

Syntheses and Vibrational Spectra of Some Tris(alkanethiolato)mercurate(II) Complexes, and Crystal Structure of the Hexakis-(methanethiolato)dimercurate(II) Dianion

Graham A. Bowmaker,^A Ian G. Dance,^B Brian C. Dobson^A and David Alan Rogers^A

^A Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand.

^B School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033.

Abstract

The complexes [cation][Hg(SR)₃] (R = Me, cation = Et₄N⁺; R = Bu^t, cation = Et₄N⁺, Bu₄N⁺, [N(Ph₃P)₂]⁺) have been prepared. The crystal structure of the methanethiolate complex shows that it contains centrosymmetric dinuclear anions [(MeS)₂Hg(μ-SMe)₂Hg(SMe)₂]²⁻ with distorted tetrahedral geometry about the mercury atoms. Vibrational spectroscopic evidence suggests that this complex dissociates on dissolution in ethanol to give mononuclear [Hg(SMe)₃]⁻ species. The Bu^tS⁻ complexes appear to exist as mononuclear [Hg(SBu^t)₃]⁻ species both in the solid state and in solution. The metal-sulfur stretching frequencies are assigned for all of the complexes studied, and the vibrational spectra are discussed in terms of the structures of the complex anions involved. Crystal data for [(C₂H₅)₄N]₂Hg₂(SCH₃)₆: *a* 8.656(5), *b* 9.130(6), *c* 12.368(8) Å; α 102.16(4), β 105.51(4), γ 105.29(4)°; space group *P* $\bar{1}$, *Z* 1, *R* 0.034, *R*_w 0.042.

Introduction

Anionic thiolate complexes of the Group 2B metals include the monometallic complexes [M(SR)₄]²⁻ (R = Ph, C₆F₅, C₆H₄Cl-*p*, M = Zn, Cd, Hg; R = C₆Cl₅, M = Zn, Hg),¹⁻¹⁰ the tetrametallic complexes [M₄(SR)₁₀]²⁻ (R = Ph, M = Zn, Cd),^{4,5,11,12} and the decametallc complexes [E₄M₁₀(SPh)₁₆]⁴⁻ (E = S, Se, M = Zn,

¹ Holah, D. G., and Coucouvanis, D., *J. Am. Chem. Soc.*, 1975, **97**, 6917.

² Swenson, D., Baenziger, N. C., and Coucouvanis, D., *J. Am. Chem. Soc.*, 1978, **100**, 1932.

³ Coucouvanis, D., Murphy, C. N., Simhon, E., Stremple, P., and Draganjac, M., *Inorg. Synth.*, 1982, **21**, 23.

⁴ Dance, I. G., *Inorg. Chem.*, 1981, **20**, 2155.

⁵ Dance, I. G., Guernsey, P. J., Choy, A., and Scudder, M. L., unpublished data on [M(SPh)₄]²⁻, [M₄(SPh)₁₀]²⁻, M = Zn, Cd.

⁶ Choudhury, S., Dance, I. G., Guernsey, P. J., and Rae, A. D., *Inorg. Chim. Acta*, 1983, **70**, 227.

⁷ Liesk, J., and Klar, G., *Z. Anorg. Allg. Chem.*, 1977, **435**, 103.

⁸ Hollebhone, B. R., and Nyholm, R. S., *J. Chem. Soc. A*, 1971, 332.

⁹ Beck, W., Stetter, K. H., Tadros, S., and Schwarzhaus, K. E., *Chem. Ber.*, 1967, **100**, 3944; Beck, W., Fehlhammer, W. P., Stetter, K. H., and Tadros, S., *Chem. Ber.*, 1967, **100**, 3955.

¹⁰ Lucas, C. R., and Peach, M. E., *Inorg. Nucl. Chem. Lett.*, 1969, **5**, 73.

¹¹ Hagen, K. S., Stephan, D. W., and Holm, R. H., *Inorg. Chem.*, 1982, **21**, 3928.

¹² Hencher, J. L., Khan, M., Said, F. F., and Tuck, D. G., *Inorg. Nucl. Chem. Lett.*, 1981, **17**, 287.

Cd).¹³ Thiolate ligands have pseudo-halide characteristics,^{8,14} and the $[M(SR)_4]^{2-}$ species described above have well known halide counterparts $[MX_4]^{2-}$ ($X = Cl, Br, I$). The cage structures $[M_4(SR)_{10}]^{2-}$ have no halide counterparts, although structures in which some of the terminal thiolate groups are replaced by halide are known.⁴

In all of the above compounds the metal atom is tetrahedrally coordinated. Rather less is known about anionic thiolate complexes of mercury with coordination number three. Complexes of the type $[Hg(EPh)_3]^-$ ($E = S, Se, Te$) have been reported,⁷ and the crystal structure of $[Ph_4P][Hg(TePh)_3]$ has been determined.¹⁵ This compound contains mononuclear $[Hg(TePh)_3]^-$ ions with slightly distorted trigonal planar coordination of the mercury atom. The vibrational spectra of the compounds $[Ph_4P][Hg(EPh)_3]$ in the $\nu(HgE)$ region have been reported, and these indicate trigonal planar $HgTe_3$ coordination in $[Hg(TePh)_3]^-$, and trigonal pyramidal HgS_3 coordination in $[Hg(SPh)_3]^-$.⁷ The corresponding halogeno complexes $[HgX_3]^-$ have been identified in solution,¹⁶ and Raman results suggest the presence of an equilibrium between planar and pyramidal forms.¹⁷ In the solid state, trihalogenomercurates show a wide variety of stereochemical arrangements, depending on the nature of the cation. In general, infinite polymeric structures occur, with bridging halide ions and distorted tetrahedral, octahedral or trigonal bipyramidal coordination of the mercury atom. In a few cases, however, discrete doubly halide-bridged dimers $[Hg_2X_6]^{2-}$ have been found,¹⁸⁻²² while in $[Bu_4N][HgI_3]$ occurs the first example of a mononuclear trigonally coordinated trihalogenomercurate in the solid state.²²

In order to discover more about the properties of thiolatomercurate(II) complexes, and the factors which determine the coordination geometry about mercury, we have examined tris(thiolato)mercurate(II) species involving methanethiolate, MeS^- , and 2-methylpropane-2-thiolate, Bu^tS^- . Crystalline compounds of the type [cation]- $[Hg(SR)_3]$ (where $R = Me$, cation = Et_4N^+ ; $R = Bu^t$, cation = Et_4N^+ , Bu_4N^+ , $[N(Ph_3P)_2]^+$) have been prepared and studied by vibrational spectroscopy. The vibrational spectra of the compound $[Et_4N][Hg(SMe)_3]$ showed that the structure of the anion was more complex than those of the corresponding Bu^tS^- and PhS^- complexes, with evidence for the presence of both terminal and bridging MeS^- groups. A crystal structure determination was carried out on this compound, and showed that it contains the dinuclear complex $[(MeS)_2Hg(\mu-SMe)_2Hg(SMe)_2]^{2-}$, with a structure similar to that previously found for the halogeno complexes $[Hg_2X_6]^{2-}$.¹⁸⁻²² The vibrational

¹³ Choy, A., Craig, D., Dance, I. G., and Scudder, M. L., *J. Chem. Soc., Chem. Commun.*, 1982, 1246, and unpublished data.

¹⁴ Birckenbach, L., and Kellerman, K., *Ber. Dtsch. Chem. Ges.*, 1925, **58**, 786, 2377.

¹⁵ Behrens, U., Hoffman, K., and Klar, G., *Chem. Ber.*, 1977, **110**, 3672.

¹⁶ Short, E. L., Waters, D. N., and Morris, D. F. C., *J. Inorg. Nucl. Chem.*, 1964, **26**, 902.

¹⁷ Waters, D. N., Kantarci, Z., and Rahman, N. N., *J. Raman Spectrosc.*, 1978, **7**, 289.

¹⁸ Harris, G. S., Inglis, F., McKechnie, J., Cheung, K. K., and Ferguson, G., *Chem. Commun.*, 1967, 442.

¹⁹ Gal, A. W., Beurskens, G., Cras, J. A., Beurskens, P. T., and Willemse, J., *Recl Trav. Chim. Pays-Bas*, 1976, **95**, 157.

²⁰ Spek, A. L., *Cryst. Struct. Commun.*, 1979, **8**, 577.

²¹ Beurskens, P. T., Bosman, W. P. J. H., and Cras, J. A., *J. Cryst. Mol. Struct.*, 1972, **2**, 183.

²² Goggin, P. L., King, P., McEwan, D. M., Taylor, G. E., Woodward, P., and Sandström, M., *J. Chem. Soc., Dalton Trans.*, 1982, 875.

spectra of these complexes in the solid state and in solution have been analysed, and are discussed in terms of the structures of the complex anions involved.

Experimental

Preparation of Compounds

Commercial methanethiol (Matheson), 2-methylpropane-2-thiol (RDH, Prosynth), mercuric oxide (BDH), and 25% aqueous tetraethylammonium hydroxide solution (Fluka) were used without further purification. Bis(triphenylphosphine)iminium chloride* was prepared by a literature method.²³

All thiolate preparations were carried out under an atmosphere of dry nitrogen, standard Schlenk techniques²⁴ being used.

Bis(methanethiolato)- and Bis(2-methylpropane-2-thiolato)-mercury(II)

These were prepared by reaction of a slight excess of the appropriate thiol with a solution of HgCl_2 in absolute ethanol, and were recrystallized from ethanol.

Bis(tetraethylammonium) Hexakis(methanethiolato)dimercurate(II), $[\text{Et}_4\text{N}]_2 [\text{Hg}_2(\text{SMe})_6]$

Methanethiol (1.5 g, 30 mmol) was added to a suspension of bis(methanethiolato)mercury(II) (2.8 g, 10 mmol) in a mixture of 25% aqueous tetraethylammonium hydroxide (12 g; contains 3 g, 20 mmol, Et_4NOH) and absolute ethanol (10 cm^3). The solution became clear on warming to 60°, and was filtered and reduced in volume to give white crystals of the product, m.p. 77–78° (Found: C, 28.1; H, 6.2; Hg, 42.1; N, 3.0. $\text{C}_{11}\text{H}_{29}\text{HgNS}_3$ requires C, 28.0; H, 6.2; Hg, 42.5; N, 3.0%). The ^1H n.m.r. spectrum of this compound in (D_5)pyridine showed no signals other than those due to the thiolate methyl (δ 2.83) and cation ethyl (δ 1.26, CH_3 ; 3.38, CH_2) groups when the solution was made up under nitrogen. When the solution was made up in air, however, an additional strong singlet appeared at δ 2.03, and the solution became yellow.

Tetraethylammonium Tris(2-methylpropane-2-thiolato)mercurate(II), $[\text{Et}_4\text{N}] [\text{Hg}(\text{SBU}^t)_3]$

2-Methylpropane-2-thiol (5.4 g, 60 mmol) was dissolved in a mixture of 25% aqueous tetraethylammonium hydroxide (18.0 g; contains 4.5 g, 30 mmol) and absolute ethanol (30 cm^3). Mercury(II) oxide (2.2 g, 10 mmol) was added to the resulting solution, and the mixture was warmed to 55° and stirred until all the mercuric oxide had dissolved. The resulting solution was filtered and reduced to about half of its original volume. The white crystalline product was collected and washed with absolute alcohol. M.p. 170° (dec.) (Found: C, 40.0; H, 7.4; N, 2.1. $\text{C}_{20}\text{H}_{47}\text{HgNS}_3$ requires C, 40.1; H, 7.9; N, 2.3%). The stoichiometry of the complex was also established by determining the ratio of the number of thiolate to cation protons from the integrated ^1H n.m.r. spectrum of the compound dissolved in (D_5)pyridine. This yielded a value of 3.1 ± 0.1 (mean of four determinations from separate integral traces) for the number of t-butyl groups per tetraethylammonium cation, which establishes the formula as $[\text{Et}_4\text{N}] [\text{Hg}(\text{SBU}^t)_3]$. The ^1H n.m.r. spectrum showed no signals other than those due to the t-butyl (δ 1.76) and ethyl (δ 1.29, CH_3 ; 3.40, CH_2) groups when the solution was made up under nitrogen. When the solution was made up in air, however, an additional strong singlet appeared at δ 2.03.

$[\text{Et}_4\text{N}] [\text{Hg}(\text{SBU}^t)_3]$ was also prepared by the following method. 2-Methylpropane-2-thiol (1.19 g, 13 mmol) and bis(2-methylpropane-2-thiolato)mercury(II) (2.7 g, 7 mmol) were added to a mixture of 25% aqueous tetraethylammonium hydroxide (7.6 g; contains 1.9 g, 13 mmol) and ethanol (10 cm^3). The solution became clear on warming to 60°, and was filtered and reduced in volume to

* Systematic name: triphenyl(*P,P,P*-triphenylphosphine imidato-*N*)phosphorus(1+) chloride.

²³ Ruff, J. K., and Schlientz, W. J., *Inorg. Synth.*, 1974, **15**, 84.

²⁴ Schriver, D. F., 'The Manipulation of Air-sensitive Compounds' Ch. 7 (McGraw-Hill: New York 1969).

give white crystals of the product, m.p. 175° (dec.). The far-infrared spectrum of this compound was identical to that of the product of the first preparation.

Tetrabutylammonium Tris(2-methylpropane-2-thiolato)mercurate(II), [Bu₄N][Hg(SBu^t)₃]

2-Methylpropane-2-thiol (2.7 g, 29.6 mmol) was added to a mixture of 40% aqueous tetrabutylammonium hydroxide (13.7 g; contains 5.5 g, 21.1 mmol) and absolute ethanol (15 cm³) to produce a cloudy solution. To this was added bis(2-methylpropane-2-thiolato)mercury(II), Hg(SBu^t)₂ (2.7 g, 7.0 mmol), and the resulting mixture was stirred with heating until all the solid had dissolved. The clear solution was filtered and the volume of the filtrate was reduced to about 10 cm³, whereupon white crystals of the *product* formed. These were collected by filtration and dried under vacuum. M.p. 89–93° (Found: C, 47.3; H, 9.2; Hg, 28.9; N, 2.2. C₂₈H₆₃HgNS₃ requires C, 47.3; H, 8.9; Hg, 28.2; N, 2.0%).

Bis(triphenylphosphine)iminium Tris(2-methylpropane-2-thiolato)mercurate(II), [N(PPh₃)₂][Hg(SBu^t)₃]

2-Methylpropane-2-thiol (0.35 g, 3.9 mmol) was dissolved in a solution of sodium hydroxide (0.12 g, 3.0 mmol) in absolute ethanol (10 cm³). To the resulting solution was added [N(PPh₃)₂]Cl (0.45 g, 0.78 mmol), and bis(2-methylpropane-2-thiolato)mercury(II) (0.30 g, 0.79 mmol). The resulting mixture was heated to 60° and dimethylformamide (4.5 cm³) was added. The clear solution was filtered, and white crystals of the *product* formed on cooling. M.p. 215–225° (Found: C, 57.0; H, 5.4; N, 1.3. C₄₈H₅₇HgNP₂S₃ requires C, 57.3; H, 5.7; N, 1.4%).

Microanalyses

Microanalyses were carried out by Professor A. D. Campbell at the University of Otago, Dunedin, New Zealand.

Spectroscopy

Infrared spectra in the range 400–4000 cm⁻¹ were obtained with a Perkin–Elmer 397 spectrometer. Spectra were run on Nujol mulls between KBr plates, and were calibrated by using the spectrum of polystyrene. The far-infrared spectra (50–400 cm⁻¹) were obtained with a Grubb–Parsons Cube Mk II interferometer fitted with a 6.25 μm Mylar-film beam splitter. They were run on petroleum jelly mulls between polythene plates, and were calibrated by using the spectrum of water vapour. Far-infrared spectra at c. 125 K were recorded in the Grubb–Parsons GRM 01 low-temperature cell cooled with liquid nitrogen. Raman spectra were obtained with a Jasco R300 Raman spectrometer and were excited with a Control 540 argon ion laser (488.0 nm line) or a Coherent CR4 argon ion laser (514.5 nm line). The spectra of the solids were obtained from polycrystalline samples in glass capillary tubes, whereas solution samples were in glass cells.

¹H n.m.r. spectra were run at c. 308 K on a Varian T60 spectrometer.

X-Ray Crystallography

The available crystals of [Et₄N][Hg(SBu^t)₃] were not single. Crystals of [Et₄N]₂[Hg₂(SMe)₆], obtained from the preparation described above, were examined on a CAD4 diffractometer.

Crystal data.—C₂₂H₅₈Hg₂N₂S₆, *M* 944.26, colourless plates, triclinic, space group *P*1, *a* 8.656(5), *b* 9.130(6), *c* 12.368(8) Å, *α* 102.16(4), *β* 105.51(4), *γ* 105.29(4)°, *U* 865.9(1.1) Å³, *D_c* 1.81 g cm⁻³, *Z* 1, Mo *Kα* radiation, *λ* 0.71069 Å, *μ* 92.1 cm⁻¹, temperature 21°, scan mode *θ/2θ*, *2θ_{max}* 50°, 3047 intensity measurements, intensity decay 1 → 0.74 (corrected). Observed [*I* > 3σ(*I*)] reflections 2593.

Computational procedures were standard, and have been described previously.²⁵ Mercury and sulfur atom positions were determined by Patterson methods, and other non-hydrogen atoms were located by Fourier methods. Least-squares refinement of *F*, with *w* = [σ(*F_o*)]⁻², converged at *R* 0.088 with all atoms isotropic, at which stage a difference synthesis revealed 22 of the 29 hydrogen atoms. Methylene hydrogen atoms were included at calculated positions, and all methyl hydrogen

²⁵ Dance, I. G., *Inorg. Chem.*, 1981, **20**, 1487.

atoms were included after idealization of and addition to the locations indicated by the difference map. All hydrogen atoms were assigned isotropic temperature factors equal to those of the carbon atoms to which they were bonded.

Refinement was completed with anisotropic thermal parameters for the non-hydrogen atoms, converging at R 0.034, R_w 0.042. Standard scattering curves for neutral atoms, and corrections for anomalous dispersion for mercury and sulfur, were from International Tables.²⁶

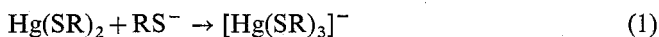
A difference electron-density map based on the final atomic parameters showed three peaks greater than $2 e \text{ \AA}^{-3}$. One of these (of height $5 e \text{ \AA}^{-3}$) was at the mercury position, and the other two ($2.5 e \text{ \AA}^{-3}$) were within 1.3 \AA of the mercury. These probably arise as a result of inadequate correction for decomposition of the crystal during data collection.

Atomic coordinates are listed in Table 1 (the atom labelling within the anion is shown in Fig. 1). Atomic thermal parameters, together with observed and calculated structure factors, are deposited as an Accessory Publication.*

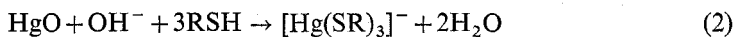
Results and Discussion

Preparation of Compounds

The complexes were prepared in ethanol by reaction of $\text{Hg}(\text{SR})_2$ with RS^- according to



or by reaction of HgO with RSH and OH^- according to



Tris(thiolato)mercurates(II), $[\text{Cat}] [\text{Hg}(\text{SR})_3]$, were crystallized from solutions containing the appropriate organic cation Cat^+ . As in the preparation of thiolato-cuprates(I) and -argentates(I) by similar methods,²⁷ it was found necessary to use an excess of thiolate over that required by the above equations. In preparations involving reaction (1), for example, it was found that 1:1 mole ratio of RS^- to $\text{Hg}(\text{SR})_2$ was insufficient to allow complete dissolution of the $\text{Hg}(\text{SR})_2$ under the experimental conditions used. Mole ratios of RS^- to $\text{Hg}(\text{SR})_2$ in the range 2.0–5.0 were used, but the only solids to crystallize from these reaction mixtures were the tris(thiolato)mercurates(II). This contrasts with the situation found by Liesk and Klar⁷ in the preparation of $[\text{Ph}_4\text{P}] [\text{Hg}(\text{SPh})_3]$ where a 1:1 mole ratio of PhS^- to $\text{Hg}(\text{SPh})_2$ was used, and a 2:1 mole ratio produced the tetrakis(thiolato)mercurate(II) $[\text{Ph}_4\text{P}]_2 [\text{Hg}(\text{SPh})_4]$. However, this is possibly a function of the solvent, since these workers used liquid ammonia as the solvent for the initial reactions, and the crude $[\text{Ph}_4\text{P}]_2 [\text{Hg}(\text{SPh})_4]$ was recrystallized from chloroform. When this compound was dissolved in methanol it decomposed to $[\text{Ph}_4\text{P}] [\text{Hg}(\text{SPh})_3]$ and $[\text{Ph}_4\text{P}] [\text{SPh}]$.⁷ However, reaction of 4 equiv. of 4-chlorobenzenethiol and triethylamine with 1 equiv. of mercuric nitrate in alcohols readily yielded $[\text{Hg}(\text{SC}_6\text{H}_4\text{Cl})_4]^{2-}$, as the Me_4N^+ salt.⁶

Solutions of $[\text{Et}_4\text{N}] [\text{Hg}(\text{SR})_3]$ ($\text{R} = \text{Me}, \text{Bu}^t$) in pyridine are air-sensitive, a strong singlet appearing at δ 2.03 in the ^1H n.m.r. spectra of both compounds in the presence of air (see Experimental).

* Copies are available on application to the Editor-in-Chief, Editorial and Publications Service, CSIRO, 314 Albert Street, East Melbourne, Vic. 3002.

²⁶ Ibers, J. A., and Hamilton, W. C., (Eds) 'International Tables for X-Ray Crystallography' Vol. 4, Tables 2.2A and 2.3.1 (Kynoch Press: Birmingham 1974).

²⁷ Bowmaker, G. A., and Tan, L.-C., *Aust. J. Chem.*, 1979, **32**, 1443.

Table 1. Atomic coordinates for $[\text{Et}_4\text{N}]_2 [(\text{MeS})_2\text{Hg}(\mu\text{-SMe})_2\text{Hg}(\text{SMe})_2]$

Atom	x	y	z	Atom	x	y	z
Hg	0.6057(0)	0.1073(0)	0.6557(0)	H2(C1)	0.8929	-0.1442	0.5117
S(1)	0.7246(2)	0.0231(2)	0.4866(2)	H3(C1)	0.6907	-0.2522	0.4539
S(2)	0.6432(2)	-0.0672(2)	0.7816(2)	H2(C2)	0.3704	-0.2430	0.6567
S(3)	0.6712(3)	0.3925(3)	0.7390(2)	H3(C2)	0.4799	-0.3387	0.7276
C(1)	0.7752(10)	-0.1514(10)	0.5143(7)	H2(C3)	0.8170	0.4250	0.6057
C(2)	0.4842(13)	-0.2562(11)	0.6865(9)	H3(C3)	0.8500	0.5808	0.6825
C(3)	0.7456(13)	0.4817(12)	0.6375(10)	H1(C11)	0.2605	0.4193	0.9859
N	0.2121(6)	0.1922(7)	0.8757(5)	H2(C11)	0.2678	0.2950	1.0554
C(11)	0.1995(9)	0.3059(9)	0.9796(6)	H2(C21)	0.0221	0.3694	1.0493
C(21)	0.0188(10)	0.2890(10)	0.9786(7)	H3(C21)	-0.0416	0.1766	0.9755
C(12)	0.1032(9)	0.1966(9)	0.7579(7)	H1(C12)	-0.0205	0.1485	0.7469
C(22)	0.1370(12)	0.3586(11)	0.7415(8)	H2(C12)	0.1192	0.1236	0.6923
C(13)	0.1489(9)	0.0249(9)	0.8845(7)	H2(C22)	0.1093	0.4307	0.8028
C(23)	0.1768(11)	-0.1022(10)	0.7975(7)	H3(C22)	0.0504	0.3551	0.6674
C(14)	0.3949(9)	0.2380(9)	0.8814(7)	H1(C13)	0.0243	-0.0072	0.8756
C(24)	0.5213(9)	0.2357(11)	0.9920(8)	H2(C13)	0.2053	0.0232	0.9676
H1(C1)	0.7743	-0.1572	0.5986	H2(C23)	0.1538	-0.2056	0.8177
H1(C2)	0.5217	-0.2905	0.6135	H3(C23)	0.3010	-0.0750	0.8084
H1(C3)	0.6736	0.5049	0.5741	H1(C14)	0.4330	0.3469	0.8710
H1(C21)	-0.0472	0.3125	0.8967	H2(C14)	0.4042	0.1680	0.8105
H1(C22)	0.2343	0.4061	0.7430	H2(C24)	0.4689	0.1405	1.0156
H1(C23)	0.1140	-0.1249	0.7159	H3(C24)	0.5539	0.3358	1.0567
H1(C24)	0.6285	0.2248	0.9745				

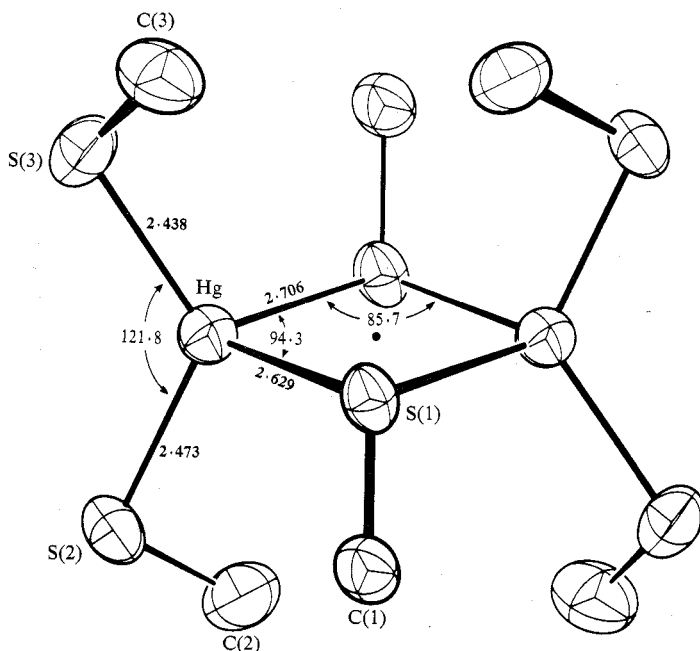
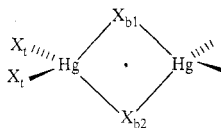


Fig. 1. The centrosymmetric $[\text{Hg}_2(\text{SMe})_6]^{2-}$ ion. Thermal vibrations are represented by 50% probability ellipsoids. (Distances in Å, angles in degrees.)

Table 2. Bond lengths and angles for $[\text{Et}_4\text{N}]_2[\text{Hg}_2(\text{SMe})_6]$

Atoms	Distance (Å)	Atoms	Angle (degrees)
Hg-S(1)	2.629(2)	S(1)-Hg-S(1) ^A	94.27(5)
Hg-S(1) ^A	2.706(2)	S(1)-Hg-S(2)	106.98(6)
Hg-S(2)	2.473(2)	S(1)-Hg-S(3)	116.09(7)
Hg-S(3)	2.438(2)	S(2)-Hg-S(1) ^A	104.94(6)
S(1)-C(1)	1.834(8)	S(2)-Hg-S(3)	121.87(7)
S(2)-C(2)	1.811(10)	S(3)-Hg-S(1) ^A	108.68(7)
S(3)-C(3)	1.800(10)	Hg-S(1)-Hg ^A	85.73(5)
		Hg-S(1)-C(1)	101.8(3)
		Hg ^A -S(1)-C(1)	102.3(3)
		Hg-S(2)-C(2)	101.4(3)
		Hg-S(3)-C(3)	105.2(4)
N-C(11)	1.522(9)	C(11)-N-C(12)	112.3(5)
N-C(12)	1.525(9)	C(11)-N-C(13)	107.6(5)
N-C(13)	1.519(9)	C(11)-N-C(14)	108.9(5)
N-C(14)	1.504(9)	C(12)-N-C(13)	108.5(5)
		C(12)-N-C(14)	108.6(5)
		C(13)-N-C(14)	111.1(5)
C(11)-C(21)	1.53(1)	N-C(11)-C(21)	115.5(6)
C(12)-C(22)	1.50(1)	N-C(12)-C(22)	114.9(6)
C(13)-C(23)	1.53(1)	N-C(13)-C(23)	114.7(6)
C(14)-C(24)	1.51(1)	N-C(14)-C(24)	115.7(6)

^A 1-x, -y, 1-z.Table 3. Comparison of dimensions of centrosymmetric $[\text{Hg}_2\text{X}_6]^{2-}$, X = SMe, Cl

Atoms	X = SMe (Et_4N^+) ^A	(Bu_4N^+) ^B	X = Cl (tff^+) ^C
	Distances (Å)		
Hg-X _{b1}	2.629(2)	2.587(4)	2.600(5)
Hg-X _{b2}	2.706(2)	2.662(5)	2.696(5)
Hg-X _t	2.438(2), 2.473(2)	2.387(6), 2.390(5)	2.381(5), 2.386(5)
Angles (degrees)			
X _{b1} -Hg-X _{b2}	94.3(1)	87.7(2)	90.1(2)
X _t -Hg-X _t	121.8(1)	121.5(2)	132.2(2)
X _t -Hg-X _{b1}	107.0(1), 116.1(1)	108.4(2), 118.1(2)	106.4(2), 111.3(2)
X _t -Hg-X _{b2}	105.0(1), 108.7(1)	103.8(2), 111.9(2)	98.9(2), 109.1(2)

^A This work.^B Goggin, P. L., King, P., McEwan, D. M., Taylor, G. E., Woodward, P., and Sandström, M., *J. Chem. Soc., Dalton Trans.*, 1982, 875.^C Tetrathiafulvalene radical cation; Kistenmacher, T. J., Rossi, M., Chiang, C. C., van Duyne, R. P., and Siedle, A. R., *Inorg. Chem.*, 1980, **19**, 3604.

Structure of $[\text{Et}_4\text{N}]_2 [\text{Hg}_2(\text{SMe})_6]$

The structure of the centrosymmetric bitetrahedral $[(\text{MeS})_2\text{Hg}(\mu\text{-SMe})_2\text{Hg}(\text{SMe})_2]^{2-}$ molecular anion is shown in Fig. 1. The methyl substituents on the sulfur atoms of the planar HgS_2Hg bridge adopt the *anti* configuration, and the conformations of the methyl substituents at the terminal thiolate ligands are such that each $\text{Hg}(\text{S}-\text{C})_4$ coordination tetrahedron has pseudo- S_4 symmetry* about the Hg-Hg vector. The complete anion has pseudo- C_{2h} symmetry.

At the bridging thiolate the angle between the S-C bond and the HgSHg plane is unusually large, 73.5° . At the terminal thiolates the conformational torsional angles are $\text{C}(2)-\text{S}(2)-\text{Hg}-\text{S}(1')$ 28.1° and $\text{C}(3)-\text{S}(3)-\text{Hg}-\text{S}(1)$ 14.0° . The angle between the $\text{S}(1)-\text{Hg}-\text{S}(1')$ and $\text{S}(2)-\text{Hg}-\text{S}(3)$ planes is 91.3° .

Molecular dimensions are listed in Table 2. Bond angles at mercury are distorted by the bridge constraints, $\text{S}_{\text{br}}-\text{Hg}-\text{S}_{\text{br}}$ 94.3° . The bond distances at mercury are also distorted, in addition to the normal elongation by *c.* 0.2 \AA of the bridging Hg-S distance relative to the terminal Hg-S distance. The two independent Hg-S_{br} distances, $2.629(2)$ and $2.706(2) \text{ \AA}$, are significantly different. A corresponding differentiation by *c.* 0.1 \AA of apparently equivalent Hg-Cl_{br} bonds occurs in $[\text{Hg}_2\text{Cl}_6]^{2-}$ with the Bu_4N^+ cation²² and the tetrathiafulvalene radical cation.²⁸ There is close correspondence of all individual distances and angles in $[\text{Hg}_2(\text{SMe})_6]^{2-}$ and $[\text{Hg}_2\text{Cl}_6]^{2-}$, as shown in Table 3. In comparable complexes $(\text{Ph}_3\text{PSe})\text{Hg}_2\text{Cl}_4$ ²⁹ and $(\text{Ph}_3\text{P})_2\text{-Cu}(\mu\text{-SPh})_2\text{Cu}(\text{PPh}_3)_2$ ³⁰ the dissymmetry of otherwise equivalent bridge bonds amounts to 0.18 and 0.07 \AA respectively. In contrast, there is no significant differentiation of Zn-S_{br} distances in $[\text{Cl}_2\text{Zn}(\mu\text{-SR})_2\text{ZnCl}_2]^{2-}$ ($\text{R} = \text{C}_5\text{H}_9\text{NHMe}$).³¹

We have examined the crystal environment of the $[\text{Hg}_2(\text{SMe})_6]^{2-}$ ion for dissymmetry which might be responsible for the observed slight dissymmetry of bridge bonding, but can find no extramolecular explanation. It may be that this dissymmetry of $\text{Hg}(\mu\text{-X})_2\text{Hg}$ bridging with $\text{X} = \text{Cl}^-$ or ^-SMe has an inherent bonding origin, although it is not mentioned in Hoffmann's comprehensive study of tetrahedral M_2L_6 molecules.³² (The bridge dissymmetry in two $[\text{Cu}_2(\text{H}_2\text{NCSNH}_2)_6]^{2+}$ structures can be readily rationalized through the lower electronic symmetry of the bridging ligand.³³)

Vibrational Spectra

Selected far-infrared (i.r.) and low-wavenumber Raman (R) spectra are shown in Figs 2 and 3 respectively, and band assignments are listed in Table 4.

The low-wavenumber vibrational spectra of $[\text{Et}_4\text{N}]_2 [\text{Hg}_2(\text{SMe})_6]$ (Figs 2a and 3a) are similar to those of halogeno complexes of the type $[\text{Hg}_2\text{X}_6]^{2-}$, and can be assigned in the same way. The best comparison is with $[\text{Bu}_4\text{N}]_2 [\text{Hg}_2\text{Cl}_6]$, since the $\nu(\text{HgCl})$

* The full $[\text{Hg}(\text{SC}_6\text{H}_4\text{Cl})_4]^{2-}$ ion has pseudo- D_{2d} molecular symmetry.⁶

²⁸ Kistenmacher, T. J., Rossi, M., Chiang, C. C., van Duyne, R. P., and Siedle, A. R., *Inorg. Chem.*, 1980, **19**, 3604.

²⁹ Glasser, L. S. D., Ingram, L., King, M. G., and McQillan, G. P., *J. Chem. Soc. A*, 1969, 2501.

³⁰ Dance, I. G., Guerny, P. J., Rae, A. D., and Scudder, M. L., *Inorg. Chem.*, 1983, **22**, 2883.

³¹ Briansó, M. C., Briansó, J. L., Gaete, W., Ros, J., and Suner, C., *J. Chem. Soc., Dalton Trans.*, 1981, 852.

³² Summerville, R. H., and Hoffman, R., *J. Am. Chem. Soc.*, 1976, **98**, 7240.

³³ Taylor, I. F., Jr, Weininger, M. S., and Amma, E. L., *Inorg. Chem.*, 1974, **13**, 2835.

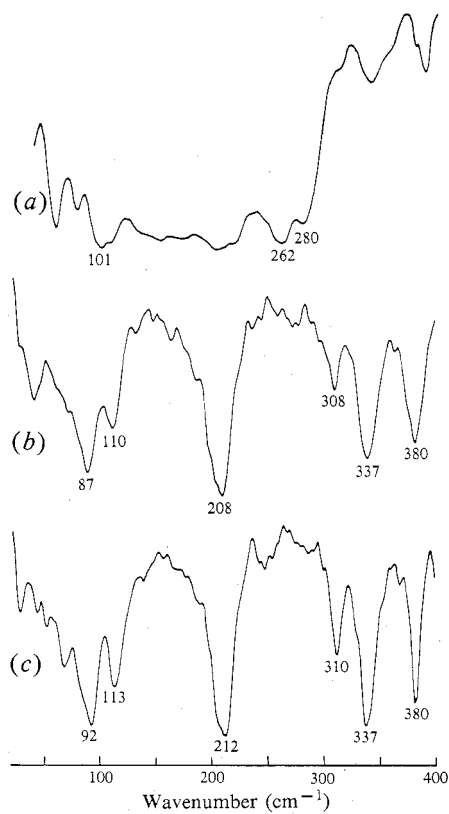
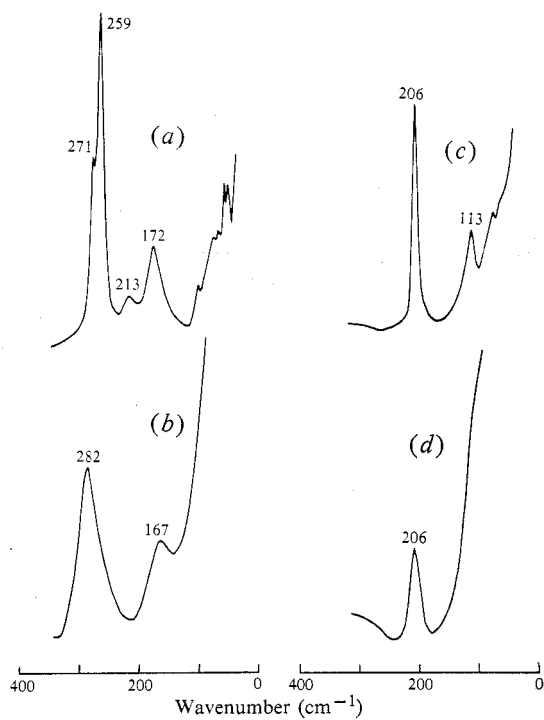


Fig. 2. Far-infrared spectra of:
 (a) $[\text{Et}_4\text{N}]_2 [\text{Hg}_2(\text{SMe})_6]$ at 125 K;
 (b) $[\text{Et}_4\text{N}] [\text{Hg}(\text{SBu}^t)_3]$ at 298 K;
 (c) $[\text{Et}_4\text{N}] [\text{Hg}(\text{SBu}^t)_3]$ at 125 K.

Fig. 3. Raman spectra (at 298 K) of:
 (a) $[\text{Et}_4\text{N}]_2 [\text{Hg}_2(\text{SMe})_6]$ (solid);
 (b) $[\text{Et}_4\text{N}] [\text{Hg}(\text{SMe})_3]$ (ethanol solution);
 (c) $[\text{Et}_4\text{N}] [\text{Hg}(\text{SBu}^t)_3]$ (solid);
 (d) $[\text{Et}_4\text{N}] [\text{Hg}(\text{SBu}^t)_3]$ (ethanol solution).



frequencies are similar to the $\nu(\text{HgS})$ frequencies in the thiolate complex. Thus the bands at 280 and 262 cm^{-1} in the infrared spectrum and at 271 and 259 cm^{-1} in the Raman spectrum can be assigned as $\nu(\text{HgS})$ vibrations of the terminal Hg-S groups. The bands between 250 and 180 cm^{-1} are assigned as $\nu(\text{HgS})$ modes involving the bridging thiolate groups. As in the case of the $[\text{Hg}_2\text{Cl}_6]^{2-}$ complex,²² the bridging modes are of comparable intensity to the terminal modes in the infrared spectrum, but are much weaker in the Raman spectrum.

Table 4. Bands (cm^{-1}) assigned to $\nu(\text{CS})$, $\nu(\text{HgS})$ and $\delta(\text{SHgS})$ vibrations

Compound	Method	$\nu(\text{CS})$		$\nu(\text{HgS})$		$\delta(\text{SHgS})$	
		I.r.	R	I.r.	R	I.r.	R
[Et ₄ N] [Hg(SMe) ₃]	solid	698	697	A	271	A	172
		690	692		259		
	EtOH solution		700		282		167
[Et ₄ N] [Hg(SBu ^t) ₃]	solid	584	592	206	208	110	113
				180		87	
	EtOH solution				206		
[Bu ₄ N] [Hg(SBu ^t) ₃]	solid	585	590	201	203	95	
[N(PPh ₃) ₂] [Hg(SBu ^t) ₃]	solid		588	212	211	114	112
						91	
[Ph ₄ P] [Hg(SPh) ₃] ^B	solid			178	180		
				158			

^A Several overlapping absorption bands in the range 60–280 cm^{-1} (Fig. 2).

^B Ref. 7.

The Raman spectrum (Fig. 3b) of [Et₄N]₂ [Hg₂(SMe)₆] dissolved in ethanol is significantly different from that (Fig. 3a) of the solid. Only two bands at 282 and 167 cm^{-1} are observed. The disappearance of the $\nu(\text{HgS})$ bridging mode at 213 cm^{-1} suggests that the $[\text{Hg}_2(\text{SMe})_6]^{2-}$ complex dissociates on dissolution to give a mono-nuclear $[\text{Hg}(\text{SMe})_3]^-$ species. The increase in the frequency of the $\nu(\text{HgS})$ terminal modes from 260–270 to 282 cm^{-1} also suggests a change in structure on dissolution, and is consistent with a change from fourfold to threefold coordination of the mercury. The possibility that the dissociation is more extensive, leading to the formation of $\text{Hg}(\text{SMe})_2$ and MeS^- , can be ruled out since the frequency of the symmetric $\nu(\text{HgS})$ mode of $\text{Hg}(\text{SMe})_2$ is 298 cm^{-1} ,^{34–36} significantly higher than the value 282 cm^{-1} found in the Raman spectrum of the solution. The most likely structure for an $[\text{Hg}(\text{SMe})_3]^-$ species would be one with trigonal planar coordination of the mercury atom. If the local symmetry of the HgS_3 group is considered to be D_{3h} , the predicted symmetry and activity of the vibrations of this group are $A_1'(\text{R})$ and $E'(\text{i.r.},\text{R})$ (HgS stretches), $E'(\text{i.r.},\text{R})$ (in-plane bend), and $A_2''(\text{i.r.})$ (out-of-plane bend). There should therefore be three bands in the Raman spectrum, but only two are observed. The separation in frequency seems too large for these to be both due to $\nu(\text{HgS})$ modes, so the 167 cm^{-1} band is assigned as the E' in-plane bending mode $\delta(\text{SHgS})$. The 282 cm^{-1} Raman band is probably due to the A_1' $\nu(\text{HgS})$ mode, the E' stretching

³⁴ Canty, A. J., Kishimoto, R., Deacon, G. B., and Farquharson, G. J., *Inorg. Chim. Acta*, 1976, **20**, 161.

³⁵ Biscarini, P., Fusina, L., and Nivelini, G., *J. Chem. Soc., Dalton Trans.*, 1974, 2140.

³⁶ Iwasaki, N., Tomooka, J., and Toyoda, K., *Bull. Chem. Soc. Jpn*, 1974, **47**, 1323.

mode being much weaker (as in the case of $[\text{HgI}_3]^-$ in $[\text{Bu}_4\text{N}][\text{HgI}_3]^{22}$) or accidentally degenerate with the A_1' mode. Similar results were obtained for the $[\text{Hg}(\text{SBU})_3]^-$ complex (see below).

There are two very sharp $\nu(\text{CS})$ bands, split by about 7 cm^{-1} , in the infrared and Raman spectra of solid $[\text{Et}_4\text{N}]_2[\text{Hg}_2(\text{SMe})_6]$. This splitting is most likely to be due to the presence of the two different bonding modes (terminal and bridging), and this splitting disappears in the Raman spectrum of the solution. This further supports the conclusion that the bridged structure breaks down on dissolution to give mononuclear $[\text{Hg}(\text{SMe})_3]^-$ species.

The far-infrared and Raman spectra of $[\text{Et}_4\text{N}][\text{Hg}(\text{SBU})_3]$ in the solid state at room temperature (Figs 2b and 3c) show bands in the $290\text{--}400\text{ cm}^{-1}$ region which can be assigned to internal vibrations of the thiolate ligand,^{34,37} and very strong $\nu(\text{HgS})$ bands at $206\text{--}208\text{ cm}^{-1}$. $\nu(\text{HgS})$ vibrations in $\text{Hg}(\text{SBU})_2$ have been assigned at 172 cm^{-1} (i.r.) and 188 cm^{-1} (R) in the solid,³⁴ and at 246 cm^{-1} (i.r.) and 223 cm^{-1} (R) in pyridine solution.³⁵ The reason for the low values in the solid state is that solid $\text{Hg}(\text{SBU})_2$ is an infinite polymer in which the mercury atoms are bridged by thiolate groups; this results in a coordination number of four for mercury.³⁸ Thus, the present assignment of $\nu(\text{HgS})$ at $206\text{--}208\text{ cm}^{-1}$ for $[\text{Hg}(\text{SBU})_3]^-$, involving three-coordinate mercury, lies between the values for two- and four-coordinate mercury in $\text{Hg}(\text{SBU})_2$. A solution of $[\text{Et}_4\text{N}][\text{Hg}(\text{SBU})_3]$ in EtOH shows a strong $\nu(\text{HgS})$ band unshifted from the value 206 cm^{-1} for the solid. This indicates that the same $[\text{Hg}(\text{SBU})_3]^-$ species is present in the solid and solution phases.

Previous workers have reported that $[\text{Ph}_4\text{P}][\text{Hg}(\text{SPh})_3]$ shows two $\nu(\text{HgS})$ bands in the infrared at 178 and 158 cm^{-1} , and on the basis of this observation they concluded that the complex had trigonal pyramidal rather than trigonal planar HgS_3 coordination geometry.⁷ The observation of only a single $\nu(\text{HgS})$ band at 208 cm^{-1} in the infrared spectrum of $[\text{Et}_4\text{N}][\text{Hg}(\text{SBU})_3]$ suggests that this complex has trigonal planar HgS_3 geometry. As in the case of the $\text{Hg}(\text{SMe})_3^-$ ion (see above), the Raman spectrum should contain two $\nu(\text{HgS})$ bands rather than the single one observed. However, it is likely that this is due to accidental coincidence of the A_1' and E' $\nu(\text{HgS})$ modes, since the strongest Raman band is expected to correspond to the totally symmetric A_1' mode, but the frequency of the Raman band is almost coincident with that of the infrared band, which must be the E' mode. Near coincidence of this type has previously been found to occur for the infrared- and Raman-active $\nu(\text{AuS})$ modes in $[\text{Au}(\text{SMe})_2]^-$ and $[\text{Au}(\text{SCN})_2]^-$.^{39,40} Thus, the results can be most readily explained in terms of trigonal planar HgS_3 geometry. Essentially the same conclusions apply to the compound $[\text{Bu}_4\text{N}][\text{Hg}(\text{SBU})_3]$, the only difference being a slight shift of the $\nu(\text{HgS})$ modes to lower frequency.

The Raman spectrum of the solution containing $[\text{Hg}(\text{SMe})_3]^-$ (Fig. 3b) is similar in appearance to that of $[\text{Et}_4\text{N}][\text{Hg}(\text{SBU})_3]$ (Fig. 3c). The ratio of the $\nu(\text{MS})$ frequencies $282/206 = 1.4$ is the same as that previously observed for $[\text{Au}(\text{SMe})_2]^-$ and $[\text{Au}(\text{SBU})_2]^-$,³⁹ and is equal to the ratio of the square roots of the masses of the ligands. The band at 113 cm^{-1} in the Raman spectrum of $[\text{Et}_4\text{N}][\text{Hg}(\text{SBU})_3]$ appears

³⁷ Gaufres, R., Perez, A., and Bribes, J. L., *Bull. Soc. Chim. Fr.*, 1971, 2898.

³⁸ Kunchur, N. R., *Nature (London)*, 1964, **204**, 468.

³⁹ Bowmaker, G. A., and Dobson, B. C., *J. Chem. Soc., Dalton Trans.*, 1981, 267.

⁴⁰ Bowmaker, G. A., and Rogers, D. A., *J. Chem. Soc., Dalton Trans.*, 1982, 1873.

to be the counterpart of the 167 cm^{-1} band in $[\text{Hg}(\text{SMe})_3]^-$, and is therefore assigned as the in-plane bending mode of the HgS_3 group. The infrared spectrum (Fig. 2*b*) contains a corresponding band at 110 cm^{-1} , and an additional band at 87 cm^{-1} which is tentatively assigned as the out-of-plane bending mode (infrared-active only). A slight shift to higher wavenumber and some splitting of the bands in the 100 cm^{-1} region occurs on cooling the sample to 120 K, and additional bands (possibly lattice modes) below 80 cm^{-1} become resolved at this temperature (Fig. 2*c*).

The vibrational spectra of $[\text{N}(\text{PPh}_3)_2][\text{Hg}(\text{SBu}^t)_3]$ are more difficult to assign than those of the Et_4N^+ and Bu_4N^+ salts due to interference by cation bands in the regions of interest. Nevertheless, bands at nearly the same wavenumbers occur in both compounds, and these are assigned in Table 4. There is no doubt about the assignment of the $\nu(\text{HgS})$ band in the Raman spectrum and the corresponding band in the far-infrared, as these are quite strong. This band occurs at almost exactly the same wavenumber in all three complexes, which indicates that the same anion is present in each.

Thus, the structures of tris(thiolato)mercurates in the solid state appear to depend on the nature of the thiolate group present. This parallels the situation for the neutral thiolates, $\text{Hg}(\text{SR})_2$, in the solid state, where essentially monomeric structures with two-coordinate mercury are found for $\text{R} = \text{Me}^{41}$ and Et^{42} and an infinite polymeric structure with four-coordinate mercury is found for $\text{R} = \text{Bu}^t^{38}$. In the case of the anionic complexes, the structure could also depend on the nature of the cation. It is generally found that anionic complexes with fewer bridging interactions are found in compounds where the cation size is large relative to that of the anion.⁴³ On this basis, and on the basis of the four-coordinate polymeric structure found for the neutral compound, it might have been expected that the Bu^tS^- complex could have been the one to show a polymeric structure in the solid, but the opposite situation is found, and the reason for this is not clear at present.

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⁴² Bradley, D. C., and Kunchur, N. R., *Can. J. Chem.*, 1965, **43**, 2786.

⁴³ Wells, A. F., 'Structural Inorganic Chemistry' 4th Edn, p. 920 (Clarendon Press: Oxford 1975).