Preparation and Crystal Structure of a Binuclear Compound of Methylmercury(II) containing Bismuthiol I as a Bridging Ligand[†]

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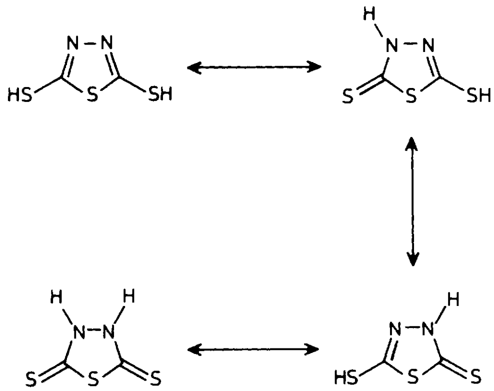
Solid [$(HgMe)_2L$] (H_2L = 2,5-dimercapto-1,3,4-thiodiazole, bismuthiol I) has been isolated and its crystal structure determined. This compound crystallizes in the tetragonal space group $I4_1/a$ (no. 88) with a = 21.600(6), c = 9.470(4) Å, and Z = 16 (R = 0.064, R' = 0.065). The ligand binds to the mercury atoms *via* its two exocyclic sulphur atoms, and secondary ligand–metal interactions are involved in the lattice structure.

Bismuthiol I (2,5-dimercapto-1,3,4-thiodiazole, H_2L) is a versatile ligand with tautomeric forms. In some of its co-ordination compounds it remains fully protonated,[1a,2a,b] while in others it is known to be monodeprotonated,[1b,c,2,3] but only one complex has been isolated for which the possibility of the ligand's being doubly deprotonated has been suggested (with HL as a possible alternative).[1c]

In this work we report the preparation and characterization of the bimetallic complex [$(HgMe)_2L$] in which bismuthiol I is doubly deprotonated.



Experimental

Synthesis.—To a stirred aqueous solution of methylmercury(II) hydroxide [obtained by stirring methylmercury(II) chloride (Ventron) for several hours with an aqueous suspension of freshly prepared silver oxide] was slowly added a H_2L solution in methanol until a metal:ligand molar ratio of about 2:1 was reached. A light yellow precipitate was formed which was filtered off, washed with water and methanol, and dried under reduced pressure, m.p. 188 °C (Found: C, 8.60; H, 1.00; N, 5.00; S, 16. 30. $C_4H_6Hg_2N_2S_3$ requires C, 8.30; H, 1.05; N, 4.85; S, 16.60%). Data obtained from Galbraith Lab. Inc., Knoxville, Tennessee, U.S.A.

Determination of the Crystal Structure.—A transparent crystal of irregular shape and maximum and minimum linear dimensions 0.25 and 0.14 mm respectively was used.

Crystal data. $C_4H_6Hg_2N_2S_3$, M_r = 579.5, tetragonal, a = 21.600(6), c = 9.470(4) Å, U = 4 418(4) $Å^3$, space group $I4_1/a$ (no. 88), Z = 16, D_c = 3.484 g cm^{-3}, $\lambda(Mo\text{-}K_\alpha)$ = 0.71 073 Å, μ = 27.2 mm^{-1}, $F(000)$ = 4 032, T = 296 K.

Data collection. Enraf-Nonius CAD-4 diffractometer, graphite monochromated Mo-K_α radiation. Cell parameters by least squares on setting angles from 25 reflections, $10.3 < \theta < 13.5$, ω—2θ scans, scan width $0.70 + 0.35 \tan\theta°$, maximum scan speed 7.6° min^{-1}. Data were collected for a triclinic unit cell related to the tetragonal cell by the transformation matrix with rows (0, 0, 1), $(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$; $-10 < h < 10$, $-17 < k < 17$, $l < 17$, $\theta_{max.} = 22°$. After transformation to space group $I4_1/a$ (origin at $\bar{1}$), the hkl range was $-16 < h < 17$, $k < 23$, $l < 10$. The mean intensity of a standard reflection 077 varied by ±4.9% over the period of data collection, 5 300 reflections measured, 1 344 unique, R_{int} = 7.1%, 725 observed with $I > 3\sigma(I)$, Lorentz polarization corrections.

Determination and refinement of the structure. The structure was solved by Patterson and Fourier methods. In the final cycles of full-matrix least-squares refinement only Hg and S atoms were anisotropic. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + 0.0018F_o^{\,2}]^{-1}$, 71 parameters refined. Correction for secondary extinction: $F_{corr.} = F_c/(1.0 - \chi F_c^{\,2}/\sin\theta)$, where χ refined to 9.0×10^{-8} in the final run; excluding unobserved reflections, R = 0.064, R' = 0.065; maximum shift/estimated standard deviation (e.s.d.) = 0.01; $\Delta\rho$ excursions between 2.0 and −1.6 e $Å^{-3}$. Scattering factors for non-H atoms were taken from ref. 4 with corrections for anomalous dispersion from ref. 5. Programs used: SHELX 76[6] and ORTEP.[7] Calculations were performed on a VAX11/780 computer.

Final atomic parameters are listed in Table 1, and interatomic

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[†] μ-1,3,4-Thiodiazole-2,5-dithiolato-*S′S″*-bis[methylmercury(II)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Positional parameters for [$(HgMe)_2L$] with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Hg(1)	0.3209(1)	0.4416(1)	0.2764(2)
Hg(2)	0.1119(1)	0.2077(1)	0.0088(2)
S(1)	0.2702(5)	0.3927(6)	0.473(1)
S(2)	0.1077(6)	0.1994(6)	0.258(1)
S(3)	0.1860(6)	0.2797(6)	0.459(1)
N(1)	0.216(1)	0.342(2)	0.233(3)
N(2)	0.181(2)	0.296(1)	0.182(3)
C(1)	0.228(2)	0.340(2)	0.379(4)
C(2)	0.161(2)	0.260(2)	0.296(4)
C(3)	0.364(2)	0.488(2)	0.113(5)
C(4)	0.117(3)	0.217(3)	−0.201(8)

Table 2. Bond distances (Å) and angles (°) for [$(HgMe)_2L$][a]

Hg(1)–S(1)	2.40(1)	S(1)–Hg(1)–C(3)	177(1)
Hg(1)–C(3)	2.07(4)	S(1)–Hg(1)–N(1)	81.1(7)
Hg(2)–S(2)	2.37(1)	C(3)–Hg(1)–N(1)	98(1)
Hg(2)–C(4)	2.00(7)	S(2)–Hg(2)–C(4)	178(1)
S(1)–C(1)	1.71(4)	Hg(1)–S(1)–C(1)	98(1)
S(2)–C(2)	1.78(4)	Hg(2)–S(2)–N(2)	69.9(7)
S(3)–C(1)	1.76(4)	Hg(2)–S(2)–C(2)	97(1)
S(3)–C(2)	1.69(4)	C(1)–S(3)–C(2)	88(1)
N(1)–N(2)	1.34(4)	N(2)–N(1)–C(1)	116(1)
N(1)–C(1)	1.41(5)	N(1)–N(2)–C(2)	108(1)
N(2)–C(2)	1.40(5)	S(1)–C(1)–S(3)	123(1)
Hg(1)–N(1)	2.76(3)[b]	S(1)–C(1)–N(1)	126(1)
Hg(1)–N(1)	3.15(3)[c]	S(3)–C(1)–N(1)	111(1)
		S(2)–C(2)–S(3)	125(1)
		S(2)–C(2)–N(2)	117(1)
		S(3)–C(2)–N(2)	118(1)

[a] Numbers in parentheses are e.s.d.s for the least significant digits. [b] Corresponds to the intermolecular contact shown in Figure 1. [c] Corresponds to the intramolecular contact shown in Figure 1.

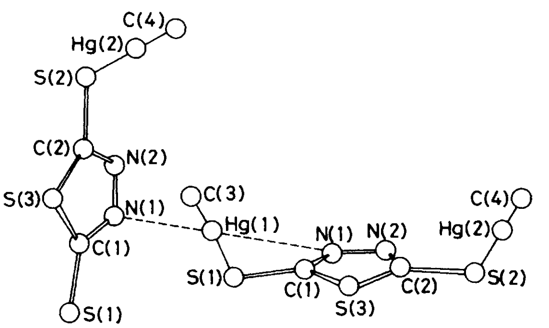

Figure 1. ORTEP drawing of [$(HgMe)_2L$], showing the atomic numbering scheme

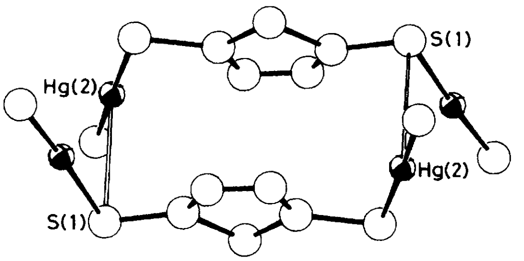

Figure 2. ORTEP drawing of a molecule pair held together by secondary S(1)–Hg(2) interactions (hollow lines)

bond distances and angles in Table 2. The irregular shape of the crystal prevented application of analytical absorption corrections. To minimize the effects of absorption, a highly redundant set of data was collected and the equivalent reflections averaged. The noisy final difference map shows that some systematic error still remained, but the structure nevertheless refined to reasonable accuracy.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Other Physicochemical Measurements.—Proton n.m.r. spectra were recorded in $(CD_3)_2SO$ solutions using a Bruker WM250 spectrometer. Conductivity was measured with a WTW LF3 conductimeter.

Results and Discussion

The compound [$(HgMe)_2L$] was insoluble in water and in all the common organic solvents except dimethylformamide (dmf) and dimethyl sulphoxide, which suggests association in the solid state. Its molar conductivity in dmf (4.8 ohm^{-1} cm^2 mol^{-1}) shows that it is not an electrolyte.[8]

Crystal Structure.—The structure of the compound is shown in Figure 1, which includes the atomic numbering scheme. The L part of the molecule is practically planar ($\chi^2 = 27$). The two Me–Hg–S groups are nearly linear [177(1) and 178(1)°] and slant towards the nitrogen atoms of the ring; the Hg–S and Hg–C bond lengths are normal.[9,10] Although the differences between the ring parameters in free H_2L[11] and in [$(HgMe)_2L$] compounds are not easily evaluated because of the large standard deviations of the interatomic distances shown in Table 2, the C(1)–S(1) and C(2)–S(2) distances both appear to increase significantly as the result of the thione $\longrightarrow$ thiol transformation during complexation, with the former of these bonds retaining rather more double-bond character than the latter.[12]

The two Hg atoms are not symmetrically located with respect to the bismuthiol ring, the torsion angle Hg(1)–S(1)–C(1)–N(1) −16(4)° being of clearly greater absolute value than Hg(2)–S(2)–C(2)–N(2) 7(3)°. Even though the angles C(1)–S(1)–Hg(1) and C(2)–S(2)–Hg(2) are quite similar (Table 2), the distance Hg(2)–N(2), 2.93(3) Å, is significantly less than the sum of the van der Waals radii (3.2 Å),[9] indicating that these atoms are involved in a secondary interaction;[13] the distance Hg(1)–N(1), 3.15(3) Å, does seem to suggest a very weak or not significant interaction between Hg(1) and N(1).

The difference between the two MeHg groups as regards their orientation with respect to the plane of the ring is important for the intermolecular interactions in the crystal. As Figure 2 shows, the molecules are arranged in the lattice in pairs whose members are related by the symmetry operation $0.5 - x$, $0.5 - y, 0.5 - z$, and whose S(1) atoms are located at a distance of just 3.35(3) Å from the Hg(2) atom of their partner. Since this distance is considerably less than the sum of the corresponding van der Waals radii (3.5 Å),[9] it may be concluded that the molecule pairs are held together by significant S(1) ⋯ Hg(2) interactions. It may be noted that these interactions are facilitated by the small Hg(2)–S(2)–C(2)–N(2) torsion angle.

Neighbouring molecule pairs are held together by strong interactions between one Hg(1) of one pair and one N(1) of the other, the Hg(1)–N(1) distance being 2.76(3) Å. The interacting molecules are related by the symmetry operation $\frac{1}{4} + x, \frac{3}{4} - y$, $\frac{1}{4} + z$ (Figures 1 and 3). This strong intermolecular interaction explains why N(1) interacts weakly or not at all with the Hg(1) atom of its own molecule (see above), and may help to increase the torsion angle Hg(1)–S(1)–C(1)–N(1).

In view of the above, the two mercury atoms of each molecule

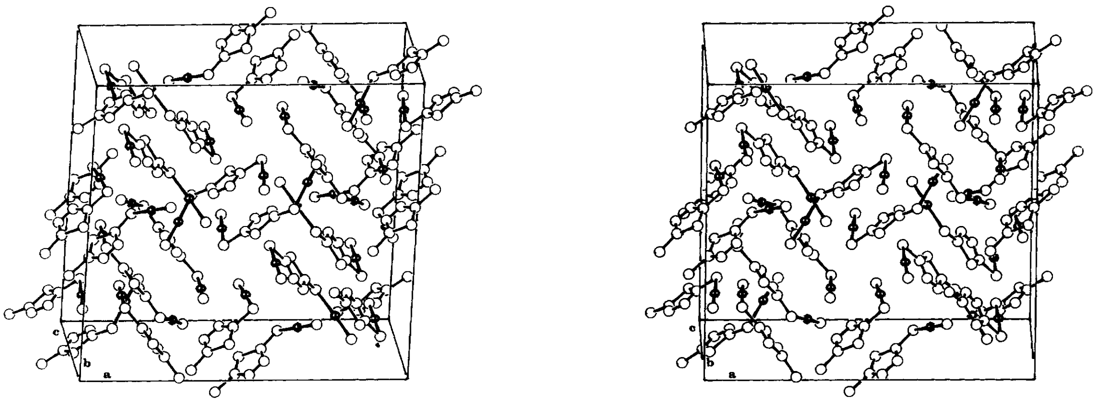

Figure 3. A stereoscopic view of the unit cell of [$(HgMe)_2L$]

have significantly different environments. As well as bonding to S(1) and the methyl carbon C(3), Hg(1) is also involved in a strong intermolecular interaction with the N(1) of another molecule and, possibly, a weak or not significant intramolecular interaction with the N(1) of its own molecule, while the bonds of Hg(2) with S(2) and the methyl carbon C(4) are complemented by a secondary intramolecular bond with N(2) and a significant intermolecular interaction with the S(1) of the partner molecule. All other intermolecular distances, such as N(2)–Hg(1) [3.24(3) Å], Hg(1)–S(1) [3.97(1) Å], or Hg(2)–S(2) [3.79(1) Å], are too large for significant interaction between the corresponding atoms.

Proton N.M.R. Spectrum.—The coupling constant $^2J(^{199}Hg-^1H)$ (190.9 Hz) is within the usual range for systems in which mercury is bonded to a thiol sulphur atom.[14] The presence of just a single methyl signal suggests that, as in the solid state, the two MeHg groups have roughly the same orientation, though an alternative explanation which cannot be ruled out would be the averaging of the signals of two magnetically non-equivalent groups as the result of their rapid interconversion.

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