

Homoleptic Cyclohexanethiolato Complexes of Mercury(II)†

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The complexes $\text{Hg}(\text{SR})_2$ **1** and $[\text{NR}'_4][\text{Hg}(\text{SR})_3]$ ($\text{R}' = \text{Et}$ **2** or Me **3**) have been obtained from the reaction of HgCl_2 with NaSR in acetonitrile, with $[\text{NR}'_4]\text{Cl}$ also present for complexes **2** and **3**; SR is cyclohexanethiolate. Complex **1** has a polymeric structure consisting of rather bent $\text{Hg}(\text{SR})_2$ units [$\text{Hg}-\text{S}$ 2.372(2) and 2.374(2) Å, $\text{S}-\text{Hg}-\text{S}$ 160.4(1)°] linked together by weaker $\text{Hg}-\text{S}$ bonds [3.004(2) and 2.959(2) Å]; the Hg atoms have highly distorted tetrahedral co-ordination and each thiolate acts as a very asymmetric bridge between two Hg atoms. Complex **2** contains Hg atoms in a distorted trigonal-planar co-ordination environment, the monomeric anions being well separated from each other. The distortion is mostly in-plane, producing one angle considerably less than, and one considerably greater than, the ideal 120°; the largest angle lies opposite the longest $\text{Hg}-\text{S}$ bond, and the smallest angle opposite the shortest $\text{Hg}-\text{S}$ bond. Proton and ^{13}C NMR, far-IR and Raman, and low-energy UV spectroscopic data are discussed. The UV data afford additional support for the proposal of a trigonal-planar $[\text{Hg}(\text{CysS})_3]^-$ co-ordination environment for the metal receptor site of the MerR metalloregulatory protein. A correlation of co-ordination geometry, $\text{Hg}-\text{S}$ bond lengths, and $\text{Hg}-\text{S}$ stretching frequencies is developed for these and other homoleptic thiolate complexes of mercury.

The chemistry of thiolate complexes of zinc, cadmium and mercury has been extensively studied. The particular affinity of thiols for mercury has been known for a long time, and is well expressed in the alternative name of mercaptans for this class of compounds. Thiolate and related complexes play an important part in the biological chemistry of these metals; the co-ordination of cysteine residues of metallothioneins and metalloregulatory protein to zinc, cadmium^{1,2} and mercury³⁻⁵ is of particular interest in current research.

The co-ordination geometry of thiolate complexes of the Group 12 metals is rich and varied. While tetrahedral four-fold co-ordination predominates for Zn and Cd, linear two-fold and trigonal-planar three-fold co-ordination are also very important for Hg.⁶ All three geometries have been proposed for mercury atoms in biological systems.^{4,5,7} It is far from clear what factors determine the co-ordination of mercury in thiolate (or other) complexes. Even if we restrict our consideration to homoleptic complexes of general formula $[\text{Hg}(\text{SR})_n]^x$ there are unexpected variations in observed structures. Depending on the thiolate: mercury stoichiometric ratio n and the presence of other functional groups on the thiolate substituent R , complexes may be overall neutral, cationic or anionic.

For bis(thiolato)mercury(II) complexes of general formula $\text{Hg}(\text{SR})_2$ both linearly co-ordinated monomeric^{3,8,9} and distorted tetrahedrally co-ordinated polymeric⁹⁻¹¹ structures have been found, and there is no obvious relationship between the chemical nature of the substituent R and the observed structure.

A few tris(thiolato)mercurate(II) complexes $[\text{Hg}(\text{SR})_3]^-$ have been crystallographically investigated, and all but one are mononuclear with essentially trigonal-planar co-ordination^{3,4b,12,13} (distortions from regular trigonal co-ordination are a subject to which we return later). The exception is the dinuclear doubly bridged structure observed for the $[\text{Hg}_2(\text{SMe})_6]^{2-}$ anion in its tetraethylammonium salt;¹⁴ spectroscopic data indicate, however, that this dissociates in solution to give mononuclear $[\text{Hg}(\text{SMe})_3]^-$ ions. By contrast, dinuclear

$[\text{M}_2(\text{SR})_6]^{2-}$ species with tetrahedral co-ordination geometry and two bridging thiolates¹⁴⁻¹⁶ seem to be more common than mononuclear $[\text{M}(\text{SR})_3]^-$ species^{3,13,17} for Zn and Cd, unless the lower co-ordination number is dictated by a bulky substituent R , reflecting the greater tendency of these metals to adopt tetrahedral co-ordination in preference to lower co-ordination numbers. This is perhaps best illustrated by the fact that $[\text{Hg}(\text{SPh})_3]^-$ is mononuclear,¹² while the corresponding anions of Zn and Cd are dinuclear $[\text{M}_2(\text{SPh})_6]^{2-}$ species.¹⁵

A tetrahedrally co-ordinated Hg atom is found in the mononuclear $[\text{Hg}(\text{SC}_6\text{H}_4\text{Cl-}p)_4]^{2-}$ dianion,¹⁸ and is probably typical of other $[\text{Hg}(\text{SR})_4]^{2-}$ species which have been synthesised but for which structures have not been reported¹³ (for further references, see ref. 12).

Homoleptic mercury thiolate complexes of higher finite nuclearity are unknown for simple thiolate ligands. Although tetranuclear complexes $[\text{M}_4(\text{SR})_{10}]^{2-}$ and $[\text{M}_4\text{X}_4(\text{SR})_6]^{2-}$ (and also decanuclear complexes $[\text{M}_{10}\text{S}_4(\text{SR})_{16}]^{4-}$ and other derivatives) are known for Zn and Cd,^{19,20} attempts to prepare analogous complexes of Hg have been largely unsuccessful, and only recently has a $[\text{Hg}_4\text{I}_4(\text{SR})_6]^{2-}$ complex been synthesised and spectroscopically characterised.¹⁹ The discrete trinuclear complex ion $[\text{Hg}_3(\text{SCH}_2\text{CH}_2\text{S})_4]^{2-}$ and polymeric $[\{\text{Hg}_2(\text{SCH}_2\text{CH}_2\text{S})_3\}_n]^{2n-}$ contain ethane-1,2-dithiolate with both chelating and bridging ligand functions.²¹

We report here some of our synthetic and structural investigations of mercury complexes with cyclohexanethiolate as a ligand. Benzenethiolate has been used frequently in studies of metal thiolate complexes, and substituted derivatives have been important in the steric control of low co-ordination numbers for complexes of Zn and Cd in particular.^{3,13,17} We preferred to use the aliphatic cyclohexyl substituent in this work in order to compare ultraviolet spectroscopic data with those available for cysteine complexes of biological importance. The relevant ligand-to-metal charge-transfer transitions are obscured in the spectra by features due to aromatic substituents.^{4b}

Experimental

General Considerations.—All preparations were carried out by standard Schlenk techniques under an atmosphere of dry

† *Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1992, Issue 1, pp. xx-xxv.*

dinitrogen. Solvents were dried by conventional methods. Commercial cyclohexanethiol, tetraalkylammonium chlorides, and analytical grade HgCl_2 were not further purified. Microanalyses were performed with a Carlo Erba NA-1500 analyser. Infrared spectra were recorded from KBr discs on a Perkin-Elmer 1710 spectrometer for the range 4000–400 cm^{-1} and from polyethylene discs on a Bomem DA3 spectrometer for the range 400–100 cm^{-1} , Raman spectra from powdered samples on a Dilor spectrophotometer with 514.5 nm excitation, NMR spectra from CDCl_3 and CD_3CN solutions on a Bruker AM400 spectrometer operating at 400 MHz for ^1H , and electronic spectra from acetonitrile solutions on a Kontron Uvikon 8609 spectrometer.

Preparation of $\text{Hg}(\text{SC}_6\text{H}_{11})_2$ 1.—A solution of HgCl_2 (407 mg, 1.5 mmol) in acetonitrile (25 cm^3) was slowly added with stirring to acetonitrile (10 cm^3) containing $\text{NaSC}_6\text{H}_{11}$ (3.0 mmol) (from equimolar amounts of thiol and NaOMe) and some additional ethanol (*ca.* 1 cm^3) to keep the sodium thiolate in solution. The mixture, from which a white solid (NaCl) separated, was stirred for 2 h and then warmed to *ca.* 60 °C and filtered. The residue was washed several times with hot acetonitrile and the washings added to the filtrate. On cooling to room temperature the product separated as very small colourless needle crystals. A second crop was obtained by reducing the volume of the mother-liquor. The crystals were filtered off and dried under vacuum. Total yield 85–90% (Found: C, 33.55; H, 5.40; S, 14.75. Calc. for $\text{C}_{12}\text{H}_{22}\text{HgS}_2$: C, 33.45; H, 5.15; S, 14.90%). The compound is insoluble in water, soluble in MeOH and MeCN (both hot), and very soluble in Et_2O , CHCl_3 and CH_2Cl_2 . Infrared spectrum: 2923vs, 2849s, 1443s, 1332m, 1297m, 1262m, 1201s, 994s, 887w, 814s, 730m and 211w cm^{-1} . NMR data are given in Table 1.

Preparation of $[\text{NR}_4][\text{Hg}(\text{SC}_6\text{H}_{11})_3]$ (R = Et 2 or Me 3).—A solution of HgCl_2 (271 mg, 1 mmol) in acetonitrile (15 cm^3) was slowly added with stirring to acetonitrile (5 cm^3) containing $\text{NaSC}_6\text{H}_{11}$ (3 mmol) (prepared as above) and ethanol (*ca.* 1 cm^3). After precipitation of NaCl and addition of the appropriate solvent (10 cm^3) containing 1 mmol NR_4Cl (R = Et, 166 mg in MeCN ; R = Me, 110 mg in EtOH), the resulting mixture was stirred for several hours. Sodium chloride was filtered off and the filtrate evaporated to dryness. Extraction of the residue with hot acetonitrile, filtration to remove some insoluble material, and addition of diethyl ether to the filtrate caused separation of a white crystalline solid. This material was recrystallised from acetonitrile–ether at –20 °C to give the product as colourless crystals, which were filtered off at low temperature, washed with acetonitrile–ether (2:1), and dried under vacuum. Total yield 70–75% [Found: C, 46.20; H, 8.05; N, 2.20; S, 13.65. Calc. for $\text{C}_{26}\text{H}_{53}\text{HgNS}_3$ (R = Et 2): C, 46.15; H, 7.90; N, 2.15; S, 14.20. Found: C, 42.05; H, 7.40; N, 2.35; S, 15.05. Calc. for $\text{C}_{22}\text{H}_{45}\text{HgNS}_3$ (R = Me 3): C, 42.60; H, 7.30; N, 2.25; S, 15.50%]. Both compounds are very soluble, the NMe_4^+ salt less so, in MeCN , MeOH , dimethyl sulfoxide and dimethylformamide. Infrared spectrum of the NMe_4^+ salt 3: 3015w, 2924vs, 2847s, 1480s, 1446s, 1331m, 1294w, 1257s, 1198s, 997s, 949s, 884m, 817m, 733m and 511w cm^{-1} . NMR data for salt 2 are given in Table 1.

X-Ray Crystallography.—Crystals of $\text{Hg}(\text{SC}_6\text{H}_{11})_2$ 1 and of $[\text{NEt}_4][\text{Hg}(\text{SC}_6\text{H}_{11})_3]$ 2 were examined on a Stoe-Siemens diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.710$ 73 Å).

Crystal data for complex 1. $\text{C}_{12}\text{H}_{22}\text{HgS}_2$, $M = 431.0$, triclinic, space group $P\bar{1}$, $a = 6.510(1)$, $b = 10.707(1)$, $c = 10.971(1)$ Å, $\alpha = 89.10(1)$, $\beta = 84.37(1)$, $\gamma = 82.65(1)^\circ$, $U = 754.76$ Å³ (from 20 values of 32 reflections in the range 20–25°, measured at $\pm\omega$), $Z = 2$, $D_c = 1.896$ g cm^{-3} , $\mu = 10.43$ mm⁻¹, $F(000) = 412$, $T = 295$ K.

Data collection and processing. Intensities were measured

from a crystal of size $0.08 \times 0.12 \times 0.36$ mm, with ω – θ scans and on-line profile fitting,²² to $2\theta_{\text{max}} = 50^\circ$. A whole sphere of data was collected, with $h_{\text{max}} = 7$, $k_{\text{max}} = 12$, $l_{\text{max}} = 13$; no significant variation was observed in the intensities of three periodically measured standard reflections. Semiempirical absorption corrections were applied, with transmission factors 0.076–0.141. The 5306 measured data yielded 2653 unique reflections, 2256 of them with $F > 4\sigma_c(F)$ (σ_c from counting statistics only, $R_{\text{int}} = 0.032$) for use in structure determination.

Structure solution and refinement.²³ Atoms were located from Patterson and difference syntheses. Blocked-cascade least-squares refinement on F included anisotropic thermal parameters for all non-hydrogen atoms, and constrained hydrogen atoms [C-H 0.96 Å, H-C-H 109.5°, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. The weighting scheme²⁴ was $w^{-1} = \sigma^2(F) = \sigma_c^2(F) - 19 + 162G - 29G^2 + 30H - 4H^2 - 247GH$ ($G = F_o/F_{\text{max}}$, $H = \sin\theta/\sin\theta_{\text{max}}$); extinction effects were negligible. Atomic scattering factors were taken from ref. 25. At the termination of refinement, $R = 0.036$, $R' = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0.035$, goodness of fit = 1.23 for 136 parameters. The mean and maximum ratios of parameter shift to estimated standard deviation were 0.001 and 0.004:1 and all features in a final difference electron-density synthesis lay in the range ± 1.0 e Å⁻³.

Crystal data for salt 2. $\text{C}_{26}\text{H}_{53}\text{HgNS}_3$, $M = 676.5$, triclinic, space group $P\bar{1}$, $a = 10.724(4)$, $b = 12.440(5)$, $c = 12.643(5)$ Å, $\alpha = 72.40(2)$, $\beta = 79.36(2)$, $\gamma = 73.33(2)^\circ$, $U = 1531.3$ Å³ (obtained as above), $Z = 2$, $D_c = 1.467$ g cm^{-3} , $\mu = 5.23$ mm⁻¹, $F(000) = 688$, $T = 240$ K with the aid of an Oxford Cryostream cooler.²⁶

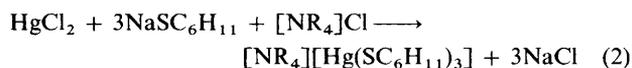
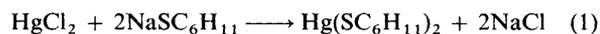
Data collection and structure determination. Similar procedures were followed as described above for complex 1, with the following differences: crystal size $0.34 \times 0.36 \times 0.52$ mm; maximum indices 12, 14, 15; correction for *ca.* 7% decay in intensity of standard reflections; transmission factors 0.169–0.248; 10 990 measured data, 5412 unique, 5088 with $F > 4\sigma_c(F)$, $R_{\text{int}} = 0.018$; $w^{-1} = \sigma_c^2(F) + 10 - 17G + 125G^2 - 15H + 10H^2 - 41GH$; $R = 0.033$, $R' = 0.027$, goodness of fit = 1.27 for 293 parameters; mean and maximum shift/estimated standard deviation (e.s.d.) 0.006 and 0.084; largest difference electron-density peak 2.29 e Å⁻³ (close to Hg atom), largest hole -1.58 Å⁻³.

Refined coordinates are given in Tables 2 and 3, selected bond lengths and angles in Tables 4 and 5.

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

Results and Discussion

Synthesis.—Reactions of HgCl_2 with 2–2.5 molar equivalents of $\text{NaSC}_6\text{H}_{11}$ in acetonitrile lead to complex 1 according to equation (1), while the use of 3–7 equivalents of the ligand give



rise to $[\text{Hg}(\text{SR})_3]^-$ anionic species, which have been isolated as quaternary ammonium salts 2 (R = Et) and 3 (R = Me), according to equation (2). Attempts to prepare $[\text{Hg}(\text{SR})_4]^{2-}$ species¹⁸ by using excess of ligand (> 4 equivalents) have been unsuccessful in our case; all such attempts have resulted in the separation of tris(thiolato) complexes.

Alternative preparative methods previously reported for $[\text{Hg}(\text{SR})_3]^-$ complexes employ as starting materials either HgO or $\text{Hg}(\text{SR})_2$ together with SR^- ,^{12,14,27} or HgCl_2 with LiSR .^{3,13} In order to improve yields, all but one²⁷ of these methods need a large excess of the thiolate reagent (4–7 equivalents) over the reaction stoichiometry. The $[\text{Hg}(\text{SPh})_3]^-$

Table 1 NMR data for complexes **1** and **2**

$\delta(^1\text{H})^a$	$\Delta\delta(^1\text{H})^b$	$\delta(^{13}\text{C})^a$	$\Delta\delta(^{13}\text{C})^b$
Complex 1 , CDCl_3 solution			
3.38 (1 H, tt, J 10.9 and 3.7, 1- H_{ax})	0.65	43.77 (C^1)	5.60
2.16 (2 H, d, J 12.7, 2,6- H_{eq})	0.23	41.88 ($\text{C}^{2,6}$)	4.17
1.80 (2 H, d, J 12.7, 2,6- H_{ax})	0.13	27.03 ($\text{C}^{3,5}$)	0.95
1.65 (1 H, d, J 12.3, 4- H_{eq})	0.11	25.17 (C^4)	≈ 0
1.42 (2 H, qd, J 12.1 and 3.0, 3,5- H_{eq})	0.16		
1.32 (2 H, qt, J 12.6 and 3.0, 3,5- H_{ax})	0.06		
1.18 (1 H, tt, J 12.3 and 3.5, 4- H_{ax})	0.03		
Complex 2 , CD_3CN solution			
3.18 (8 H, q, NCH_2)		53.06 (NCH_2)	
2.90 (3 H, unresolved multiplet, 1- H_{ax})	0.17	43.10 (C^1)	3.7
1.93 (6 H, overlapping solvent, 2,6- H_{eq})	≈ 0	41.89 ($\text{C}^{2,6}$)	3.0
1.67 (6 H, br s, 2,6- H_{ax})	≈ 0	27.98 ($\text{C}^{3,5}$)	0.7
1.55 (3 H, d, J 12, 4- H_{eq})	≈ 0	26.45 (C^4)	≈ 0
1.30–1.10 (27 H, unresolved, NCCCH_3 and others)	≈ 0	7.64 (NCCCH_3)	

^a All chemical shifts are given relative to SiMe_4 ; J in Hz. ^b Co-ordination shift, *i.e.* the difference between the chemical shifts for the complex and the free ligand in the same solvent.

Table 2 Atomic coordinates ($\times 10^4$) for complex **1**

Atom	x	y	z
Hg	2260.6(3)	5517.1(3)	5614.8(2)
S(1)	5014(2)	4667(2)	6766(1)
C(11)	5560(9)	6041(6)	7577(5)
C(12)	3691(11)	6702(9)	8338(7)
C(13)	4255(14)	7790(8)	9045(8)
C(14)	6041(13)	7365(9)	9858(8)
C(15)	7892(13)	6719(9)	9121(8)
C(16)	7324(10)	5605(6)	8385(6)
S(2)	-710(2)	6838(2)	5046(1)
C(21)	282(9)	7643(5)	3661(5)
C(22)	1848(10)	8504(6)	3945(6)
C(23)	2517(12)	9253(8)	2814(8)
C(24)	766(14)	9894(8)	2199(8)
C(25)	-765(14)	9018(8)	1938(8)
C(26)	-1495(10)	8324(7)	3076(7)

Table 3 Atomic coordinates ($\times 10^4$) for complex **2**

Atom	x	y	z
Hg	7 301.3(2)	5 726.8(2)	7 150.8(1)
S(1)	6 224(1)	7 052(1)	5 522(1)
C(11)	6 923(4)	8 329(3)	5 053(3)
C(12)	8 404(4)	8 008(4)	4 801(4)
C(13)	8 964(5)	9 073(5)	4 347(5)
C(14)	8 322(7)	9 898(5)	3 341(5)
C(15)	6 853(6)	10 221(5)	3 584(5)
C(16)	6 287(5)	9 156(5)	4 029(4)
S(2)	7 365(1)	3 807(1)	6 903(1)
C(21)	8 041(4)	2 714(3)	8 135(3)
C(22)	7 112(4)	2 731(5)	9 178(4)
C(23)	7 662(5)	1 763(5)	10 190(4)
C(24)	9 014(5)	1 830(5)	10 326(4)
C(25)	9 939(5)	1 770(5)	9 276(4)
C(26)	9 377(4)	2 723(4)	8 270(3)
S(3)	8 064(1)	5 932(1)	8 734(1)
C(31)	7 585(4)	7 470(5)	8 707(4)
C(32)	8 393(5)	8 203(5)	7 818(5)
C(33)	8 040(6)	9 460(6)	7 871(7)
C(34)	6 598(8)	9 996(7)	7 798(9)
C(35)	5 772(6)	9 301(8)	8 654(8)
C(36)	6 131(5)	8 026(6)	8 625(6)
N	2 678(3)	5 227(3)	7 062(3)
C(41)	1 272(4)	5 181(5)	7 045(4)
C(42)	1 003(4)	4 950(4)	6 027(4)
C(43)	3 624(4)	4 068(5)	7 061(4)
C(44)	3 379(10)	3 078(8)	8 054(8)
C(45)	2 685(4)	5 576(6)	8 109(4)
C(46)	3 996(5)	5 667(7)	8 300(5)
C(47)	3 096(5)	6 093(5)	6 024(4)
C(48)	2 307(11)	7 295(7)	5 776(10)

complexes have been obtained from two different synthetic routes: whereas a HgO-SPh^- (1:4) system in methanol was used in the preparation of the $[\text{NBu}_4]^+$ salt,¹² only $\text{Hg}(\text{SPh})_2\text{-SPh}^-$ (1:1) is required in liquid ammonia to obtain the $[\text{PPh}_4]^+$ salt.²⁷ In contrast to these reactions, we have obtained complexes **2** and **3** in 70–75% purified yields from the stoichiometric molar ratio of reaction (2), carried out in acetonitrile.

Spectroscopic Properties.—The strongest absorptions in the infrared spectra between 4000 and 400 cm^{-1} are very similar for all three complexes, except for those due to the cation (for complex **3** at 3015, 1480 and 949 cm^{-1}); they all arise from the cyclohexanethiolato ligands.

The ^1H NMR spectrum of complex **1** in CDCl_3 consists of seven signals which are well resolved. The assignments given in Table 1 are based on those for free cyclohexanethiol. The ligands are clearly equivalent in the solution of the complex, in accordance with the expected linear two-fold co-ordination for monomeric **1**. Co-ordination to mercury causes a downfield shift of the proton resonances, the degree of deshielding increasing with proximity to the metal atom. For protons bonded to the same carbon atom the equatorial is more deshielded than the axial position. The largest downfield shift thus occurs for the α -carbon proton, which resonates at δ 2.73 for the free ligand and at δ 3.38 for the complex. The coupling constants observed for this proton [$^3J(\text{H}_{\text{ax}}\text{-H}_{\text{ax}}) = 10.9$ and $^3J(\text{H}_{\text{ax}}\text{-H}_{\text{eq}}) = 3.7$ Hz] are consistent with an equatorial site for the S atom on the cyclohexyl ring, as is usual for bulky groups.

Similar assignments can be made for the cyclohexanethiolato

Table 4 Selected bond lengths (\AA) and angles ($^\circ$) for complex **1**

Hg-S(1)	2.372(2)	Hg-S(2)	2.374(2)
Hg-S(1a)	3.004(2)	Hg-S(2b)	2.959(2)
S(1)-C(11)	1.823(7)	S(2)-C(21)	1.838(6)
S(1)-Hg-S(2)	160.4(1)	S(1)-Hg-S(1a)	93.2(1)
S(2)-Hg-S(1a)	101.1(1)	S(1)-Hg-S(2b)	99.7(1)
S(2)-Hg-S(2b)	94.2(1)	S(1a)-Hg-S(2b)	88.1(1)
Hg-S(1)-C(11)	102.5(2)	Hg-S(1)-Hg(a)	86.8(1)
C(11)-S(1)-Hg(a)	107.7(2)	Hg-S(2)-C(21)	103.6(2)
Hg-S(2)-Hg(b)	85.8(1)	C(21)-S(2)-Hg(b)	110.3(2)

protons of salt **2** in CD_3CN solution. Apart from the additional peaks due to the cation, however, there are also some other differences between this spectrum and that of **1**. The signals for **2**

Table 5 Selected bond lengths (Å) and angles (°) for complex **2**

Hg–S(1)	2.453(1)	Hg–S(2)	2.480(2)
Hg–S(3)	2.402(2)	S(1)–C(11)	1.840(5)
S(2)–C(21)	1.835(4)	S(3)–C(31)	1.825(6)
S(1)–Hg–S(2)	101.2(1)	S(1)–Hg–S(3)	135.9(1)
S(2)–Hg–S(3)	122.8(1)	Hg–S(1)–C(11)	107.5(1)
Hg–S(2)–C(21)	106.2(2)	Hg–S(3)–C(31)	108.2(2)

Table 6 Low-energy UV spectra of mercury(II) thiolate complexes

Complex	λ_{\max}/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (MeCN)	Ref.
Hg(SET) ₂	228 (sh, 4700), 282 (sh, 740)	4b
Hg(SPr') ₂	228 (sh, 3400), 262 (sh, 650)	4b
Hg(SC ₆ H ₁₁) ₂	220 (9100), 234 (sh, 4200), 270 (sh, 900)	This work
[NEt ₄][Hg(SBu') ₃]	235 (24 000), 260 (sh, 17 700)	4b
[NEt ₄][Hg(SC ₆ H ₁₁) ₃]	230 (23 200), 255 (sh, 14 200)	This work
Hg–MerR*	240 (16 620), 260 (sh, 11 150), 290 (sh, 4210)	4b

* Difference spectrum; aqueous 0.01 mol dm⁻³ sodium phosphate at pH 7.0.

are much less well resolved, and significant co-ordination shifts are not seen, except for the α -carbon proton; the downfield shift of 0.17 ppm for this proton is much less than the corresponding value of 0.65 ppm for **1**. It is possible that the weaker Hg–S bonds in the trigonal co-ordination in **2** relative to two-co-ordination in solutions of **1** leads to a smaller deshielding effect, but a more probable explanation, supported by the signal broadening in the NMR spectra of **2**, is in terms of a rapid intermolecular chemical exchange of ligands. This may occur between anionic species, or between these and neutral Hg(SC₆H₁₁)₂ produced by partial dissociation in solution. Such a rapid chemical exchange of thiolate ligands has been previously shown to occur in related anionic complexes.^{15,28} It gives rise to observed chemical shifts which are intermediate between those corresponding to the complexes in the absence of chemical exchange and those corresponding to the free ligand.

The observed chemical shifts in the ¹³C NMR spectra are affected by co-ordination of the ligands in a similar manner to those of the protons. Once again, the effects are greater for complex **1**, for which the downfield co-ordination shifts are larger than those for **2**. For **2** measurable effects extend further around the ring from the substitution position in the ¹³C than in the ¹H NMR spectrum.

Both complexes absorb in the low-energy UV region between 210 and 280 nm, giving in each case a clear maximum together with unresolved shoulders. Data are given in Table 6, together with corresponding data for some other mercury aliphatic thiolate complexes. The magnitudes of the absorption coefficients are consistent with the assignment of these absorptions to ligand-to-metal charge-transfer transitions of the SHg chromophore. The spectra resemble closely in both band positions and intensities those for the other related complexes in Table 6, which have two- or three-fold co-ordination of mercury. Three-co-ordinate species give absorption intensities several times higher than those for linear two-fold co-ordination, and this may provide a simple spectroscopic method for distinguishing between these geometrical arrangements around mercury. Our data thus support the proposal of a trigonal-planar [Hg(CysS)₃]⁻ co-ordination environment for the metal-receptor site of the MerR metalloregulatory protein, which was based on the similarity between the electronic spectrum of [Hg(SBu')₃]⁻ and the UV difference spectrum of the mercury complex of MerR,^{4b} as well as on a comparison of crystallographically determined Hg–S bond lengths in [Hg(SBu')₃]⁻

and estimates of Hg–S distances in Hg–MerR from extended X-ray absorption fine structure (EXAFS) studies,^{4a} and provide in complexes **2** and **3** a further suitable spectroscopic probe for the Hg–MerR biosensor.

The most intense peaks of the far-IR and Raman spectra in the range 400–100 cm⁻¹ for the solid complexes **1** and **2** are listed in Table 7. Bands of weak to medium intensity at 340–345, 310–316 and 196–202 cm⁻¹ in both IR and Raman spectra are common to the two complexes and are also present in the spectra of cyclohexanethiol itself. They can be derived from the fundamental vibrations of the six-membered ring of free cyclohexane at 381 (A_{1g}) and 216 (E_u) cm⁻¹.²⁹ Other bands not involved in M–L vibrations are those appearing at 352 cm⁻¹ in the spectra of complex **2**, which are due to the [NEt₄]⁺ cation.

The repeat unit of the polymeric chain of complex **1** (see below) contains two crystallographically independent Hg₂S₂ centrosymmetric rings. Since their dimensions are very similar the vibrational behaviour can be qualitatively understood by considering just one of them. The symmetry point group for the unit is C_i. Thus four Hg–S stretching (2A_u + 2A_g) and two ring deformation (A_u + A_g) vibrational modes are expected, all of which should be either IR or Raman active.³⁰ On this basis, and ignoring the absorptions due to the ligand itself, the IR-active bands at 375 and 221 cm⁻¹ and those in the Raman spectrum at 365 and 206 cm⁻¹ are assigned to asymmetric and symmetric Hg–S stretches respectively.^{8e,30,31} The assignment of the remaining peaks at 157 (IR) and 152 (Raman) cm⁻¹ to the two ring deformation modes is not so straightforward because they are so close in frequency. Furthermore, skeletal bending modes $\delta(\text{C–S–Hg})$ have been reported to occur in the range 180–120 cm⁻¹ for related complexes.³¹ In one of these, Hg(SBu')₂, whose polymeric structure also contains Hg₂S₂ rings, no significant coupling across the mercury atom has been detected between vibrations involving some carbon atoms of the alkyl chains of the ligands.³¹ This might account for the small separation between our two observed bands, suggesting that they might be ascribed to almost uncoupled $\delta(\text{C–S–Hg})$ modes.

While the two highest frequencies (375 and 365 cm⁻¹) assigned to Hg–S stretching vibrations of the Hg₂S₂ rings in complex **1** are not much lower than those reported for isolated linear HgS₂ units [405 and 394 cm⁻¹ for Hg(SET)₂^{8e,32}], the two lowest ones (221 and 206 cm⁻¹) lie between those ascribed to two tetrahedral HgS₄ co-ordination environments [172 and 188 cm⁻¹ for Hg(SBu')₂;³² 252 and 218 cm⁻¹ for Hg(SBuⁿ)₂³¹]. These figures are consistent with the description of the structure of complex **1** as diagonal Hg(SR)₂ units (Hg–S 2.37 Å) linked by secondary Hg–S interactions (3.0 Å), giving a polymeric chain with very distorted tetrahedral co-ordination of mercury. The secondary interactions would account for the lowering of $\nu(\text{Hg–S})$ corresponding to linear HgS₂ units from its characteristic value of ca. 400 cm⁻¹ to 375 and 365 cm⁻¹ for the complex. Thus, the structural features of this complex are well reflected in its vibrational spectroscopic behaviour.

The idealised local geometry of [Hg(SR)₃]⁻ anions in complex **2** is D_{3h}. The predicted fundamental vibrations and activity for this point group are HgS₃ stretches A'₁ (Raman) and E' (IR, Raman), in-plane bend E' (IR, Raman) and out-of-plane bend A''₂ (IR).^{30b} Lowering of the symmetry to C_{2v}, and further to C_s, the actual symmetry of the anion in this structure, renders all modes active in both spectra and, in principle, removes degeneracy.³³ Thus, the bands at 280 (IR, Raman) and 250 (IR, Raman) cm⁻¹ have been assigned respectively to $\nu_a(\text{A}' + \text{A}'')$ and $\nu_{\text{sym}}(\text{A}')$ Hg–S stretching modes.¹⁴ The resolution of the spectra has not permitted the observation of A' and A'' components of ν_a as separate lines. The peak at 159 (IR, Raman) cm⁻¹ is very close to those observed at 152–157 cm⁻¹ in the spectra of complex **1**, so it is also associated with skeletal bending $\delta(\text{C–S–Hg})$.³¹ The remaining band at 146 (IR, Raman) cm⁻¹ is ascribed to $\delta_a(\text{S–Hg–S})$ in-plane bending (A' + A''), as for some related complexes.¹⁴

Table 8 lists the Hg–S stretching frequencies and bond

Table 7 Solid-state far-IR and Raman spectra (400–100 cm⁻¹)* of complexes **1** and **2**

Hg(SC ₆ H ₁₁) ₂ 1			[NEt ₄][Hg(SC ₆ H ₁₁) ₃] 2		
IR	Raman	Assignment	IR	Raman	Assignment
375s	365s	<i>v</i> _{asym} (Hg–S) (A _u) <i>v</i> _{sym} (Hg–S) (A _g)	351s	352w	NEt ₄ ⁺
345m	344w	Ligand related	339m	343w	Ligand related
316m	317w	Ligand related	309m	311w	Ligand related
			280s	281m	<i>v</i> _d (Hg–S) (A' + A'')
			251m	250s	<i>v</i> _{sym} (Hg–S) (A')
221m	206s	<i>v</i> _{asym} (Hg–S) (A _u) <i>v</i> _{sym} (Hg–S) (A _g) Ligand related	196m	200w	Ligand related
202w			159w	159w	δ (C–S–Hg) (2A' + A'')
157s	152m	δ (C–S–Hg) (A _u + A _g)	145w	146m	δ _d (S–Hg–S) (A' + A'')

* Bands mainly related to the ligands or to the cation are shown in italics.

Table 8 Geometry, metric parameters and Hg–S stretches for mercury sites in thiolate complexes

Primary co-ordination ^a	Compound	<i>d</i> (Hg–S) ^b	Secondary co-ordination ^c	<i>v</i> (Hg–S) ^d	Ref.
Primary c.n. = 2 Linear geometry	Hg(SEt) ₂ ^e	2.36 ^f	—	405 (IR) 394 (Raman) 395 (IR) 372 (Raman)	5, 8b 32 8e
Primary c.n. = 2 Essentially linear geometry	[Hg(SC ₅ H ₉ NHMe) ₂] ²⁺	2.33	—	375 (IR) 365 (Raman) 354 (IR) 326 (Raman)	This work 9
	Hg(SC ₆ H ₁₁) ₂ ^g	2.37	2 at 3.0 Å	337 (IR) 297 (Raman)	8a, 32
	[Hg{S(CH ₂) ₃ NMe ₃ } ₂] ²⁺ ^g	2.34	2 to 3 at 2.98–3.42 Å	340–320 (IR)	8g
	Hg(SMe) ₂	2.36	3 at 3.25 Å	280 (IR, Raman) 250 (IR, Raman)	This work
	[Hg(SC ₆ H ₄ SiMe ₃) ₂]	2.35	2 at 3.23 Å	282 (Raman)	14
	[Hg(SC ₅ H ₃ NSiMe ₃) ₂]	2.34	2(N) at 2.8 Å	210 (IR, Raman)	4b, 14
Primary c.n. = 3 Trigonal-planar geometry	[NEt ₄][Hg(SC ₆ H ₁₁) ₃]	2.44	—	252 (IR) 218 (Raman)	11, 31
	[Hg(SMe) ₃] ^{-h}	2.44	—	172 (IR)	10, 32
Primary c.n. = 4 Distorted-tetrahedral geometry	[NR ₄][Hg(SBu ^t) ₃]	2.54 (bridging)	—	188 (Raman) 230–180 (IR)	14
	Hg(SBu ^t) ₂	2.63 (bridging)	—	213 (Raman)	14
	[NEt ₄] ₂ [Hg ₂ (SMe) ₆]	2.67 (bridging)	—	275 (IR, Raman) 260 (IR, Raman)	
		2.45 (terminal)	—		

^a Co-ordination number (c.n.) and geometry for primary co-ordination. ^b Average primary bond length in Å. ^c Number and distances of secondary interactions. ^d In cm⁻¹. ^e Interatomic distances in ref. 8b are not very accurate (see text and ref. 5). The mercury is also surrounded by four sulfur atoms at 3.54 Å, larger than the Hg–S van der Waals distance. ^f From EXAFS data. ^g Only the bands mainly related to the primary co-ordination are included (see text). ^h In EtOH solution.

distances for the co-ordination sphere of mercury in different thiolate complexes, including those reported here. The expected correlation between *v*(Hg–S) and the number of atoms bonded to the metal is not observed, unless a primary co-ordination number is considered rather than the full co-ordination sphere.³² This would not take into account either sulfur or any other atoms bonded to mercury through weaker interactions at distances above *ca.* 2.8 Å. The sum of the covalent radii of sulfur and mercury atoms is about 2.33 Å, and the sum of the van der Waals radii 3.5 Å.^{8e,g} Thus, in going from primary two-co-ordination in discrete molecular species to three-co-ordination in monomeric species, and to tetrahedral co-ordination in di- or poly-meric structures, *v*(Hg–S) are lowered and the average Hg–S distance increases.

From the vibrational spectra of numerous complexes it is possible to assign a range of 400–300 cm⁻¹ for homoleptic thiolate complexes with two-fold mercury co-ordination. Within these limits, genuinely discrete species have *v*(Hg–S)

towards the upper limit (400–380 cm⁻¹), but secondary interactions reduce the frequencies of both asymmetric and symmetric vibrations towards the lower limit. For three-fold co-ordination, *v*(Hg–S) values fall within the range 285–210 cm⁻¹, though this is based on rather few data at present. The few known examples of tetrahedral co-ordination give frequencies for bridging Hg–S in the range 250–170 cm⁻¹, partially overlapping the range for three-co-ordination. The only reported vibrations for terminal Hg–S bonds with tetrahedral co-ordination {in [Hg₂(SMe)₆]²⁻} give wavenumbers of 275 and 260 cm⁻¹, outside the range for bridging Hg–S and close to the upper limit of the three-co-ordination range, appropriate to the shorter terminal than bridging Hg–S bond lengths, the terminal Hg–S bonds being very similar in length to those in the three-co-ordinate complexes. Identification of two-fold co-ordination can, therefore, be made confidently from the Hg–S observed stretching frequencies, but a distinction between three- and four-co-ordination is more difficult.

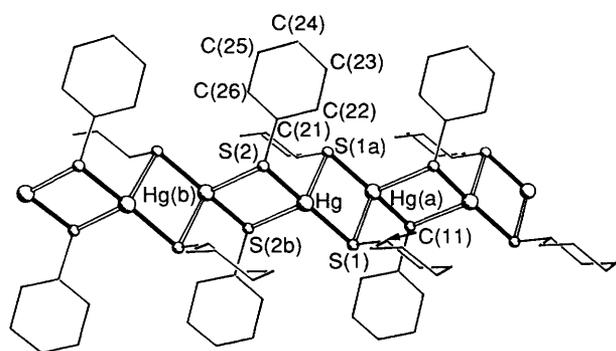


Fig. 1 Part of the polymeric chain structure of complex 1. Hydrogen atoms are omitted; the atom numbering of both independent ligand rings follows the same scheme. Primary Hg-S bonds are shown filled, secondary bonds hollow

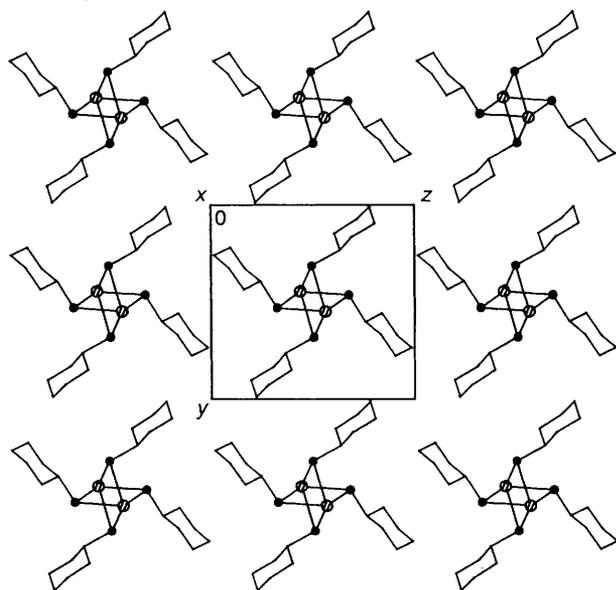


Fig. 2 The structure of complex 1 seen in projection along the crystallographic *a* axis

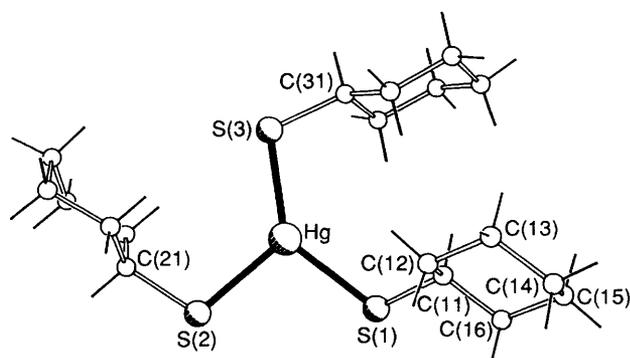


Fig. 3 The structure of the anion of complex 2 viewed along the normal to the plane of the three sulfur atoms. All ligand rings follow the same numbering scheme

Structure of Complex 1.—Among about a dozen known structures of complexes of formula $\text{Hg}(\text{SR})_2$, that of 1 stands out as unique. The majority have essentially linear two-fold co-ordination of mercury atoms with Hg-S bond lengths in the fairly narrow range 2.32–2.37 Å [the value 2.45 Å for $\text{Hg}(\text{SEt})_2$ reported in 1965^{8b} must be regarded as of lower reliability]; weak $\text{Hg}\cdots\text{S}$ interactions between monomer units, with distances ranging from about 3.2 Å upwards (there is a single exceptionally short $\text{Hg}\cdots\text{S}$ distance of 2.98 Å in one struc-

ture⁹) link these into various oligo- or poly-meric arrangements, but scarcely affect the essential linear co-ordination geometry, with bending of the S-Hg-S unit up to only about 10°. Two reported $\text{Hg}(\text{SR})_2$ structures^{9,10} have approximately symmetrical sulfur bridges between Hg atoms to give a linear polymeric chain of linked $\text{Hg}_2(\mu\text{-S})_2$ rings, with Hg-S bond lengths 2.56–2.66 Å and distorted tetrahedral co-ordination of Hg, the distortion consisting of a stretching along the polymer chain direction, so that S-Hg-S angles are much smaller within the approximately square Hg_2S_2 rings and larger otherwise. In one case the same $\text{Hg}(\text{SR})_2$ compound is known with both monomeric and linear polymeric structures.⁹

A quite different polymeric $\text{Hg}(\text{SR})_2$ structure has also been reported, for $\text{Hg}(\text{SBU}^n)_2$.¹¹ It consists of $\text{Hg}(\text{SR})_4$ distorted tetrahedra which are linked by corner- and edge-sharing to give a three-dimensional network. Corner sharing gives rise to $[\text{Hg}(\mu\text{-SR})(\text{SR})_2]_\infty$ helical chains, and SR groups are additionally bonded to $\text{Hg}_2(\mu\text{-SR})_2$ units to form Hg_3S_3 and Hg_2S_2 rings which connect each helix to four neighbouring ones.

Complex 1 has a structure intermediate between the monomeric and linear-chain polymeric forms. Each mercury atom forms two primary Hg-S bonds, with lengths 2.372(2) and 2.374(2) Å at the top of the range observed for $\text{Hg}(\text{SR})_2$ monomers. This HgS_2 unit is markedly bent, with an angle of 160.4(1)° at Hg, owing to the formation of two secondary $\text{Hg}\cdots\text{S}$ interactions of length 2.959(2) and 3.004(2) Å with adjacent units, *ca.* 0.2 Å shorter than the $\text{Hg}\cdots\text{S}$ distances observed in most $\text{Hg}(\text{SR})_2$ structures. The result is a polymeric chain, shown in Fig. 1. The complete co-ordination of mercury is irregular, highly distorted tetrahedral, and the sulfur bridges are very asymmetric. Each Hg_2S_2 ring is strictly planar, with a crystallographic inversion centre, and is approximately rectangular.

The $(\text{HgS}_2)_\infty$ chains run parallel to the crystallographic *a* axis and are well separated from each other by the surrounding sheaths of cyclohexyl groups (Fig. 2), so that inter-chain $\text{Hg}\cdots\text{S}$ and $\text{Hg}\cdots\text{Hg}$ distances are all >8 Å. The chains dissociate readily, solubility being high in most common organic solvents, to give probably linear monomeric $\text{Hg}(\text{SC}_6\text{H}_{11})_2$ molecules in solution, as evidenced by spectroscopic measurements.

Structure of Complex 2.—This consists of discrete $[\text{NEt}_4]^+$ cations of unremarkable geometry and mononuclear $[\text{Hg}(\text{SC}_6\text{H}_{11})_3]^-$ anions (Fig. 3). Interactions among the ions appear to be of normal electrostatic and van der Waals character with no additional secondary covalent bonding. The anions are well separated, the closest $\text{Hg}\cdots\text{S}$ and $\text{Hg}\cdots\text{Hg}$ distances being 6.970 and 7.392 Å respectively.

Mercury has trigonal-planar co-ordination in complex 2, the Hg atom lying only 0.04 Å out of the S_3 plane. In-plane distortions from regular-trigonal geometry are, however, considerable, with one S-Hg-S angle much higher and another much lower than the ideal 120°. The three Hg-S bonds are also of significantly different lengths. The longest bond lies opposite the largest angle, and the shortest bond lies opposite the smallest angle. Very similar distortions from ideal trigonal-planar geometry have been observed for three other $[\text{Hg}(\text{SR})_3]^-$ anionic thiolate complexes,^{3,12,13} and the pattern is well established for other three-co-ordinate d^{10} metal complexes,¹³ not only with thiolate ligands. It has been considered as a tendency towards the more commonly observed two-fold co-ordination for d^{10} metal centres, with lengthening of one metal-ligand bond and opening up of the opposite angle,^{3,13} an example of the interpretation of distorted molecular structures in the crystalline state as intermediate points on chemical reaction pathways.³⁴ Interestingly, there is one known $[\text{Hg}(\text{SR})_3]^-$ structure which is much closer to ideal trigonal-planar geometry (with $\text{R} = \text{Bu}^t$).^{4b} Its S-Hg-S angles all lie within 2.1° of 120°, and the range of Hg-S bond lengths is only 2.436(1)–2.451(1) Å. The mean Hg-S bond length of 2.442 Å is

very similar to that found in complex **2** (2.445 Å) and the other known $[\text{Hg}(\text{SR})_3]^-$ structures, markedly longer than the 2.32–2.37 Å typical of linear two-fold co-ordination in $\text{Hg}(\text{SR})_2$ structures and shorter than the 2.50–2.65 Å in polymeric $\text{Hg}(\text{SR})_2$ structures with distorted-tetrahedral co-ordination or 2.537–2.552 Å in the monomeric tetrahedral $[\text{Hg}(\text{SC}_6\text{H}_4\text{-Cl-p})_4]^{2-}$ anion.¹⁸

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