Complexes of Methylmercury(II) with Dithiol Ligands: Spectroscopic and Crystallographic Studies. The Crystal Structure of *trans*-1,2-Dimercaptocyclohexanebis[methylmercury(II)],† [$Hg_2Me_2(S_2C_6H_{10})$]

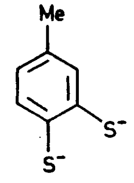
By **Nathaniel W. Alcock, Paul A. Lampe,** and **Peter Moore,*** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

Bis[methylmercury(II)] complexes have been prepared with the potentially bidentate dithiol ligands *trans*-1,2-dimercaptocyclohexane (1), 3,4-dimercaptotoluene (2), and *endo,cis*-2,3-dimercaptobicyclo[2.2.1]heptane (3). The crystal structure of [Hg_2Me_2L][L = (1)] has been determined by *X*-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, with a = 9.609(3), b = 13.428(3), c = 10.268(3), β = 112.87(2)°, and Z = 4. A total of 1 794 intensities with $I/\sigma(I) \geqslant 3.0$ were recorded at 123 K with a four-circle diffractometer and the structure refined by the least-squares method to yield a final R value of 0.037. One $Hg^{II}Me$ group is bound to one of the sulphur atoms [Hg(2)–S(2) 2.363(4) Å] with a nearly linear S(2)–Hg(2)–C(2) bond angle [177.1(5)°], whereas the second $Hg^{II}Me$ co-ordinates strongly to the other sulphur atom [Hg(1)–S(1) 2.367(4) Å] but forms a weaker bond with the first sulphur atom [Hg(1)–S(2) 2.857(3) Å] and a significantly bent S(1)–Hg(1)–C(1) bond angle [167.8(5)°]. Spectroscopic studies in solution indicate a similar type of bonding in the complexes formed by (1), (2), and (3).

It is well known that methylmercury(II) forms linear two-co-ordinate complexes, and only in rather special cases has evidence been reported for chelation with a potentially bidentate ligand. Even with rigid chelating ligands like 1,10-phenanthroline and the *NN*-diethyldithiocarbamate ion, this tendency to stay linear is apparent and results in distorted structures with almost linear co-ordination to one donor atom, and a weaker angled link to the second donor atom.[1,2] Another type of chelation has been observed in the complexes formed with the *N*-bound amino-acid ions of tyrosine, phenylalanine, and L-dopa [3-(3,4-dihydroxyphenyl)alanine]. Here evidence has been found for an 'edge-on' interaction of the mercury atom with the 1,2-carbon atoms of the phenyl ring.[3,4]

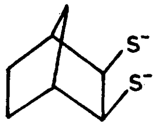
(1)

Cyclohexane-1,2-dithiolate



(2)

Toluene-3,4-dithiolate



(3)

Bicyclo[2.2.1]heptane-2,3-dithiolate

In the hope of forcing a higher co-ordination number on methylmercury(II), we have investigated the complexes formed with three potentially bidentate dithiol ligands (1), (2), and (3). Thiolate ions are known to form very strong bonds with methylmercury(II) (only selenides co-ordinate more strongly),[5] and ligands (1)—(3) were chosen because of their rigid carbon backbone, which was expected to enhance the stability of any chelate complexes they form. A previous study of the binding of methylmercury(II) to 2,3-dimercaptopropan-1-ol (British Anti Lewisite, bal) has shown that this more flexible ligand, which is used for the treatment of heavy-metal poisoning, forms bis complexes of the type [Hg_2Me_2L] (L = bal) with no evidence of enhanced stability due to chelation.[6] Ligands (1)—(3) have also been found to form bis[methylmercury(II)] complexes in this work, but a crystal structure of the complex formed by (1), and solution spectroscopic studies of all three complexes shows that chelation does occur in the bonding to at least one of the methylmercury(II) moieties.

EXPERIMENTAL

Synthesis and Study of the Bis[*methylmercury*(II)] *Complex formed with Ligand* (1).—The compound DL-*trans*-cyclohexane-1,2-dithiol was prepared by the method of Taguchi *et al.*[7] Solutions of methylmercury(II) chloride (0.251 g, 1 mmol) in methanol (50 cm³) and DL-*trans*-cyclohexane-1,2-dithiol (0.148 g, 1 mmol) with Na[OH] (0.4 g, 1 mmol) in methanol (30 cm³) were mixed and a white precipitate formed. The solvent was removed by filtration, and the solid washed with water (5 × 10 cm³). The solid was then recrystallised from acetone, and crystals of the bis[methylmercury(II)] complex suitable for crystallography were obtained by slow evaporation from aqueous acetone solution (Found: C, 16.8; H, 3.05. Calc. for $C_8H_{16}Hg_2S_2$: C, 16.65; H, 2.75%). The same complex was also prepared by mixing ligand and $Hg^{II}Me$ in a 1 : 2 mol ratio. *X*-Ray intensity data from a crystal bonded by planes {001}, {010}, and {111}, and of size 0.017 × 0.032 × 0.012 mm were collected with a Syntex $P2_1$ four-circle diffractometer in the range $3 \leqslant 2\theta \leqslant 50°$ by the θ—2θ scan technique. In an attempt to reduce crystal decomposition, the temperature was kept at 123 K with the Syntex LT-1 attachment.

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† More systematically named μ-*trans*-(cyclohexane-1,2-dithiolato)-bis[methylmercury(II)].

Five check reflections were monitored after every 50 reflections, and showed a gradual decay of *ca.* 5%. These reflections were used to scale the data to a common level. A total of 1 794 observed reflections [$I/\sigma(I) \geqslant 3.0$] were measured and corrected for absorption by the method of Alcock,[8] giving transmission factors in the range 0.096 7 to 0.021 5. The systematic extinctions $h0l$, $l \neq 2n$, $0k0$ $k \neq 2n$ were observed, indicating space group $P2_1/c$. The crystal density, measured by flotation in an aqueous cadmium tungstoborate solution, indicated four molecules per unit cell. The unit-cell dimensions and their estimated standard deviations were obtained by a least-squares fit to 15 strong reflections. For crystal data, see Table 1.

TABLE 1

Crystal data (123 K)

Colour	White	Space group	$P2_1/c$
Habit	Hexagonal block	μ/cm^{-1}	260.0
Crystal system	Monoclinic	M	576
a/Å	9.609(3)	D_m/g cm^{-3}	3.06 (295 K)
b/Å	13.428(3)	D_c/g cm^{-3}	3.14 (123 K)
c/Å	10.268(3)	Z	4
β/°	112.87(2)	N (3σ)	1 794
U/Å^3	1 220.6(6)	λ (Mo-K_α)/Å	0.710 69

Crystal Structure Solution.—The structure was solved using the heavy-atom method involving a three-dimensional Patterson synthesis to locate the positions of the mercury atoms. The remaining carbon and sulphur atoms were located in subsequent electron-density maps and refined by minimising the function $\Sigma w(|F_o| - |F_c|)^2$. The contribution from the hydrogen atoms in calculated positions was included before the final refinement with anisotropic temperature factors for mercury, sulphur, and carbon atoms which gave an R factor of 0.037. Weights $W = X*Y$ were used, where $X = 1.0$ or $[(\sin\theta)/\lambda]/0.35$ for $(\sin\theta)/\lambda < 0.35$, $Y = 1.0$ or $100/F$ for $F > 100$ or $F/40$ for $F < 40$. Atomic co-ordinates are in Table 2. Structure factors and temperature factors are listed in Supplementary Publication No. SUP 22773 (19 pp.).* Bond lengths and angles are included in Table 3. Scattering factors and anomalous dispersion corrections from ref. 9 were used, and all computing was carried out with the '*X*-ray '76' programs on a Burroughs B6700 computer.

TABLE 2

Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	x	y	z
Hg(1)	1 854.8(6)	194.9(4)	4 513.4(6)
Hg(2)	−1 478.0(6)	−1 749.1(4)	2 478.6(6)
S(1)	32(4)	1 485(3)	3 843(4)
S(2)	34(4)	−629(3)	1 822(4)
C(1)	3 751(17)	−744(14)	5 455(20)
C(2)	−2 875(19)	−2 675(12)	3 060(18)
C(3)	−1 169(15)	476(10)	1 212(14)
C(4)	−1 573(18)	1 002(11)	2 300(15)
C(5)	−2 568(19)	1 919(11)	1 675(16)
C(6)	−4 029(19)	1 595(2)	446(16)
C(7)	−3 659(19)	1 062(12)	−682(18)
C(8)	−2 620(18)	179(10)	−55(14)
H(31)	−594	934	892
H(41)	−2 180	528	2 602
H(51)	−2 814	2 256	2 375
H(52)	−2 037	2 370	1 312
H(61)	−4 662	2 166	49
H(62)	−4 594	1 155	802
H(71)	−3 161	1 512	−1 094
H(72)	−4 572	839	−1 445
H(81)	−2 383	−128	−780
H(82)	−3 188	−292	252

Synthesis of the Bis[methylmercury(II)] *Complexes formed with Ligands* (2) *and* (3).—These complexes were prepared by the method described for (1), using both 1 : 1 and 2 : 1 mol ratios of Hg^{II}Me to ligand. Both reactant ratios gave the same products of 2 : 1 stoicheiometry. The products were recrystallised from toluene [Found: C, 18.85; H, 2.15. Calc. for $C_9H_{12}Hg_2S_2$: C, 18.45; H, 2.05% for the complex with (2); Found: C, 18.75; H, 2.85. Calc. for $C_9H_{16}Hg_2S_2$: C, 18.35; H, 2.70% for the complex with (3)].

Physical Measurements.—Hydrogen-1 (90 MHz) and ^{13}C (22.63 MHz) n.m.r. spectra were obtained with a Brüker WH 90 Fourier-transform spectrometer. Chemical shifts are quoted relative to SiMe$_4$, using 1,4-dioxan as internal standard (δ = 3.56 p.p.m. for ^{1}H and δ = 67.4 p.p.m. for ^{13}C). Typically, a sweep width of 1 200 Hz (^{1}H) or 6 000 Hz (^{13}C) and 8 K data points were used for data acquisition. Estimated errors are ±0.5 Hz for coupling constants and ±0.01 p.p.m. for the chemical shifts of ^{1}H spectra, and ±1 Hz for coupling constants and ±0.04 for the chemical shifts of ^{13}C spectra. Mass spectra were recorded with an AEI MS902 instrument.

TABLE 3

Bond lengths and angles with standard deviations in parentheses

(*a*) Bond lengths (Å)

Hg(1)–S(1)	2.367(4)	C(3)–C(4)	1.50(2)
Hg(1)–S(2)	2.857(3)	C(4)–C(5)	1.54(2)
Hg(1)–C(1)	2.12(2)	C(5)–C(6)	1.54(2)
Hg(2)–S(2)	2.363(4)	C(6)–C(7)	1.52(3)
Hg(2)–C(2)	2.08(2)	C(7)–C(8)	1.52(2)
S(1)–C(4)	1.85(1)	C(8)–C(3)	1.55(2)
S(2)–C(3)	1.83(1)		

(*b*) Bond angles (°)

S(1)–Hg(1)–C(1)	167.8(5)	S(2)–C(3)–C(8)	116(1)
S(2)–Hg(1)–C(1)	107.8(5)	S(1)–C(4)–C(3)	116(1)
S(1)–Hg(1)–S(2)	84.0(1)	S(1)–C(4)–C(5)	105(1)
S(2)–Hg(2)–C(2)	177.1(5)	C(4)–C(5)–C(6)	110(1)
Hg(1)–S(1)–C(4)	105.6(5)	C(5)–C(6)–C(7)	110(1)
Hg(1)–S(2)–C(3)	94.8(4)	C(6)–C(7)–C(8)	110(1)
Hg(1)–S(2)–Hg(2)	100.6(1)	C(7)–C(8)–C(3)	113(1)
Hg(2)–S(2)–C(3)	103.7(5)	C(8)–C(3)–C(4)	110(1)
S(2)–C(3)–C(4)	108.7(9)	C(3)–C(4)–C(5)	112(1)

RESULTS AND DISCUSSION

The perspective view of the complex formed with ligand (1) is shown in Figure 1. Atom Hg(1) is co-ordinated principally through S(1) [Hg(1)–S(1) 2.367(4) Å] and has a further weaker bond with S(2) [Hg(1)–S(2) 2.857(3) Å], considerably less than the sum of the van der Waals radii (3.35 Å). The S(1)–Hg(1)–C(1) angle is significantly distorted from 180° [167.8(5)°], being bent away from the S(2)–Hg(1) bond, with S(1), S(2), Hg(1), and C(1) co-planar. The Hg(2) atom is bonded almost linearly [S(2)–Hg(2)–C(2) 177.1(5)°] to

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

S(2) [Hg(2)–S(2) 2.363(4) Å]. The atom Hg(1) also has one intermolecular interaction with $S^{I}(1)$ (Figure 2) and a further weak packing interaction with $Hg^{I}(2)$, whilst Hg(2) has interactions with both $S^{I}(1)$ and $S^{II}(1)$. Overall, these packing forces produce a three-dimensional network with each mercury within a contact distance of four sulphur atoms. These packing interactions are listed in Table 4. The Hg–C bond lengths [2.12(2) and 2.08(2) Å] are within the expected range for methylmercury(II) complexes. The cyclohexyl ring is in the chair conformation, with all bonds and angles within the expected range.

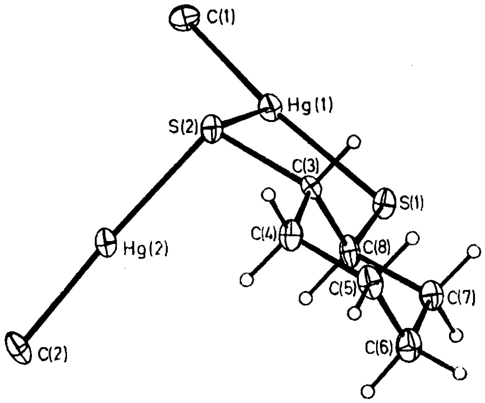


FIGURE 1 Structure of $[Hg_2Me_2L]$, L = (1)

In solution there is also evidence for chelation as shown by the $^{2}J(^{199}Hg-^{1}H)$ coupling constants in Table 5. Values of ^{2}J for the methylmercury(II) complexes formed with (1)—(3) are larger than for compounds formed with related unidentate thiolate ligands; for example we observe $^{2}J = 163.2$ Hz for the complex of (1) in pyridine solution, whereas for (mercaptocyclohexane)methylmercury(II), $^{2}J = 157.0$ Hz in the same solvent. Similarly, for the complex formed with (2), $^{2}J = 170.2$ Hz compared with 161.5 Hz in methyl(phenylmercapto)mercury(II). These increases in the values of ^{2}J for complexes of (1)—(3) agree with previous evidence of non-linear co-ordination. For example, in the complex formed by methylmercury(II) with 2,2′-bipyridine there is a 16° deviation from linearity, and ^{2}J increases by *ca.* 9 Hz.[1] The increases in ^{2}J values observed in polar solvents have also been ascribed to bending,[10] and on going from [HgMe(SCN)] to the $[HgMe(SCN)_3]^{2-}$ ion, ^{2}J increases from 205.6 to 220 Hz.[11] The reasons for the increase in the ^{2}J values have been considered previously.[1,5,10]

TABLE 4

Packing interactions between Hg and S atoms

(*a*) Distances (Å)

$Hg(1)-S^{I}(1)$	3.689(4)	$Hg(2)-S^{I}(1)$	3.499(4)
$Hg(1)-Hg^{I}(2)$	3.859(1)	$Hg(2)-S^{II}(1)$	3.295(4)

(*b*) Angles (°)

$S(1)-Hg(1)-S^{I}(1)$	98.1(1)	$S(2)-Hg(2)-S^{I}(1)$	102.3(1)
$S(1)-Hg(1)-Hg^{I}(2)$	63.25(9)	$S(2)-Hg(2)-S^{II}(1)$	86.3(1)

Roman numeral superscripts refer to the following co-ordinate transformations:

I $-x, -y, 1 - z$
II $-x, y - \frac{1}{2}, \frac{1}{2} - z$

Further evidence that one of the sulphur atoms is co-ordinated to both mercury atoms comes from the mass spectra of the complexes formed with both (1) and (3). Both spectra contain peaks with a Hg_2 isotope pattern around *m*/*e* 436 ($^{202}Hg_2{}^{32}S$) which most probably arises from chelation of the type found in the crystal structure (Figure 1).

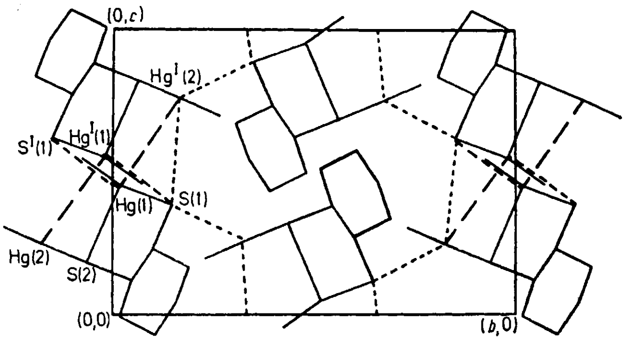


FIGURE 2 Crystal-packing diagram for $[Hg_2Me_2L]$, L = (1)

TABLE 5

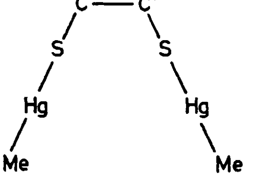
Shifts (p.p.m.) and coupling constants (Hz) of the complexes $[Hg_2Me_2L]$ formed by (1)—(3)

			^{1}J		^{2}J
L	Solvent	δ (^{13}C)	(C–Hg)	δ (^{1}H)	(H–Hg)
(1)	$[^{2}H_5]$pyridine	10.06	1 276.6	0.47	163.2
	$[^{2}H_6]$dmso			0.61	166.6
$C_6H_{11}S^{-}$ [a]	$[^{2}H_5]$pyridine				157.0 [b]
(2)	$[^{2}H_8]$toluene	12.02	1 247.2	0.72	170.2
	$[^{2}H_6]$dmso			0.66	178.0
PhS^{-}	Dichloromethane				161.5 [c]
(3)	$[^{2}H_2]$dichloromethane	10.05	1 216.3	0.82	163.0

dmso = Dimethyl sulphoxide.

[a] Cyclohexyl mercaptate. [b] L. F. Sytoma and R. J. Kline, *J. Organometallic Chem.*, 1973, **54**, 15. [c] R. D. Bach and A. T. Weibel, *J. Amer. Chem. Soc.*, 1976, **98**, 6241.

Conclusions.—Whereas flexible dithiols such as bal do not chelate to methylmercury(II) but give binuclear complexes of type (4),[6] those dithiols with sterically constrained carbon backbones such as (1)—(3) do chelate in a distorted fashion as shown in (5). The distorted chelation found in the complex of methylmercury(II) with 2,2′-bipyridine (bipy) [1] results in an increase in the stability from 5.3 × 10^{4} with pyridine to 5.6 × 10^{5} dm^{3} mol^{-1} with bipy.[12] It is to be expected, therefore,



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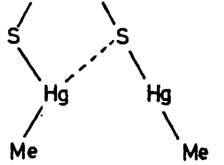

(5)

that the complexes of methylmercury(II) formed with (1)—(3) are more stable than those of bal and similar flexible dithiol ligands.

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