

Reactivity of the Tripodal Trithiol 1,1,1-Tris-(mercaptomethyl)ethane toward Methyl- and Ethyl-mercury Halides *

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The reaction of the tripod-like trithiol $\text{MeC}(\text{CH}_2\text{SH})_3$ with MeHgI or EtHgCl in organic solutions, in presence of a base such as pyridine or triethylamine, allows the isolation of the trimetallic derivatives $\text{MeC}(\text{CH}_2\text{SHgR})_3$ ($\text{R} = \text{Me}$ or Et). An X-ray structure determination for the methylmercury complex has been carried out. Crystal data: monoclinic, space group $P2_1/a$, $a = 11.892(9)$, $b = 18.621(2)$, $c = 13.932(2)$ Å, $\beta = 90.95(3)^\circ$ and $Z = 8$. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by least squares to a conventional R value of 0.036. The complex can be essentially described as an aggregate of three, virtually independent, linear two-co-ordinated methylmercury thiolates. However ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra have shown that the trend of the reaction of methylmercury iodide with the trithiol, in pyridine solution, is quite different from that of the corresponding reaction with a related monothiol such as propane-1-thiol. This discrepancy has been ascribed to the potential chelating ability of the tripodal thiol, which should allow the formation of intermediate chelated species, in which the metal atom has co-ordination numbers greater than two.

Organomercurials, namely methyl- and aryl-mercury compounds, are the most deleterious mercury contaminant agents in environmental water.¹ Their extremely high affinity for thiols, which renders them very toxic to living organisms, has been variously investigated.²⁻⁶ Recently it has been found that bacteria are capable of neutralizing organomercurials by an enzymatic process. This essentially consists of the uptake of the contaminant agent, the cleavage of the mercury-carbon bond and the reduction of the mercury(II) ion to mercury metal. On the basis of mechanistic analyses, it has been suggested that the carbon-mercury bond cleavage step could involve the co-ordination of the organomercurial by more than one cysteinic group, in the enzyme active site.⁷

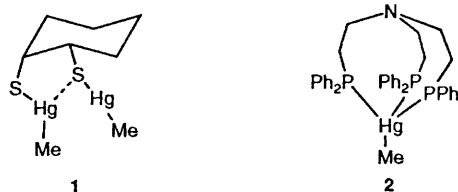
The methylmercury ion is known to link to co-ordinating groups to form only two-co-ordinate mercury(II) complexes, even if, in some cases, secondary interactions at the metal centre have been ascertained.⁸ Concerning thiolate ligands such interactions have been documented by X-ray structural studies on the complex *trans*- $[(\text{HgMe})_2(\text{S}_2\text{C}_6\text{H}_{10})]$ **1**.⁹ Moreover the chelation of MeHg^{II} by some dithiolates has been suggested in solution on the basis of NMR and potentiometric investigations.^{3,6}

We have recently found that the tripod-like ligand tris(2-diphenylphosphinoethyl)amine is capable of forming a pseudo-tetrahedral species **2** with MeHg^{II} both in the solid state and in solution.¹⁰

We report here our investigations on the interaction of the trithiol 1,1,1-tris(mercaptomethyl)ethane with MeHg^{II} and EtHg^{II} . The related ligand 1,1,1-tris(sulfidomethyl)ethane has been found to form only few complexes, which are either mono-¹¹ or tri-metallic.^{12,13} In the latter each sulfur atom bridges two metal centres to form an overall 'adamantane-like' geometry.

Experimental

The operations were carried out under purified dry nitrogen. A



literature route was used for the preparation of $\text{MeC}(\text{CH}_2\text{SH})_3$.¹⁴ The reagents MeHgI and EtHgCl were purchased from Strem Chemicals and used without further purification. Reagent grade propane-1-thiol (Fluka) was also used as supplied.

Syntheses.— $\text{MeC}(\text{CH}_2\text{SHgMe})_3$ **3**. (i) A solution of methylmercury iodide (343 mg, 1 mmol) in CH_2Cl_2 (30 cm^3) was treated with a solution of the trithiol (56 mg, 0.33 mmol) in 20 cm^3 of the same solvent. Triethylamine (101 mg, 1 mmol) was added and the solution was stirred for 15 min, at room temperature. After addition of ethanol (30 cm^3) and solvent evaporation in a current of nitrogen, colourless crystals precipitated. These were washed with ethanol, then with *n*-hexane and dried in a current of nitrogen. Yield 246 mg (91%) (Found: C, 11.75; H, 2.15; S, 11.7. Calc. for $\text{C}_8\text{H}_{18}\text{Hg}_3\text{S}_3$: C, 11.85; H, 2.25; S, 11.85%). NMR (295 K): ^1H (CD_2Cl_2), δ 0.80 (s with satellites, HgCH_3 , 9 H, $^2J_{\text{HgH}}$ 156 Hz), 1.06 (s, CH_3C , 3 H) and 3.04 (s, CH_2S , 6 H); ($\text{C}_5\text{D}_5\text{N}$), δ 0.76 (s, with satellites, HgCH_3 , 9 H, $^2J_{\text{HgH}}$ 160 Hz), 1.39 (s, CH_3C , 3 H) and 3.36 (s, CH_2S , 6 H); $^{13}\text{C}\{-^1\text{H}\}$ ($\text{C}_5\text{D}_5\text{N}$), δ 12.40 (HgCH_3), 22.52 (CH_3C), 34.56 (CH_2) and 41.40 (CH_3C).

(ii) Alternatively the complex can be prepared in equally high yield (85%), by treating MeHgI (1 mmol) with the trithiol (0.33 mmol), in pyridine (4 cm^3), at room temperature. Addition of ethanol (20 cm^3) leads to the precipitation of a yellowish material. By washing repeatedly with portions of acetone (5 cm^3) $[\text{C}_5\text{H}_5\text{NH}]\text{I}$ is eliminated and the virtually pure complex can be isolated.

$\text{MeC}(\text{CH}_2\text{SHgEt})_3$ **4**. The complex was prepared analogously

* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii-xxviii.

Table 1 Crystal data and data collection details for MeC(CH₂-SHgMe)₃ 3

Formula	C ₈ H ₁₈ Hg ₃ S ₃
<i>M</i>	812.19
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> /Å	11.892(9)
<i>b</i> /Å	18.621(2)
<i>c</i> /Å	13.932(2)
β/°	90.95(3)
<i>U</i> /Å ³	3084.7
<i>Z</i>	8
<i>D</i> _c /g cm ⁻³	3.497
Colour	White
Habit	Parallelepiped
Dimensions/mm	0.02 × 0.10 × 0.40
Linear absorption coefficient/cm ⁻¹	301.39
Absorption corrections range	0.487–1.942
Radiation, λ(Mo-Kα)	0.7107
Monochromator	Graphite crystal
Method	ω-2θ scan technique
Scan speed/° min ⁻¹	8.24
Scan width/°	0.70 + 0.35tanθ
Background time	Half scan time
Standards	3 every 120 min
Maximum deviation of standards	0.30
2θ Limits/°	5 ≤ 2θ ≤ 50
Total number of data	5906
Number of data with <i>I</i> ≥ 3σ(<i>I</i>)	2694
Final number of variables	173
Final max. and min. features in Δ <i>F</i> / <i>e</i> Å ⁻³	+1.5, -1.5
<i>S</i> (goodness of fit)	2.89

Table 2 Final atomic parameters (× 10⁴) of MeC(CH₂SHgMe)₃ 3

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Hg(1)	3995(1)	3049(1)	4605(1)
Hg(2)	1283(1)	3968(1)	4981(1)
Hg(3)	637(1)	3291(1)	8222(1)
Hg(4)	-1473(1)	1967(1)	-518(1)
Hg(5)	1250(1)	894(1)	-22(1)
Hg(6)	1917(1)	1510(1)	3197(1)
S(1)	3874(5)	1812(3)	4967(5)
S(2)	2143(5)	3298(3)	6227(5)
S(3)	926(6)	2042(3)	8180(5)
S(4)	-1351(6)	3169(3)	1(6)
S(5)	295(6)	1561(3)	1164(5)
S(6)	1652(6)	2762(3)	3217(5)
C(1)	1778(21)	1096(13)	6302(19)
C(2)	2308(17)	1822(11)	6533(15)
C(3)	3574(19)	1831(12)	6280(17)
C(4)	1613(17)	2407(11)	6005(16)
C(5)	2285(19)	1956(12)	7608(17)
C(6)	4208(28)	4129(18)	4217(27)
C(7)	784(20)	4715(13)	3921(19)
C(8)	281(23)	4390(14)	8310(22)
C(9)	846(23)	3754(14)	1363(22)
C(10)	266(17)	3027(11)	1557(15)
C(11)	-987(21)	3077(13)	1293(19)
C(12)	902(18)	2451(11)	1008(16)
C(13)	275(19)	2881(12)	2612(17)
C(14)	-1631(27)	987(17)	-1264(25)
C(15)	1882(23)	168(14)	-1032(22)
C(16)	2237(26)	385(16)	3257(25)

to the methylmercury derivative, by using EtHgCl in place of MeHgI. Yield 94% (Found: C, 15.5; H, 2.1; S, 11.25. Calc. for C₁₁H₂₄Hg₃S₃: C, 15.60; H, 2.00; S, 11.35%). NMR (295 K): ¹H (CD₂Cl₂), δ 1.06 (s, CH₃C, 3 H), 1.30–1.70 (m with satellites, CH₃CH₂Hg, 15 H) and 3.02 (s, CH₂S, 6 H); (C₅D₅N), δ 1.15–1.55 (m with satellites, CH₃CH₂Hg, 15 H) and 1.28 (s, CH₂S,

6 H); ¹³C-{¹H} (C₅D₅N), δ 14.54 (CH₃CH₂), 22.62 (CH₃C), 28.40 (CH₂Hg), 34.67 (CH₂S) and 41.89 (CH₃C).

PrSHgMe 5. To a solution of MeHgI (432 mg, 1 mmol) and NaOH (40 mg) in MeOH (20 cm³) was added PrSH (76 mg, 1 mmol). After stirring for 15 min, water (20 cm³) was added and the product was extracted with three 20 cm³ portions of pentane. Removal of the solvent afforded 276 mg (95%) of the product as a clear oil (Found: C, 16.6; H, 3.55; S, 11.05. Calc. for C₄H₁₀HgS: C, 16.50; H, 3.45; S, 11.20%). NMR (295 K): ¹H (CD₂Cl₂), δ 0.77 (s with satellites, CH₃Hg, 3 H, ²*J*_{HgH} 152), 0.99 (t, CH₃CH₂, 3 H, ²*J*_{HH} 7 Hz), 1.66 (m, CH₃CH₂, 2 H) and 2.95 (m, CH₂S, 2 H); (C₅D₅N), δ 0.70 (s with satellites, CH₃Hg, 3 H, ²*J*_{HgH} 155), 0.98 (t, CH₃CH₂, 3 H, ²*J*_{HH} 7 Hz), 1.72 (m, CH₃CH₂, 2 H) and 3.06 (m, CH₂S, 2 H); ¹³C-{¹H} (C₅D₅N), δ 12.33 (CH₃Hg), 13.76 (CH₃CH₂), 29.82 (CH₃CH₂) and 30.91 (CH₂S).

NMR Spectra (295 K) of MeC(CH₂SH)₃.—¹H (CD₂Cl₂), δ 1.00 (s, CH₃C, 3 H), 1.27 (t, SH, 3 H, ³*J*_{HH} 8) and 2.60 (d, CH₂S, 6 H, ³*J*_{HH} 8 Hz); (C₅D₅N), δ 1.00 (s, CH₃C, 3 H), 2.11 (d, SH, 3 H, ³*J*_{HH} 8) and 2.68 (d, CH₂S, 6 H, ³*J*_{HH} 8 Hz); ¹³C-{¹H} (C₅D₅N), δ 21.35 (CH₃C), 31.68 (CH₂S) and 40.0 (CH₃C).

Physical Measurements.—Proton and ¹³C-{¹H} NMR spectra were recorded on a Bruker ACP200 spectrometer at 200.13 and 50.33 MHz, respectively. Chemical shifts are relative to internal SiMe₄, with downfield values reported as positive. The trithiol and propane-1-thiol concentrations of the [H₅]pyridine solutions used in the ¹³C NMR measurements were 0.15 and 0.55 mol dm⁻³, respectively. Distortionless enhancement by polarization transfer (DEPT) experiments were performed to assign the ¹³C resonances.

Single-crystal Structure Determination of MeC(CH₂-SHgMe)₃.—Diffraction data were collected at room temperature on an Enraf-Nonius automatic diffractometer. Unit-cell parameters were determined by least-squares refinement of the setting angles of 25 carefully centred reflections. Crystal data collection details are given in Table 1. The intensities *I* as well as the standard deviations σ(*I*) were calculated as described elsewhere, by using the value of 0.03 for the instability factor *k*.¹⁵ Owing to the intensity decay during the collection, the observed intensities were appropriately rescaled. After rescaling the intensities were corrected for Lorentz-polarization and for absorption effects (empirical methods).¹⁶

All the calculations were carried out on a HP 486/25 PC, using the SHELX 76¹⁷ and PLUTO¹⁸ programs. Atomic scattering factors were taken from ref. 19. Both Δ*f*' and Δ*f*" components of anomalous dispersion were included for all atoms.²⁰ Patterson and Fourier maps enabled the location of all the atoms. Full-matrix least-squares refinements were carried out with anisotropic thermal parameters assigned to mercury and sulfur atoms. During the refinement the function Σ*w*(|*F*_o - |*F*_c||)² was minimized, the weights *w* being defined as *w* = 1/σ²(*F*_o). The refinements converged at *R* = *R*' = 0.036. Final positional parameters are reported in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre, comprises H-atom coordinates and thermal parameters.

Results and Discussion

The trithiol MeC(CH₂SH)₃ does not react with MeHgI in organic solvents such as acetone or dichloromethane (the reaction is easily monitored by ¹H NMR). However in the presence of triethylamine a rapid reaction occurs which allows the isolation of colourless crystals of composition MeC(CH₂-SHgMe)₃. When the solvent is pyridine (py), the basicity of the solvent itself is sufficient to promote the reaction. We were able to recover only the above solid product independent of the metal to ligand ratio used, even in the presence of large cations.

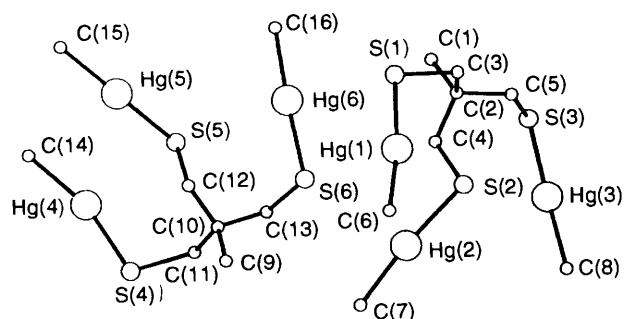


Fig. 1 Perspective view (drawn with PLUTO) of the contents of the asymmetric unit (molecules A and B) of $\text{MeC}(\text{CH}_2\text{SHgMe})_3$ **3**

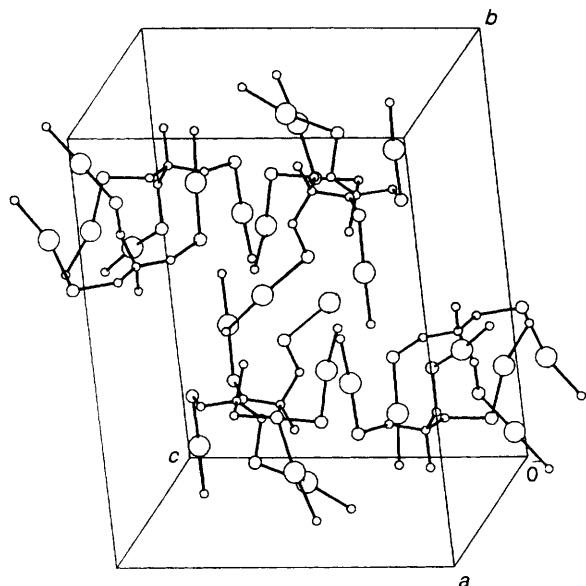


Fig. 2 Packing diagram of $\text{MeC}(\text{CH}_2\text{SHgMe})_3$ **3** within the crystal

The corresponding ethylmercury(II) derivative was prepared by an analogous reaction. The complexes appear air stable; they are sparingly soluble in dichloromethane, but more so in pyridine.

The molecular structure of **3** consists of $\text{MeC}(\text{CH}_2\text{SHgMe})_3$ molecules and a perspective view is given in Fig. 1, Fig. 2 shows the packing diagram and bond distances and angles are given in Table 3. In the asymmetric unit there are two independent trimetallic molecules of $\text{MeC}(\text{CH}_2\text{SHgMe})_3$ (A and B), in which the tripod ligand $[\text{MeC}(\text{CH}_2\text{S})_3]^{3-}$ links three HgMe^+ ions, in very similar conformations. Each HgMe group is linearly coordinated to the sulfur atoms of the thiolate ligand, the S–Hg–Me bond angles ranging from $168.2(9)^\circ$ to $176.1(8)^\circ$. The distances between the mercury atoms, all greater than 3.70 \AA , preclude any metal–metal interaction. The mercury centres in both molecules are essentially two-co-ordinated, weak secondary interactions appearing to be relatively insignificant. It is known that the concept of secondary bonding in organomercurials is recurring with a large range of weak interactions.^{8,9,21} In this instance, if we take the value of 3.3 \AA as the sum of the van der Waals radii of mercury and sulfur,²² there are only three contacts just below this limit: $\text{Hg}(1) \cdots \text{S}(2^I)$ (3.22 \AA), $\text{Hg}(2) \cdots \text{S}(1^{II})$ (3.21 \AA) and $\text{Hg}(4) \cdots \text{S}(5^I)$ (3.21 \AA) where the superscripts I and II refer to the symmetry operations x, y, z and $x - \frac{1}{2}, y + \frac{1}{2}, z$, respectively. The methyl groups are not involved in any important intermolecular contacts.

The Hg–S primary bond distances, averaging $2.359(2) \text{ \AA}$, appear somewhat shorter than the sum of covalent radii (2.51 \AA); they are close however to the value found for typical inorganic mercury sulfides (2.36 \AA).²³ Within the HgMe

Table 3 Bond distances (\AA) and angles ($^\circ$) for $\text{MeC}(\text{CH}_2\text{SHgMe})_3$ **3**

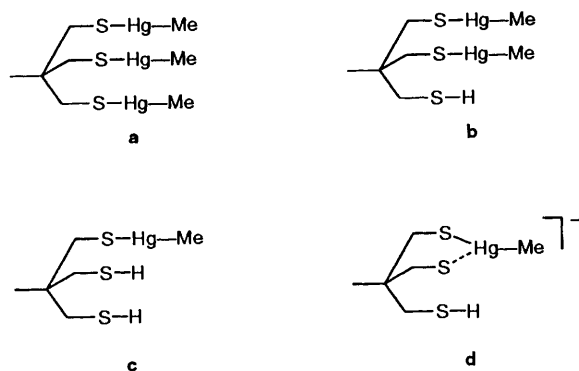
Molecule A		Molecule B	
Hg(1)–S(1)	2.363(6)	Hg(4)–S(4)	2.357(7)
Hg(2)–S(2)	2.358(6)	Hg(5)–S(5)	2.371(7)
Hg(3)–S(3)	2.351(6)	Hg(6)–S(6)	2.353(6)
Hg(1)–C(6)	2.10(3)	Hg(4)–C(14)	2.11(3)
Hg(2)–C(7)	2.11(2)	Hg(5)–C(15)	2.10(3)
Hg(3)–C(8)	2.09(3)	Hg(6)–C(16)	2.13(3)
S(1)–C(3)	1.87(2)	S(4)–C(11)	1.85(3)
S(2)–C(4)	1.80(2)	S(5)–C(12)	1.82(2)
S(3)–C(5)	1.82(2)	S(6)–C(13)	1.84(2)
C(1)–C(2)	1.52(3)	C(9)–C(10)	1.54(3)
C(2)–C(3)	1.55(3)	C(10)–C(11)	1.53(3)
C(2)–C(4)	1.55(3)	C(10)–C(12)	1.53(3)
C(2)–C(5)	1.52(3)	C(10)–C(13)	1.49(3)
S(1)–Hg(1)–C(6)	175.6(10)	S(4)–Hg(4)–C(14)	168.2(9)
S(2)–Hg(2)–C(7)	168.3(7)	S(5)–Hg(5)–C(15)	170.1(8)
S(3)–Hg(3)–C(8)	176.1(8)	S(6)–Hg(6)–C(16)	176.1(9)
Hg(1)–S(1)–C(3)	101.7(7)	Hg(4)–S(4)–C(11)	102.8(8)
Hg(2)–S(2)–C(4)	102.4(7)	Hg(5)–S(5)–C(12)	101.5(8)
Hg(3)–S(3)–C(5)	103.2(8)	Hg(6)–S(6)–C(13)	103.4(8)
C(1)–C(2)–C(3)	111.2(17)	C(9)–C(10)–C(11)	109.9(18)
C(1)–C(2)–C(4)	108.0(17)	C(9)–C(10)–C(12)	107.6(18)
C(1)–C(2)–C(5)	109.9(18)	C(9)–C(10)–C(13)	109.6(19)
C(3)–C(2)–C(4)	113.4(17)	C(11)–C(10)–C(12)	114.2(18)
C(3)–C(2)–C(5)	104.8(17)	C(11)–C(10)–C(13)	103.8(18)
C(4)–C(2)–C(5)	109.5(17)	C(12)–C(10)–C(13)	111.7(18)
C(2)–C(3)–S(1)	115.0(15)	C(10)–C(11)–S(4)	116.7(17)
C(2)–C(4)–S(2)	112.7(14)	C(10)–C(12)–S(5)	112.3(15)
C(2)–C(5)–S(3)	118.4(15)	C(10)–C(13)–S(6)	117.6(16)

moieties the Hg–C bond distances [av. $2.106(5) \text{ \AA}$] are in good agreement with the values reported for a variety of methylmercury compounds.²⁴ The values of the Hg–S–C angles [$101.5(8)$ – $103.4(8)^\circ$] fall in the range of values reported in the literature.²⁵ Concerning the trithiolate ligand $\{\text{MeC}(\text{CH}_2\text{S})_3\}^{3-}$, no particular features are envisaged, and all the bond distances and angles appear as expected. Only three X-ray crystal structures have been previously reported for this ligand, a monomeric species, in which the ligand imposes a facial geometry on the metal ion ($M = \text{Re}$),¹¹ and two trimetallic complexes, where the thiolate ligand, acting as a 12-electron donor, bridges a triangle of three non-bonded metals ($M = \text{Ir}^{12}$ or Pt^{13}).

The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR data of the complexes are reported in the Experimental section. The remarkably low value of the $^2J_{\text{HgH}}$ coupling constant (156 and 160 Hz , in dichloromethane and pyridine, respectively) of the tris(methylmercury) complex is consistent with those previously reported for analogous linear RSHgMe derivatives^{3,26} ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}$ or CPh_3) and the increase of $^2J_{\text{HgH}}$ values in polar solvents has been noted previously.^{4,9} As reported elsewhere for other thiolate–mercury derivatives,³ no mercury coupling associated with the SR moiety is observed, due to the rapid exchange of the mercaptide ligands. Accordingly, the ^1H NMR spectra of pyridine solutions of mixtures of $\text{MeC}(\text{CH}_2\text{SHgMe})_3$ and MeHgI show single resonances for the MeHg protons, with chemical shifts and $^2J_{\text{HgH}}$ coupling constants which are averages of the chemical shifts and the coupling constants of the individual compounds. In addition, the chemical shifts of the thiolate ligand are not affected by the presence of free MeHgI , so excluding any further co-ordination.

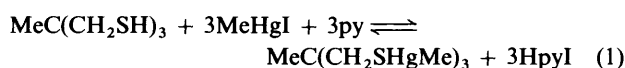
Even if only the trimetallic species **a** (Scheme 1) could be isolated as a solid, the species **b** and **c** can be likely assumed to be present in pyridine solution, depending on the molar ratio of MeHgI to $\text{MeC}(\text{CH}_2\text{SH})_3$. An even more intriguing question concerns the presence in solution of chelated species such as **d**.

Of course these species cannot be directly characterized by NMR spectroscopy due to the fast-exchange situation. In the



Scheme 1

attempt to follow the complexation of the methylmercury by the trithiol we have measured the $^{13}\text{C}\{-^1\text{H}\}$ chemical shifts of the ligand carbon atoms, in pyridine solution, as a function of the $\text{MeHgI}:\text{MeC}(\text{CH}_2\text{SH})_3$ molar ratio. In particular we have considered the chemical shift of the CH_2S carbon atoms which are most affected upon complexation. Assuming that (i) $\text{MeC}(\text{CH}_2\text{SHgMe})_3$ is the only complex species formed in solution according to reaction (1), and (ii) the changes in the



chemical shift of each CH_2S carbon of the ligand molecule are primarily due to the formation of the Hg-S bond, then the observed chemical shift δ_{obs} of the exchange-averaged resonances should be given by expression (2), where δ_{obs} is the

$$\delta_{\text{obs}} = p_f \delta_f + (1 - p_f) \delta_c \quad (2)$$

weighted average of the chemical shifts of the species present in solution, δ_f and δ_c are the chemical shifts and p_f and $(1 - p_f)$ the mole fractions of free $\text{MeC}(\text{CH}_2\text{SH})_3$ and of the complex $\text{MeC}(\text{CH}_2\text{SHgMe})_3$, respectively.²⁷ If the equilibrium of the reaction (1) lies far to the right, then the dashed line in Fig. 3 represents the expected trend of the chemical shift; on the other hand if the equilibrium does not lie so far toward product formation a smooth curve beneath the dashed line is expected which approaches the dashed line only at molar ratio > 3 . If mono- and bi-metallic species **b** and **c** are also formed in solution, below the equivalence point, a similar situation would be expected. The substitution of a thiol hydrogen by methylmercury will produce a major deshielding of the contiguous CH_2S group and a minor effect upon the two farther located groups. In complexes **b** and **c**, the ^{13}C chemical shift of CH_2SH will be slightly higher than δ_f , whereas that of CH_2SHgMe will be slightly lower than δ_c . By assuming these two effects are comparable, the curve of the averaged chemical shifts might be near to the predicted dashed line. On the other hand, if a chelated species such as **d** is formed, this is expected to give a higher contribution to the averaged chemical shift.

Measurements show that the CH_2S is deshielded continuously (as shown in Fig. 3) upon increasing the metal-to-ligand ratio, the chemical shift reaching, at a ratio of 2.95:1, a value slightly higher than δ_c . Unfortunately it was not possible to record spectra for ratios higher than 3:1 due to the precipitation of the complex. The experimental values in the ratio interval 0–3:1 lie above but relatively near to the dashed line, the highest deviation being *ca.* 0.5 ppm, at a ratio close to 1.5.

The most straightforward interpretation of this trend is to assume that intermediate species are formed, in addition to the trimetallic one, with the equilibrium of the overall reaction lying well to the right. However information from the ^1H NMR spectra, recorded on the same solutions, appear to contradict this interpretation. The value of the averaged coupling constant

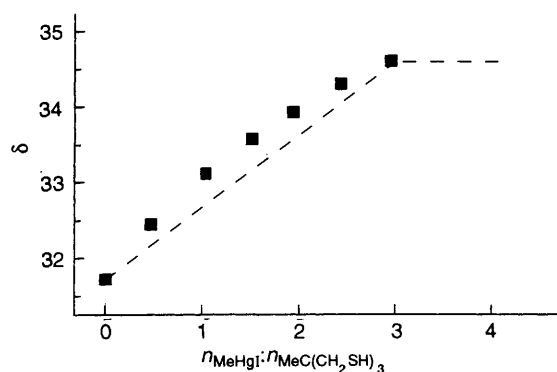


Fig. 3 Plot of the chemical shifts of the CH_2S carbons of $\text{MeC}(\text{CH}_2\text{SHgMe})_3$ versus the methylmercury:trithiol molar ratio. The dashed line represents the expected chemical shifts assuming complete conversion to products according to reaction (1)

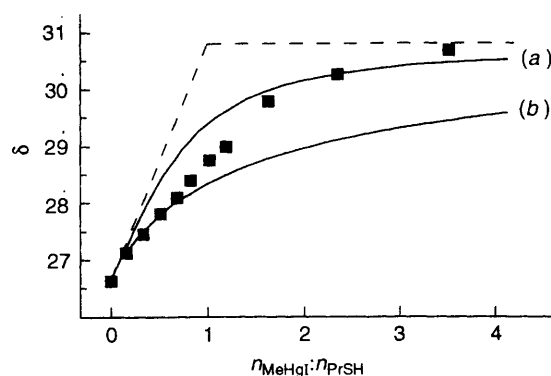
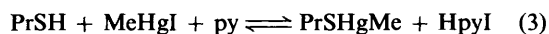


Fig. 4 Plot of the chemical shifts of the CH_2S carbon of PrSHgMe versus the methylmercury:propane-1-thiol molar ratio. The dashed line represents the expected chemical shifts assuming complete conversion to products according to reaction (3). Solid lines represent the chemical shifts calculated assuming that the equilibrium constant of reaction (3) is 4 (a) or 0.5 (b)

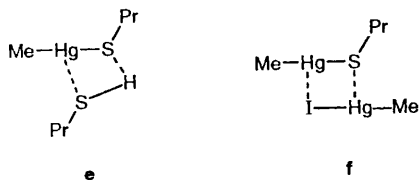
$^2J_{\text{HgH}}$, which is, at a ratio of 0.46:1, close to that of $\text{MeC}(\text{CH}_2\text{SHgMe})_3$ (162 vs. 160 Hz), becomes progressively larger as the ratio increases. At a ratio of 2.95:1, where the predominant species should be the trimetallic complex, the value of $^2J_{\text{HgH}}$ is 176 Hz. This finding suggests that increasing amounts of MeHgI ($^2J_{\text{HgH}} = 202$ Hz) are present in solution when the ratio increases and therefore that the complexation of the methylmercury ion is incomplete. A contribution to the averaged $^2J_{\text{HgH}}$ from other complexes having higher individual $^2J_{\text{HgH}}$ values (*i.e.* thiolate–methylmercury species with coordination numbers > 2 at the metal centre) cannot be excluded.

In the hope of clarifying this matter we performed analogous measurements using an aliphatic monothiol, propane-1-thiol, in place of the trithiol. The chemical shift of the CH_2S carbon versus the $\text{MeHgI}:\text{PrSH}$ molar ratio is shown in Fig. 4. In this case the titration points clearly remain under the dashed line (calculated assuming quantitative formation of the methylmercury thiolate), reaching it only at a molar ratio of *ca.* 3:1. Such a trend is approximately what one should expect if the equilibrium of reaction (3) does not lie far to the right. Likewise



the values of the averaged $^2J_{\text{HgH}}$ coupling constants in the corresponding ^1H NMR spectra are consistent with an equilibrium situation: the value of $^2J_{\text{HgH}}$ changes from 165 Hz, at a ratio of 0.13:1, to 171 Hz at a ratio of 1.0:1 ($^2J_{\text{HgH}}$ of PrSHgMe is 155 Hz). However an attempt to determine the equilibrium constant for reaction (3), using the data of the titration curve, was unsuccessful. This failure is probably due to the fact that also in this apparently even simpler case the

equilibrium is complicated by the formation of intermediates, whose presence cannot be neglected. These species could be four-centred intermediates such as **e** and **f** of the type already proposed by Bach and Weibel³ to explain the anion exchange mechanism in methylmercury thiolates.



It is worth stressing the quite different trend of the two titration curves. Thus the trithiol in this reaction cannot be regarded as a mere combination of three monothiolates, even though the only isolated species is essentially an aggregate of three virtually independent thiolates. We cannot justify invoking different acidities of the two thiols to account for their different reaction patterns: in fact, due to their similar aliphatic backbone, all the SH groups of the compounds should exhibit comparable acidity. On the contrary the potential ability of the trithiol to give rise to chelated intermediate species, with a metal:ligand ratio of 1 or 2, can reasonably explain the experimental results. In this framework, at the equivalence point of the reaction between the trithiol and MeHgI, the value of the CH₂S-averaged ¹³C chemical shift should be near to δ_c, due to the presence in solution of the trimetallic complex, methylmercury iodide and mono- or dimetallic chelated species, having chemical shifts higher than δ_c and ²J_{HgH} constants greater than 160 Hz.

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