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Crystal and Molecular Structure of Bis(2-mercaptobenzoato-*S*)mercury(II) Monodioxane

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The structure of $Hg(C_7H_5O_2S)_2 \cdot C_4H_8O_2$ has been determined from three-dimensional single-crystal X-ray diffraction data and refined to $R = 0.047$ for 703 counter intensities. The crystals are monoclinic, space group $P2_1/a$, with $a = 21.86(2)$, $b = 4.117(4)$, $c = 11.42(1)$ Å, $\beta = 111.04(5)°$ and $Z = 2$. The Hg atom, at a centre of symmetry, is linearly coordinated to the S atoms of two thiosalicylic acid molecules with the Hg–S distance 2.361(7) Å. The O atoms of the centrosymmetric dioxane molecule are hydrogen-bonded to the carboxyl groups of two bis(2-mercaptobenzoato-*S*)mercury(II) complexes, forming endless zig-zag chains.

Ortho-mercaptobenzoic (= thiosalicylic) acid forms chelate complexes with a variety of metal ions.[1] Both the carboxyl and the sulfhydryl groups usually participate in the binding.[2] With mercury(II), however, it behaves differently. Two compounds have been described; with one or two molecules thiosalicylic acid per mercury atom. Infrared spectra of the solid compounds and potentiometric studies of the complex formation in solution indicated that the carboxyl groups do not coordinate to mercury.[2] Moreover, the bis(2-mercaptobenzoato-*S*)mercury(II) complex, BTM, can bind further metal atoms, such as Zn^{2+}, Cd^{2+} or Pb^{2+}.[3] In order to investigate the surroundings of mercury and to elucidate the coordination properties of the BTM compound, the crystal structure of the BTM dioxane solvate was determined.

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EXPERIMENTAL

Preparation. The BTM-compound was prepared as described previously[2] and recrystallized from a water–dioxane mixture. Thin colourless needles were obtained when the solution was evaporated under vacuum at room temperature. The ^1H NMR spectrum of the crystals dissolved in deuterated dimethylsulfoxide-d_6 (Merck, 99.8% D) showed an additional sharp signal at 3.58 ppm at low field relative to TMS. Its area corresponded to eight protons per BTM complex. Addition of dioxane to the solution increased the area of this signal, confirming the assignment of one dioxane molecule per BTM.

Data collection. A prismatic crystal of approximate dimensions $0.04 \times 0.33 \times 0.12$ mm was chosen for the data collection and enclosed in a capillary. The cell parameters were obtained by film methods and refined by least-squares methods using 14 selected reflexions, centered on the automatic Syntex $P2_1$ diffractometer.

The intensities of 946 unique reflexions with $3° < 2\theta < 41°$ were measured using the ω scan technique with different scan speeds, from 0.5° min^{-1} upwards. Of these, 709 reflexions with $I > 2\sigma(I)$ were used in the calculations and were corrected for Lorentz and polarization effects. Two check reflexions were measured at regular intervals. Their intensities decreased about 39% with a constant rate during the 120 h of data collection. A linear correction was applied to compensate for the decrease. A semiempirical absorption correction was applied.[4] The measured maximum transmission ratio was 1:0.54.

All calculations were carried out by means of the Syntex XTL Crystallographic Program System.[5]

Crystal data. $C_{18}H_{18}O_6S_2Hg$, $M = 595.06$, monoclinic, $a = 21.86(2)$, $b = 4.117(4)$, $c = 11.42(1)$ Å, $\beta = 111.04(5)°$, $V = 959(1)$ Å^3, $D_m = ca.\ 2$ g/cm^{-3}, $Z = 2$, $D_x = 2.06$ g/cm^{-3}, $F(000)$ 572, space group $P2_1/a$:

Table 1. Final fractional atomic positional parameters and isotropic mean square amplitudes U in Å^2. Estimated standard deviations are given in parentheses.

	x	y	z	U
Hg	0	0	0	
S	0.0848(3)	−0.320(2)	−0.0226(6)	
O1	0.0579(7)	−0.504(6)	0.2142(14)	
O2	0.1401(8)	−0.588(4)	0.3865(15)	
O3	−0.0504(8)	0.111(4)	0.5390(17)	
C1	0.1646(9)	−0.284(5)	0.2370(17)	0.020(5)
C2	0.1539(10)	−0.199(6)	0.1073(19)	0.033(5)
C3	0.2042(10)	−0.014(8)	0.0842(19)	0.043(5)
C4	0.2628(11)	0.057(7)	0.1849(22)	0.048(7)
C5	0.2713(11)	−0.042(7)	0.3100(21)	0.048(6)
C6	0.2234(10)	−0.213(6)	0.3279(18)	0.027(5)
C7	0.1162(11)	−0.461(7)	0.2749(21)	0.037(6)
C8	−0.103(13)	−0.016(9)	0.3724(21)	
C9	−0.0652(12)	0.045(8)	0.3211(26)	

non-standard setting of No. 14 with general positions $\pm(x,y,z)$, $\pm(\frac{1}{2}-x,\frac{1}{2}+y,\bar{z})$, MoKα x-radiation (graphite-monochromator), $\lambda = 0.71069$ Å, $\mu(\text{MoK}\alpha) = 84.2$ cm^{-1}.

STRUCTURE DETERMINATION AND REFINEMENT

Weissenberg photographs showed the systematic extinctions $h0l$: $h=2n+1$ and $0k0$: $k=2n+1$ consistent with the space group $P2_1/a$.[6] From a listing of Patterson vectors, initial values of the Hg and S positions were deduced and refined by least-squares methods. Subsequent difference Fourier maps and full-matrix least-squares refinements revealed the positions of all non-hydrogen atoms. The function minimized was $\Sigma w_i||F_o|-|F_c||^2$ with the weighting function $w_i = 1/\{\sigma^2(F_o)+(0.04\,F_o)^2\}$.

The scattering factors used were obtained from analytical expressions for the neutral atoms, including anomalous dispersion corrections for Hg and S.[6]

With isotropic temperature factors for all atoms, the agreement factors $R=\Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.085$, $R_w=(\Sigma w_i||F_o|-|F_c||^2/\Sigma w_i|F_o|^2)^{1/2}=0.11$, were obtained. Anisotropic temperature factors could be introduced for all atoms except the carbon atoms of the aromatic ring. No definitive hydrogen atom positions could be found from the difference Fourier maps. They were therefore introduced at calculated positions with a C−H distance of 0.96 Å (omitting the proton of the carboxyl group) taking the usual underestimation of about 0.13 Å in X-ray studies into account.[7]

The final agreement factors were $R=0.047$, $R_w = 0.060$, with a largest shift of 0.01 σ in the parameter values in the last refinement cycle. The highest peaks, 0.9 e Å^{-3}, in a subsequent difference Fourier map were close to the mercury position. The final parameter values are given in Tables 1 and 2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure contains centrosymmetric molecular BTM complexes, formed by a linear S−Hg−S bond between two thiosalicylic acid molecules. The carboxyl groups of two adjacent BTM complexes are hydrogen-bonded to the oxygen atoms of the centrosymmetric dioxane molecules, forming zig-zag chains running through the crystal, Fig. 1.

These chains of molecules are stacked on top of each other along the b axis with a perpendicular distance of 4.12 Å. Two long Hg−S distances at 3.420(7) Å between adjacent S−Hg−S groups, and four Hg−O1 distances at 3.08(2) and 3.11(2) Å,

Table 2. Final anisotropic thermal parameters in Å^2 with estimated standard deviations in parentheses. The temperature factor expression used is $\exp[-2\pi^2(U_{11}h^2a^{*2}+...+2\,U_{12}hka^*b^*+...)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	0.0339(8)	0.0489(9)	0.0309(8)	0.0046(13)	0.0014(5)	−0.0009(11)
S	0.041(4)	0.042(4)	0.033(3)	−0.008(4)	0.005(3)	−0.006(4)
O1	0.039(9)	0.131(17)	0.048(9)	−0.036(16)	0.013(8)	−0.002(16)
O2	0.038(9)	0.062(17)	0.053(11)	−0.006(9)	0.002(8)	0.032(10)
O3	0.056(12)	0.057(15)	0.064(12)	−0.013(9)	0.033(11)	0.007(10)
C8	0.069(18)	0.073(18)	0.037(13)	−0.004(25)	0.021(14)	−0.009(21)
C9	0.049(15)	0.076(25)	0.065(18)	−0.010(19)	0.023(14)	0.013(20)

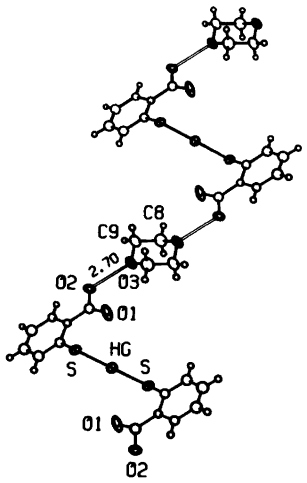

Fig. 1. The zig-zag chain of centrosymmetric BTM complexes and dioxane molecules. The hydrogen bond between O2 and O3 is indicated by the double line. The hydrogen atoms are shown in calculated positions (except for the hydrogen bond).

complete a distorted cube around each mercury atom, Fig. 2. These distances are, however, all in excess of the sum of the corresponding van der Waals radii (Hg: 1.50 Å,[7] S: 1.85 Å and O: 1.40 Å)[8] and represent therefore no significant interactions between the atoms. The length of the short Hg–S bonds, 2.361(7) Å, is typical for linearly coordinated mercury.[9] Selected interatomic distances and angles are given in Table 3.

Table 3. Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses. Symmetry codes:
$i = -x,1-y,-z$; $ii = -(x,y,z)$;
$iii = -x,-y,1-z$; $iv = -x,-y-1,1-z$

Within the BTM molecule			
Hg–S	2.361(7)	S–Hg–S^{ii}	180
S–C2	1.76(2)	Hg–S–C2	119.4(8)
C1–C7	1.47(3)	C1–C7–O1	128(2)
C7–O1	1.22(3)	C1–C7–O2	114(2)
C7–O2	1.30(3)	O1–C7–O2	118(2)
Within the dioxane molecule			
C8–O3	1.45(3)	O3^{iii}–C8–C9	109(2)
C9–O3	1.42(3)	C8^{iii}–O3–C9	110(2)
C8–C9	1.51(4)	C8–C9–O3	110(2)
Intermolecular distances and angles			
Hg–S^{i}	3.420(7)	S–Hg–S^{i}	88.9(2)
Hg–O1	3.11(2)	O1–Hg–O1^{i}	96.6(5)
Hg–O1^{i}	3.08(2)	C7–O2...O3^{iv}	114.3(15)
O2...O3^{iv}	2.70(3)	C8–O3^{iv}...O2	112.3(16)
		C9–O3^{iv}...O2	124.2(16)

The oxygen atoms O1 och O2 of the carboxyl group are twisted 0.30(2) and −0.24(2) Å, respectively, out of the plane of the benzene ring. The twist angle of 14° is probably a result of the relatively strong hydrogen bond, 2.70(3) Å, between the carboxyl oxygen O2 atom and the dioxane oxygen O3 atom, Fig. 1.

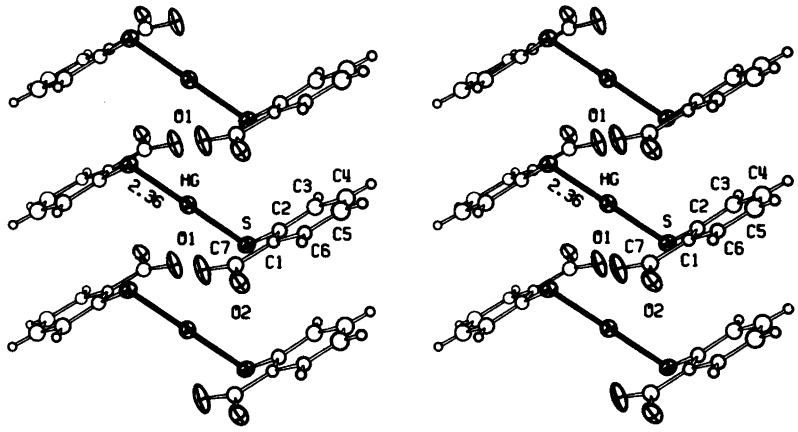

Fig. 2. BTM complexes stacked on top of each other along the monoclinic *b* axis of the unit cell. The short linear S–Hg–S bonds in the BTM complex are drawn with solid lines. The thermal ellipsoids are drawn to enclose 30% probability.

None of the carbon–carbon and carbon–oxygen distances and angles within the aromatic ring and the dioxane molecule are significantly different from their expected values.[6]

In view of the BTM dioxane structure discussed above, it seems probable that, in the mixed metal complexes formed by the ability of BTM to take up various metal ions, these additional metal ions can replace the dioxane molecule and be held between the carboxyl groups of neighbouring BTM complexes in solid state. In solution, however, intramolecular chelate bonding between the two carboxyl groups of a BTM molecule, might occur. The mode of coordination in solution will be the subject of a further study.

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