination at each Hg (Canty, Raston & White, 1978, 1979a). All chains are infinite and of the overall *trans* type with considerable deviations in the $\text{S}-\text{Hg}-\text{S}$ and $\text{Hg}-\text{S}-\text{Hg}$ angles from the ideal values of 180 and 109°.

In the present study the chains are of the *cis-trans* type with angles at the Hg and S atoms of 162.4, 143.7 and 98.1, 98.4° and with $\text{Hg}-\text{S}$ distances in the range 2.403–2.481 \AA (Table 2). The two independent Hg atoms are, in addition to the thiolate groups, also bidentate coordinated to one acetate group with $\text{Hg}-\text{O}$ bonds in the range 2.38–2.55 \AA . Hg(2) is further bonded to one acetate ligand and Hg(1) weakly bonded to two (Table 2, Fig. 1). These acetate groups link Hg(1) atoms within one chain [$\text{Hg}(1)-\text{O}$ 2.85,

2.87 \AA], while the acetate groups bonded to Hg(2) form double bridges [$\text{Hg}(2)-\text{O}$ 2.55, 2.57 \AA], crosslinking the chains into layers (Fig. 2). Distances and angles within the acetate and thiolate ligands are unexceptional.

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

In the coordination spheres of the Hg atoms			
Hg(1)–S(1)	2.403 (3)	Hg(2)–O(3)	2.378 (8)
Hg(1)–S(2)	2.410 (3)	Hg(2)–S(2 ^{III})	2.445 (3)
Hg(1)–O(1)	2.483 (9)	Hg(2)–S(1)	2.481 (3)
Hg(1)–O(2)	2.514 (8)	Hg(2)–O(4)	2.551 (10)
Hg(1)–O(1')	2.852 (9)	Hg(2)–O(3 ^{IV})	2.569 (8)
Hg(1)–O(2 ^{II})	2.873 (8)		
S(1)–Hg(1)–S(2)	162.4 (1)	S(1)–Hg(2)–S(2 ^{III})	143.7 (1)
S(1)–Hg(1)–O(1)	104.1 (2)	S(1)–Hg(2)–O(3)	97.3 (2)
S(1)–Hg(1)–O(2)	93.4 (2)	S(1)–Hg(2)–O(3 ^{IV})	103.6 (2)
S(2)–Hg(1)–O(1)	92.2 (2)	S(1)–Hg(2)–O(4)	98.7 (2)
S(2)–Hg(1)–O(2)	102.1 (2)	S(2 ^{III})–Hg(2)–O(3)	119.0 (2)
O(1)–Hg(1)–O(2)	51.9 (3)	S(2 ^{III})–Hg(2)–O(3 ^{IV})	88.9 (2)
Hg(1)–S(1)–Hg(2)	98.1 (1)	S(2 ^{III})–Hg(2)–O(4)	105.4 (2)
Hg(1)–S(2)–Hg(2 ^{II})	98.4 (1)	O(3)–Hg(2)–O(3 ^{IV})	67.8 (3)
		O(3)–Hg(2)–O(4)	52.0 (3)
		O(3 ^{IV})–Hg(2)–O(4)	117.7 (3)

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

In the thiolate ligands

S(1)–C(11)	1.79 (1)	S(2)–C(21)	1.78 (1)
C(11)–C(12)	1.38 (2)	C(21)–C(22)	1.39 (2)
C(12)–C(13)	1.39 (2)	C(22)–C(23)	1.38 (2)
C(13)–C(14)	1.37 (2)	C(23)–C(24)	1.40 (2)
C(14)–C(15)	1.37 (2)	C(24)–C(25)	1.34 (2)
C(15)–C(16)	1.37 (2)	C(25)–C(26)	1.38 (2)
C(16)–C(11)	1.39 (2)	C(26)–C(21)	1.41 (2)
S(1)–C(11)–C(12)	122.9 (8)	S(2)–C(21)–C(22)	123.8 (8)
S(1)–C(11)–C(16)	118.0 (8)	S(2)–C(21)–C(26)	117.0 (8)
C(12)–C(11)–C(16)	119 (1)	C(22)–C(21)–C(26)	119 (1)
C(11)–C(12)–C(13)	120 (1)	C(21)–C(22)–C(23)	120 (1)
C(12)–C(13)–C(14)	120 (1)	C(22)–C(23)–C(24)	119 (1)
C(13)–C(14)–C(15)	120 (1)	C(23)–C(24)–C(25)	120 (1)
C(14)–C(15)–C(16)	121 (1)	C(24)–C(25)–C(26)	122 (1)
C(15)–C(16)–C(11)	120 (1)	C(25)–C(26)–C(21)	119 (1)

In the acetate ligands

C(31)–O(1)	1.255 (14)	C(41)–O(3)	1.265 (15)
C(31)–O(2)	1.239 (13)	C(41)–O(4)	1.257 (15)
C(31)–C(41)	1.523 (18)	C(41)–C(42)	1.515 (21)
O(1)–C(31)–O(2)	122.6 (10)	O(3)–C(41)–O(4)	118.6 (12)
C(32)–C(31)–O(1)	118.4 (10)	C(42)–C(41)–O(3)	120.7 (12)
C(32)–C(31)–O(2)	119.0 (10)	C(42)–C(41)–O(4)	120.7 (12)

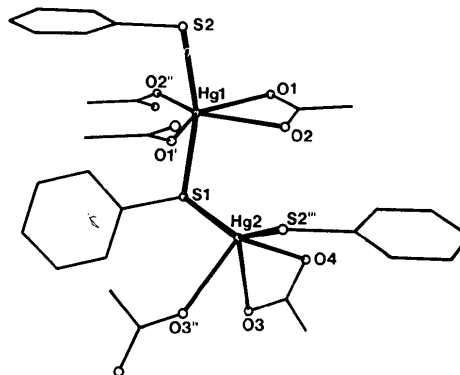


Fig. 1. The environment of the Hg atoms. Atomic-numbering scheme and superscripts are given in Table 2.

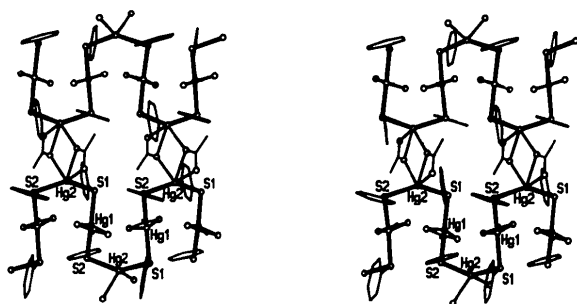


Fig. 2. Stereoview of part of the layers in the structure. Infinite $(-\text{Hg}-\text{RS}-)_n$ chains, running parallel to the b axis, are linked by the acetate ligands. $\text{Hg}-\text{O}$ bonds $>2.8 \text{ \AA}$ are not drawn.

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Structure of a Chelating Phosphine Rhenium(I) Complex: *fac*-Tricarbonylchloro-[1,1,1-tris(diphenylphosphinemethyl)ethane]rhenium(I)

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Abstract. $[\text{ReCl}(\text{CO})_3(\text{C}_{41}\text{H}_{39}\text{P}_3)]$, $M_r = 930.372$, triclinic, $P\bar{1}$, $a = 9.804(3)$, $b = 9.815(2)$, $c = 21.339(5) \text{ \AA}$, $\alpha = 103.74(2)$, $\beta = 93.25(2)$, $\gamma = 97.62(2)^\circ$, $U = 1968.7(4) \text{ \AA}^3$, $Z = 2$, $D_m = 1.58$, $D_x = 1.57 \text{ Mg m}^{-3}$ (by flotation in $\text{CCl}_4/\text{hexane}$ mixture),

$\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$, $\mu = 0.9907 \text{ mm}^{-1}$, $F(000) = 928$, $T = 296(4) \text{ K}$, $R(F) = 0.55$ for 7317 observed reflections [$I > 3\sigma(I)$]. The coordination geometry about Re is a six-coordinate octahedron comprising Cl, two P atoms and three carbonyl groups. The six-membered ring in this complex is characterized by a large ring strain and takes a chair form.

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