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Synthesis and ^{199}Hg NMR Spectra of Adamantane-like $[(\mu\text{-SAlk})_{6-m}(\mu\text{-X})_m(\text{HgX})_4]^{2-}$ Anions and Structures of $(\text{Ph}_4\text{P})_2[(\mu\text{-SEt})_5(\mu\text{-Br})(\text{HgBr})_4]$ and $(\text{Et}_4\text{N})_2[(\mu\text{-I})(\mu\text{-SPr}^n)(\text{HgI}_2)_2]$

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The self-assembly method has been used to synthesize several salts of the type $(\text{Cat})_2[(\mu\text{-SAlk})_{6-m}(\mu\text{-X})_m(\text{HgX})_4]$ ($\text{Cat}^+ = \text{R}_4\text{N}^+, \text{Ph}_4\text{P}^+$; Alk = Et, Pr^i, Bu^n; X = Cl, Br, I; m = 0–2). Mercury-199 NMR data have been measured for these and other analogous complexes that were formed in situ. The adamantane-like structures of several complexes with m = 0 have been verified by metal NMR spectra of mixtures of $[(\mu\text{-SAlk})_6(\text{HgX})_4]^{2-}$ and $[\mu\text{-SAlk})_6(\text{MX})_4]^{2-}$ (M = Zn, Cd). Attempted recrystallization of various $(\text{Cat})_2[(\mu\text{-SAlk})_6(\text{HgX})_4]$ complexes gave products of different formulas: $(\text{Ph}_4\text{P})_2[\text{HgBr}_4]$ or $(\text{Ph}_4\text{P})_2[\text{Hg}_4(\text{SEt})_5\text{Br}_5]$ (**1**), depending on conditions, from $(\text{Ph}_4\text{P})_2[(\mu\text{-SEt})_6(\text{HgBr})_4]$; $(\text{Et}_4\text{N})_2[\text{HgI}_4]$ from $(\text{Et}_4\text{N})_2[(\mu\text{-SBu}^n)_6(\text{HgI})_4]$; $(\text{Et}_4\text{N})_2[\text{Hg}_2(\text{SPr}^n)\text{I}_5]$ (**2**) from $(\text{Et}_4\text{N})_2[(\mu\text{-SPr}^n)_6(\text{HgI})_4]$. The structures of **1** and **2** were determined by single-crystal X-ray diffraction methods. Compound **1** crystallizes in the monoclinic space group $C2/c$ with Z = 8. The crystal data for **1** are a = 46.599(5) Å, b = 12.775(2) Å, c = 25.582(3) Å, β = 116.50(1)°, V = 13629(3) Å^3, d(calcd) = 2.13, g·cm^{-3}, and R = 0.0766. In **1**, the anion contains a highly distorted adamantane-like core, $[(\mu\text{-S})_5(\mu\text{-Br})(\text{HgBr})_4]$, with five sulfur atoms and a bromine atom in the bridging positions. The ethyl groups attached to the sulfur atoms have the configuration of [aae,aee,ae,ae] (a = axial, e = equatorial) in the four cyclohexane-like chairs present in the anion. Compound **2** crystallizes with Z = 4 in the orthorhombic space group $Cmc2_1$. The crystal data are a = 12.408(2) Å, b = 17.339(4) Å, c = 16.964(4) Å, V = 3650(1) Å^3, d(calcd) = 2.50 g·cm^{-3}, and R = 0.0339. The anion has a symmetric dimeric structure in which the each mercury atom is bonded to two terminal iodine atoms and the two mercury atoms are bridged by one iodine and a propanethiolate ligand. The central four-membered ring has a "butterfly" conformation, with the Pr^n substituent in the endo (axial) position.

Introduction

For the elements of the zinc group, cadmium and zinc adamantane-like anions of the type $[(\mu\text{-SR})_6(\text{MX})_4]^{2-}$ (X = Cl–I) are well-established and isolable.[1] Analogous thiolato complexes of mercury might provide models for the mercury-binding site in mercury metallothioneins,[2] but there has been no reported isolation of such complexes.[3] There is evidence from NMR that adamantanoid anions $[(\mu\text{-SR})_6(\text{HgX})_4]^{2-}$ (R = Ph, Pr^n) exist in solution at reduced temperature.[6] These complexes dissociate at ambient probe temperature, but the nature of the dissociation products is not known with certainty. Tentatively, it has been suggested[6] that dissociation of the SPh$^-$ complexes give species containing both SPh$^-$ and X$^-$, while the S(Pr^n)$^-$ complexes give HgX_4^{2-} and $\text{Hg(SPr}^n)_2$.

The purpose of the present work was to characterize a more extensive series of complexes $[(\mu\text{-SAlk})_6(\text{HgX})_4]^{2-}$ in solution and to isolate representative members of the series if possible, as well as to investigate further the products of dissociation of these species.

During the course of this study, we discovered a new family of adamantanoid complexes of Hg(II) with both halides and thiolates in bridging positions, $[(\mu\text{-SR})_{6-m}(\mu\text{-X})_m(\text{HgX})_4]^{2-}$ (m = 1, 2). To our knowledge, the only analogues of this type of complex reported to date are $[(\mu\text{-EPh})_{6-m}(\mu\text{-I})_m(\text{CdI})_4]^{2-}$ (E = S, Se), which have been identified in solution by multi-NMR (^{77}Se, ^{113}Cd).[7]

Experimental Section

Materials and General Procedures. The compounds Hg(SR)_2 (R = Et, Pr^n, Pr^i, Bu^n, Cy[8]) were synthesized by the literature method.[9] All other starting materials were from commercial sources and were used as received. Solvents were dried over 3A molecular sieves. Solvents for use in synthesis or the preparation of NMR samples were deoxygenated by sparging with Ar.

Syntheses. $(\text{Bu}^n_4\text{N})_2[(\text{Hg}_4(\text{SEt})_6\text{I}_4]$. A mixture of HgI_2 (0.136 g, 0.30 mmol), Hg(SEt)_2 (0.291 g, 0.60 mmol), and Bu^n*NI* (0.222 g, 0.60 mmol) in CH_2Cl_2 (2 mL) was stirred for 20 min, producing a pale yellow solution. To this was added Et_2O (2 mL). Refrigeration of the $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture at 0 °C overnight produced two phases. The supernatant liquid was removed, and an additional 4 mL of Et_2O was added to the syrup that remained. Further refrigeration gave the product as a white solid, which was isolated by filtration and dried under vacuum at room temperature; yield 0.30 g (46%). Anal. Calcd for $\text{C}_{44}\text{H}_{102}\text{Hg}_4\text{I}_4\text{N}_2\text{S}_2$ (mol wt 2161.62): C, 24.45; H, 4.76; N, 1.30. Found: C, 24.95; H, 4.66; N, 1.15.

The following compounds were prepared in an identical manner.

$(\text{Bu}^n_4\text{N})_2[\text{Hg}_4(\text{SEt})_6\text{Br}_4]$ formed as a white solid; yield 51%. Anal. Calcd for $\text{C}_{44}\text{H}_{102}\text{Br}_4\text{Hg}_4\text{N}_2\text{S}_6$ (mol wt 1973.63): C, 26.78; H, 5.21; N, 1.42. Found: C, 26.49; H, 5.42; N, 1.32.

$(\text{Bu}^n_4\text{N})_2[\text{Hg}_4(\text{SPr}^i)_6\text{Br}_4]$ formed as white crystals; yield 76%. Anal. Calcd for $\text{C}_{50}\text{H}_{114}\text{Br}_4\text{Hg}_4\text{N}_2\text{S}_6$ (mol wt 2057.77): C, 29.18; H, 5.58; N, 1.36. Found: C, 28.98; H, 5.37; N, 1.56.

$(\text{Bu}^n_4\text{N})_2[\text{Hg}_4(\text{SPr}^i)_6\text{Cl}_4]$ formed as white crystals; yield 53%. Anal. Calcd for $\text{C}_{50}\text{H}_{114}\text{Cl}_4\text{Hg}_4\text{N}_2\text{S}_6$ (mol wt 1879.96): C, 31.94; H, 6.11; N, 1.49. Found: C, 31.62; H, 6.30; N, 1.89.

$(\text{Ph}_4\text{P})_2[\text{Hg}_4(\text{SEt})_6\text{Br}_4]$. This was prepared in a manner similar to that for $(\text{Bu}^n_4\text{N})_2[(\text{Hg}_4(\text{SEt})_6\text{I}_4]$, except that the product was obtained as white crystals following the first addition of Et_2O and refrigeration

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(1) For a recent review see: Dean, P. A. W.; Vittal, J. J. In *Metallothioneins*; Stillman, M. J., Shaw, C. F., III, Suzuki, K. T., Eds.; VCH: New York, 1992; Chapter 14.

(2) Stillman, M. J. In *Metallothioneins*; Stillman, M. J., Shaw, C. F., III, Suzuki, K. T., Eds.; VCH: New York, 1992; Chapter 4, p 105 ff, and references therein.

(3) *Cations* of the general type $[(\mu\text{-SR})_6(\text{HgL})_4]^{2+}$ (L = ER$'_3$; E = P, As) have been isolated[4] and the structure of $[(\mu\text{-SPh})_6(\text{HgPPh}_3)_4](\text{ClO}_4)_2\cdot 2\text{CHCl}_3$ has been determined.[5]

(4) Dean, P. A. W.; Vittal, J. J.; Trattner, M. H. *Inorg. Chem.* **1987**, *26*, 4245.

(5) Vittal, J. J.; Dean. P. A. W.; Payne, N. C. *Can. J. Chem.* **1993**, *71*, 2043.

(6) Dean, P. A. W.; Manivannan, V. *Inorg. Chem.* **1990**, *29*, 2997.

(7) Dean, P. A. W.; Vittal, J. J. Unpublished results quoted in ref 1.

(8) Cy = c-C_6H_{11}

(9) Wertheim, E. *J. Am. Chem. Soc.* **1929**, *51*, 3661.

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overnight; yield 97%. Anal. Calcd for $C_{60}H_{70}Br_4Hg_4P_2S_6$ (mol wt 2167.50): C, 33.25; H, 3.25. Found: C, 32.90; H, 2.95.

Prepared in the same way was **$(Et_4N)_2[Hg_4(SBu^n)_6I_4]$**, which formed as white crystals; yield 79%. Anal. Calcd for $C_{40}H_{94}Hg_4I_4N_2S_6$ (mol wt 2105.49): C, 22.82; H, 4.50; N, 1.33. Found: C, 22.60; H, 4.55; N, 1.36.

$(Et_4N)_2[Hg_4(SEt)_6Cl_4]$. A mixture of $HgCl_2$ (0.109 g, 0.40 mmol), $Hg(SEt)_2$ (0.387 g, 1.2 mmol), and $Et_4NCl \cdot H_2O$ (0.147 g, 0.80 mmol) in CH_2Cl_2 (6 mL) was stirred for 3 h. At the end of this time, a small amount of insoluble material was removed by filtration. Et_2O (6 mL) was added to the filtrate, and the CH_2Cl_2/Et_2O mixture was refrigerated overnight. The white crystals so produced were isolated by decantation, washed with Et_2O, and dried in vacuum at room temperature; yield 0.35 g (56%). Anal. Calcd for $C_{28}H_{70}Cl_4Hg_4N_2S_6$ (mol wt 1571.40): C, 21.40; H, 4.49; N, 1.78. Found: C, 21.35; H, 4.18; N, 1.83.

$(Ph_4P)_2[Hg_4(SEt)_5I_5]$. This was prepared as white crystals by starting with HgI_2 (0.60 mmol), $Hg(SEt)_2$ (1.0 mmol), and Ph_4PI (0.8 mmol) in CH_2Cl_2 (3 mL) and using the same procedure as for $(Ph_4P)_2[Hg_4(SEt)_6Br_4]$; yield 0.94 g (97%). Anal. Calcd for $C_{58}H_{65}Hg_4I_5P_2S_5$ (mol wt 2421.28): C, 28.77; H, 2.71. Found: C, 28.87; H, 2.40.

Prepared in the same way was **$(Ph_4P)_2[Hg_4(SEt)_5Br_5]$ (1)**, which formed as white crystals; yield 81%. Anal. Calcd for $C_{58}H_{65}Br_5Hg_4P_2S_5$ (mol wt 2186.28): C, 31.86; H, 3.00. Found: C, 32.10; H, 2.58. The same material (characterized by ^1H, ^{13}C, and ^{199}Hg NMR) was obtained when $(Ph_4P)_2[Hg_4(SEt)_6Br_5]$ (see above) was recrystallized from dilute $CHCl_3/Et_2O$.

$(Ph_4P)_2[Hg_4(SPr^i)_5I_5]$. This compound was prepared as white crystals from a mixture of HgI_2 (1 mmol), $Hg(SPr^i)_2$ (3 mmol), and Ph_4PI (2 mmol) in CH_2Cl_2 (5 mL) by following the procedure used for **1**; yield 49%. Anal. Calcd for $C_{63}H_{75}Hg_4I_5P_2S_5$ (mol wt 2491.41): C, 30.37; H, 3.03. Found: C, 30.18; H, 3.05.

The following compounds were prepared in a similar manner.

$(Bu^n{}_4N)_2[Hg_4(SPr^i)_5I_5]$ formed as white crystals; yield 51%. Anal. Calcd for $C_{47}H_{107}Hg_4I_5N_2S_5$ (mol wt 2306.64): C, 24.47; H, 4.68; N, 1.21. Found: C, 24.74; H, 4.67; N, 1.21.

$(Ph_4P)_2[Hg_4(SPr^i)_5Br_5]$ formed as white crystals; yield 56%. Anal. Calcd for $C_{63}H_{75}Br_5Hg_4P_2S_5$ (mol wt 2256.41): C, 33.54; H, 3.35. Found: C, 33.71; H, 3.25.

$(Bu^n{}_4N)_2[Hg_4(SPr^i)_5Cl_5]$. This was prepared in the same way as $(Et_4N)_2[Hg_4(SEt)_6Cl_4]$ but by using $HgCl_2$, $Hg(SPr^i)_2$, and $Bu^n{}_4NCl \cdot xH_2O$ in a 3:5:4 ratio; yield 24%, as white crystals. Anal. Calcd for $C_{47}H_{107}Cl_5Hg_4S_5$ (mol wt 1840.37): C, 30.67; H, 5.87; N, 1.52. Found: C, 31.10; H, 5.69; N, 1.70.

$(Ph_4P)_2[Hg_4(SBu^n)_4I_6]$. This was synthesized in the same manner as $(Ph_4P)_2[Hg_4(SPr^i)_5I_5]$ but by using HgI_2, $Hg(SBu^n)_2$, and Ph_4PI in a 1:1:1 ratio; yield 87%, as white crystals. Anal. Calcd for $C_{64}H_{76}Hg_4I_6P_2S_4$ (mol wt 2599.28): C, 29.57; H, 2.95. Found: C, 30.06; H, 2.87.

The stoichiometry of each of the preceding new compounds was confirmed by the cation:SR^- intensity ratio in its ^1H NMR spectrum. As well, the anion that each contained was authenticated by comparison of its reduced-temperature ^{199}Hg NMR spectrum with that of the analogous anion formed in situ (see Results and Discussion).

The tetranuclear anions undergo dissociation in solution at ambient probe temperature (see Results and Discussion). Therefore $^1H/^{13}C$ NMR chemical shifts of the new compounds recorded under these conditions are exchange averages that just provide evidence for the presence of the appropriate constituents (cation and SR^-). Typical $^1H/^{13}C$ NMR results have been deposited.[10]

The synthesis of $(Ph_4P)_2[Hg_4(SPr^i)_4Br_6]$ following the procedure used for $(Ph_4P)_2[Hg_4(SBu^n)_4I_6]$ gave a foamy white solid that was pure by ^1H, ^{13}C, and ^{199}Hg NMR but did not give satisfactory microanalytical results.

An attempted recrystallization of $(Ph_4P)_2[Hg_4(SEt)_6Br_4]$ (50 mg) by dissolving it in $CHCl_3$ (2 mL), layering on Et_2O (2 mL), then allowing the mixture to stand at room temperature for 2 days gave crystals of $(Ph_4P)_2[Hg_4(SEt)_5Br_5]$ (**1**) that were suitable for crystallography (see below). When MeOH was layered onto a dilute solution of crude $(Et_4N)_2[Hg_4(SEt)_6Br_4]$, a very poorly soluble crystalline product was obtained. A determination of the unit cell parameters by X-ray analysis showed the compound to be $(Et_4N)_2[HgBr_4]$.[11] Similarly, attempted recrystallizations of $(Ph_4P)_2[Hg_4(SEt)_6Br_4]$ from CH_2Cl_2/Et_2O at room temperature and of $(Et_4N)_2[Hg_4(SBu^n)_6I_4]$ from $CHCl_3/Et_2O$ at room temperature gave $(Ph_4P)_2[HgBr_4]$ and $(Et_4N)_2[HgI_4]$, respectively, as confirmed by their unit cell parameters.[12] The recrystallization of crude $(Et_4N)_2[Hg_4(SPr^n)_6I_4]$ (prepared in the same way as the Bu^nS^- analogue and characterized by $^1H/^{13}C$ NMR) was attempted at room temperature by layering Et_2O onto a solution of the Hg_4 compound in CH_2Cl_2. The crystalline product was **$(Et_4N)_2[Hg_2(SPr^n)I_5]$ (2)**, which was characterized by ^1H NMR and by the complete X-ray analysis given below.

NMR Spectra. Proton and ^{13}C NMR spectra were obtained at ambient probe temperature using a Varian Gemini-200 spectrometer system with solutions in 5 mm o.d. NMR tubes. The ^2D resonances of the deuterated solvents were used as field-frequency locks. For ^1H NMR the solvent residuals were used as internal references (δ_H = 1.93, 7.24, and 2.04 for CHD_2CN, $CHCl_3$, and $(CH_3)(CHD_2)CO$, respectively). The solvent signals were similarly used for ^{13}C NMR (δ_C = 1.3, 77.0, and 29.8 for CD_3CN, $CDCl_3$, and $(CD_3)_2CO$, respectively).

Cadmium-111 and ^{199}Hg NMR spectra[14] were measured with samples in 10 mm o.d. NMR tubes and without the use of a ^2D field-frequency lock.[6,16] For ^{111}Cd and ^{199}Hg, samples were referenced to external 0.1 M $Cd(ClO_4)_2(aq)$ and external pure $HgMe_2$, respectively, at ambient probe temperature by sample interchange. Cadmium-111 NMR spectra were obtained using Varian XL-200 and -300 spectrometer systems, the frequencies at the reference being 42.41 and 63.59 MHz on the lower and higher field instruments, respectively. A recent paper[16] gives typical conditions used to obtain ^{111}Cd NMR spectra. In the present work, satisfactory spectra were obtained by collection of $(1-2) \times 10^3$ transients. (Cadmium-111 (as opposed to slightly more sensitive[14] ^{113}Cd) was observed to alleviate problems with artifacts when Cd NMR spectra were recorded with the Varian XL-200 and -300 spectrometer systems.[16] No primary isotope effect is expected.) Most of the ^{199}Hg NMR spectra were measured using the XL-200 and -300 spectrometers, for which the frequencies at the reference were 35.83 and 53.72 MHz, respectively. Typically $(1-3) \times 10^3$ transients were collected using the following conditions: spectral window, 50 kHz; acquisition time and recycle time, 0.3 s; tip angle, 45° (ca. 8 μs on both instruments); size of data table, 32K (with zero-filling). Later ^{199}Hg NMR spectra were measured analogously using a Varian Gemini-200 spectrometer system for which the frequency at the reference was 35.84 MHz and the 45° pulse was ca. 5.5 μs. An appropriate exponential line broadening was applied to the raw FID; e.g., a line broadening of 50 Hz was used for the spectra given in Figure 1.

X-ray Structure Determinations. The crystals of $[(C_6H_5)_4P]_2[Hg_4Br_5(SC_2H_5)_5]$ (**1**) and $[(C_2H_5)_4N]_2[Hg_2I_5(S\text{-}n\text{-}C_3H_7)]$ (**2**) were examined by employing similar procedures, as given below. The densities were measured by the neutral buoyancy method. Measurements were made using an Enraf-Nonius CAD4F diffractometer[17] at room temperature (296 K). Three standard reflections were monitored at regular intervals of time. The data were processed using NRCVAX crystal structure programs[18] running on a SUN 3/80 workstation. The faces of the data crystals were indexed, and the distances among them were measured for a Gaussian absorption correction. The crystal systems and the Laue symmetries were determined from inspection of Niggli matrices and symmetry-equivalent reflections, respectively. Both the crystals have *C* centering (*hkl*, $h + k = 2n + 1$ were absent). The space groups were deduced from the systematic absences.[19] The structures were solved by direct methods using the software SHELXS-86[20] and subsequent difference Fourier routines and were refined by full-matrix least-squares

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(10) Supplementary material.

(11) Crystal system: orthorhombic; a = 11.180(1) Å, b = 21.297(4) Å, c = 11.000(3) Å at 296 K, (proposed) space group $P2_12_12_1$, Z = 4.

(12) **$(Ph_4P)_2[HgBr_4]$** crystal system: monoclinic; a = 11.303(1) Å, b = 19.757(2) Å, c = 20.757(3) Å, β = 92.57(1)° at 296 K, proposed space group *Cc* or *C*2/*c*, Z = 4, d(obs) = 1.76(5) $g \cdot cm^{-3}$. **$(Et_4N)_2[HgI_4]$** crystal system: tetragonal; a = 13.99(8) Å, c = 14.80(8) Å at 296 K, isomorphous with $(Et_4N)_2[CdI_4]$[13a] and $(Et_4N)_2[FeI_4]$,[13b] both of which contain $[MI_4]^{2-}$ anions.

(13) (a) Vittal, J. J.; Yang, W.; Dean, P. A. W. Unpublished observations. (b) Pohl, S. Personal communication, Univrsity of Oldenberg.

(14) For the nuclei ^{111}Cd, ^{113}Cd, and ^{199}Hg, the percent natural abundances and receptivities relative to ^{13}C are 12.75 and 6.97, 12.26 and 7.67, and 16.84 and 5.57.[15]

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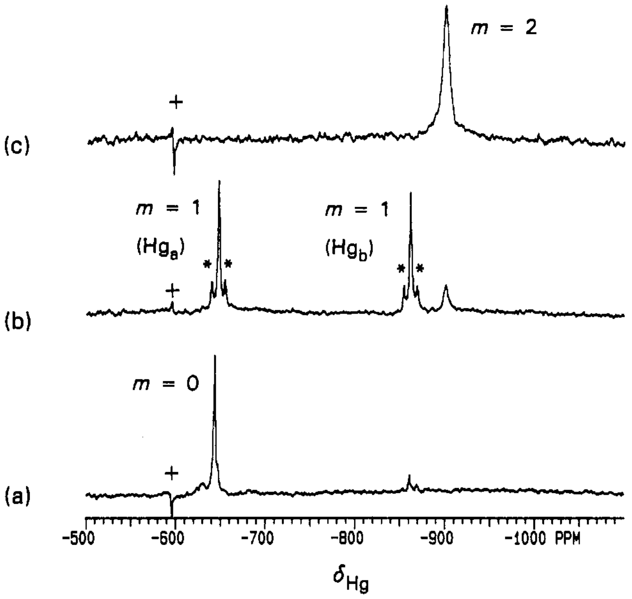

Figure 1. $^{199}Hg\{^1H\}$ NMR spectra of $HgBr_2/Hg(SPr^i)_2/(Ph_4P)Br$ mixtures in CH_2Cl_2 at 183 K, showing the formation of $[(\mu\text{-}SPr^i)_{6-m}(\mu\text{-}Br)_m(HgBr)_4]^{2-}$. $HgBr_2{:}Hg(SPr^i)_2{:}(Ph_4P)Br$ = (a) 1:3:2, (b) 1.5:2.5:2, (c) 1:1:1. * = ^{199}Hg satellite; + = artifact.

techniques on F using SHELX-76[21] software. All hydrogen atoms were placed in the calculated positions (C–H = 0.95 Å). They were included for the structure factor calculations only. A common temperature factor was assigned for all the hydrogen atoms.

Crystal 1. Colorless, hexagonal-rod shaped single crystals of the compound $(Ph_4P)_2[Hg_4Br_5(SC_2H_5)_5]$ were produced from $(Ph_4P)_2[Hg_4Br_4(SEt)_6]$ in a CH_2Cl_2/Et_2O mixture by the diffusion method. The data crystal (with approximate dimensions, 0.12 × 0.2 × 0.25 mm) was mounted with epoxy resin at the end of a glass fiber and used for the diffraction experiments. The intensity data were collected using Cu Kα radiation (λ = 1.541 84 Å) with a nickel filter. The cell dimensions (a = 46.599(5) Å, b = 12.775(2) Å, c = 25.582(3) Å, β = 116.50(1)°, V = 13629(3) Å^3, Z = 8) were obtained from least-squares refinement of 21 high-angle ($48.1 \leq 2\theta \leq 57.6°$) reflections. A total of 7527 data were collected in the 2θ range 0–100° ($-1 \leq h \leq 46$, $-1 \leq k \leq 12$, $-25 \leq l \leq 25$), with a scan speed from 0.82- to 4.12° min^{-1}. The maximum and minimum transmission factors were 0.208 and 0.029 (μ = 210.7 cm^{-1}). The systematic absences indicated that the space group could be either $C2/c$ (No. 15) or Cc (No. 9). The distribution of E suggested[20] a centric space group. The mean absolute $e^2 - 1$ observed was 0.968 (expected for centric, 0.999, and acentric, 0.736). For Z = 8, therefore, the space group $C2/c$, was assumed and the correctness of the choice of the space group was confirmed by successful solution and refinement of the structure. Equivalent reflections were averaged (R_{int} = 0.034), leaving 3495 ($I \geq 2.5\sigma(I)$) unique reflections. The phenyl rings were treated as regular hexagons with C–C distances of 1.395 Å. During the least-squares refinements, the phenyl rings containing the carbon atoms C(31)–C(36), C(61)–C(66), C(71)–C(76), and C(81)–C(86) and all the ethyl groups but one (C(131) and C(132)) showed high thermal motions and a wide range of unacceptable C–C distances and angles, indicating the possibility of disorder in these groups. A sensible orientational disorder model was achieved for only one carbon atom (C(242)) and refined. For the rest of the ethyl carbon atoms the disorder could not be resolved due to smearing of electron density, as indicated by the electron density maps. The C–C bond distances and the S–C–C angles were constrained to 1.542 Å and 109.5°, respectively. For the same reason, common isotropic thermal parameters were assigned and refined in the least-squares cycles for the phenyl ring carbon atoms. For the methyl carbon atoms C(142) and C(232) an isotropic thermal parameter was fixed (U = 0.10 Å^2) and not refined. The hydrogen atoms were not included for these ethyl groups. In the final least-squares refinement cycles, the data converged at R = 0.0766 and R_w = 0.0824 for 3242 observations with $I \geq 3\sigma(I)$ and 275 variables using the weighting scheme $w = k/\sigma^2(F_o) + gF^2$ where g = 0.001 248 and w = 2.4741. Seven peaks in the final difference Fourier synthesis had electron density more than 1.0 e·Å^{-3}; of these, the top four peaks (electron density range 2.27–1.36 e·Å^{-3}) were associated with mercury atoms (at distances 1.08–1.18 Å). The fifth peak was associated with Br(5). The rest of the peaks were near the carbon atoms of the disordered ethyl groups. The maximum shift/error in the final cycle was –0.0057. The secondary extinction coefficient was refined (6.5(6) × 10^{-5}). In another attempt, anisotropic thermal parameters were assigned and refined for all the ethyl carbon atoms (except for the one that is attached to S(24)). The refinement converged at R = 0.0735 and R_w = 0.0793 for 3243 ($I > 3\sigma(I)$) parameters and 312 variables. However, this model was not retained because of the large value of the mean U_{eq} for the ethyl group carbon atoms.

Table 1. Crystallographic Data for $(Ph_4P)_2[(\mu\text{-}SEt)_5(\mu\text{-}Br)(HgBr)_4]$ (**1**) and $(Et_4N)_2[(\mu\text{-}I)(\mu\text{-}SPr^n)(HgI_2)_2]$ (**2**)

	1	**2**
formula	$C_{58}H_{65}Br_5Hg_4S_5P_2$	$C_{19}H_{47}N_2Hg_2I_5S_1$
fw	2186.3	1371.3
crystal system	monoclinic	orthorhombic
space group	$C2/c$ (No. 15)	$Cmc2_1$ (No. 36)
a (Å)	46.599(5)	12.408(2)
b (Å)	12.775(2)	17.339(4)
c (Å)	25.582(3)	16.964(4)
β (deg)	116.50(1)	
cell vol (Å^3), Z	13629(3), 8	3650(1), 4
density (g·cm^{-3}): obsd, calcd	2.11(5), 2.13	2.51(5), 2.50
radiation, wavelength (Å)	Cu Kα, 1.541 84	Mo Kα, 0.710 73
abs coeff (cm^{-1})	210.7	126.5
final model: R, R_w	0.0766, 0.0824	0.0339, 0.0342

Crystal 2. A colorless square blocklike single crystal with approximate dimensions 0.15 × 0.17 × 0.20 mm was mounted on a glass fiber in air. Intensity data were collected using Mo Kα radiation (λ = 0.710 73 Å), and 22 high-angle ($24.0 \leq 2\theta \leq 29.0°$) reflections were used in the least-squares program to obtain the cell dimensions. Cell data: a = 12.408(2) Å, b = 17.339(4) Å, c = 16.964(4) Å, V = 3650(1) Å^3, Z = 4. A total of 1745 reflections were collected in the 2θ range 0–45° ($-1 \leq h \leq 13$, $-1 \leq k \leq 18$, $-1 \leq l \leq 18$), with a variable scan speed from 1.18 to 4.12° min^{-1}. The maximum and minimum transmission factors were 0.212 and 0.118 (μ = 126.5 cm^{-1}). The systematic absences ($h0l$, $h = 2n + 1$ and $l = 2n + 1$, and a C centering) suggested three possible space groups, namely, $Cmc2_1$, $C2cm$, and $Cmcm$. The space group $Cmc2_1$ (No. 36) was assumed, and the correctness of the choice of the space group was confirmed by successful solution and refinement of the structure. For Z = 4, a mirror symmetry is imposed on the molecule in which the bridging iodine and the propanethiolate ligand sit on the mirror. Similarly the mirror plane passes through both the $(C_2H_5)_4N^+$ cations. The C(2) carbon of the n-propyl group is off the mirror plane by 0.683 Å. High thermal parameters and unreasonable bond lengths and angles for the carbon atoms in the anion and the cations suggested that they may be disordered. The disorder appeared to be diffusional in nature since reasonable disorder models could not be found. Hence all the C–C and N–C bond distances were fixed at 1.542 and 1.485 Å, respectively, in the refinements. In the final least-squares cycles, employing 1013 observations with $I \geq 2\sigma(I)$ and 91 variables, with weights of the form $w = k/[\sigma^2(F_o) + gF_o^2]$ where k = 1.7737 and g = 0.000 1448, the refinement converged at agreement factors R = 0.0339 and R_w = 0.0342. The maximum shift/esd was 0.0123 in the final least-squares cycle. In the final difference Fourier map, the residual electron density fell in the range 1.13 to –0.70 e·Å^{-3}. The top peak, which has the electron density >1.0 e·Å^{-3}, was found near H(21a) at a distance of 1.26 Å. The secondary extinction coefficient was refined to 3.9(8) × 10^{-5}. The agreement factors for the inverted model are R = 0.0571 and R_w = 0.0569.

The experimental details and crystal data are given in Table 1, and the positional and thermal parameters for **1** and **2** are shown in Tables 2 and 3, respectively.

Elemental Microanalyses. All analyses were carried out by Guelph Chemical Laboratories Ltd.

Results and Discussion

Synthesis. The self-assembly reaction (1), starting with a 1:3:2 molar ratioof $HgX_2{:}Hg(SR)_2{:}(Cat^+)X^-$, leads to the isolable

$$HgX_2 + 3Hg(SR)_2 + 2X^- \rightarrow [Hg_4(SR)_6X_4]^{2-} \quad (1)$$

complexes $[Hg_4(SR)_6X_4]^{2-}$ for the following representative

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[21] Sheldrick, G. M. SHELX-76. University of Cambridge, Cambridge, England, 1976.

Table 2. Atomic Positional and Thermal Parameters for the Anion in $(Ph_4P)_2[(\mu\text{-SEt})_5(\mu\text{-Br})(HgBr)_4]$ (**1**)[a]

atom	*x*	*y*	*z*	B_{iso}, Å^2
Hg(1)	0.36856(5)	0.22160(16)	0.61390(9)	7.78(13)
Hg(2)	0.39614(5)	0.43705(15)	0.75839(10)	8.51(16)
Hg(3)	0.43441(4)	0.16519(16)	0.76798(9)	7.66(13)
Hg(4)	0.34395(5)	0.19784(17)	0.74155(10)	8.53(14)
Br(1)	0.3435(1)	0.2327(4)	0.4994(2)	8.7(3)
Br(2)	0.4047(1)	0.6310(3)	0.7981(2)	8.0(3)
Br(3)	0.4834(1)	0.0456(4)	0.8310(2)	8.2(3)
Br(4)	0.3005(1)	0.1131(6)	0.7668(2)	10.2(4)
Br(5)	0.3786(2)	0.4318(5)	0.6342(3)	12.3(6)
S(13)	0.4210(3)	0.1323(9)	0.6625(5)	8.1(8)
S(14)	0.3243(3)	0.1579(9)	0.6348(6)	8.0(8)
S(23)	0.4479(3)	0.3612(13)	0.7829(10)	15.1(14)
S(24)	0.3416(3)	0.4021(11)	0.7435(8)	12.0(13)
S(34)	0.3980(3)	0.1375(11)	0.8150(6)	9.1(9)
C(131)	0.4474(9)	0.2279(28)	0.6551(15)	9.1(37)
C(132)	0.4431(8)	0.2281(35)	0.5919(14)	9.8(32)
C(141)	0.2944(6)	0.2567(23)	0.5974(22)	12.3(17)
C(142)	0.2611(4)	0.2135(31)	0.5849(17)	7.9
C(231)	0.4691(12)	0.3693(37)	0.8611(10)	14.2(19)
C(232)	0.4933(7)	0.4607(30)	0.8778(13)	7.9
C(241)	0.3485(12)	0.4451(44)	0.8153(13)	15.0(21)
C(242)	0.3188(16)	0.4214(73)	0.8248(24)	8.9(24)
C(242′)	0.3535(30)	0.3490(68)	0.8548(21)	14.4(40)
C(341)	0.3962(12)	−0.0035(14)	0.8157(15)	12.2(17)
C(342)	0.3832(12)	−0.0454(23)	0.7528(19)	11.2(15)
P(1)	0.4421(2)	0.2585(8)	0.0453(4)	5.2(6)
P(2)	0.2228(3)	0.2591(9)	0.8582(5)	6.9(7)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid. The occupancy factors for C(242) and C(242′) are 0.5 and 0.5.

Table 3. Atomic Positional and Thermal Parameters for $(Et_4N)_2[Hg_2I_5(SC_3H_7)]$ (**2**)[a]

	x	*y*	*z*	B_{iso}, Å^2
Hg	0.14440(8)	0.13968(6)	0.2788	6.77(6)
I(1)	0	0.02043(13)	0.21465(14)	5.96(11)
I(2)	0.22759(15)	0.21660(12)	0.15363(14)	7.50(10)
I(3)	0.27850(16)	0.05675(12)	0.37540(14)	7.54(10)
S	0	0.2106(6)	0.3552(6)	7.01(52)
C(1)	0	0.1571(25)	0.4458(24)	10.1(8)
C(2)	−0.0550(37)	0.2028(28)	0.5124(22)	10.1(8)
C(3)	0	0.1630(24)	0.5830(26)	10.1(8)
N(1)	0	0.4766(14)	0.1298(14)	5.8(14)
C(11)	0	0.5589(16)	0.1053(20)	9.3(4)
C(12)	0	0.5692(24)	0.0151(20)	9.3(4)
C(13)	0	0.4723(18)	0.2174(15)	9.3(4)
C(14)	0	0.3913(17)	0.2553(24)	9.3(4)
C(15)	0.0931(14)	0.4314(13)	0.0997(18)	9.3(4)
C(16)	0.2036(18)	0.4664(17)	0.1208(20)	9.3(4)
N(2)	0	0.8142(14)	0.3967(14)	5.1(13)
C(21)	0	0.8030(22)	0.3099(16)	13.2(6)
C(22)	0	0.7158(21)	0.2906(37)	13.2(6)
C(23)	0	0.8989(15)	0.4074(24)	13.2(6)
C(24)	0	0.9209(30)	0.4954(24)	13.2(6)
C(25)	0.1015(17)	0.7821(19)	0.4298(20)	13.2(6)
C(26)	0.2065(26)	0.8164(22)	0.3958(25)	13.2(6)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

combinations of $Cat^+/R/X$: $Et_4N^+/Et/Cl$; $Et_4N^+/Bu^n/I$; $Bu^n{}_4N^+/Et/I$, Br; $Bu^n{}_4N^+/Pr^i/Br$, Cl; $Ph_4P^+/Et/Br$; $Ph_4P^+/Bu^n/I$. In some cases, however, a 1:3:2 ratio of reactants gave salts of $[Hg_4(SR)_5X_5]^{2-}$ as the isolated product ($Cat^+/R/X$: $Ph_4P^+/Pr^i/I$, Br; $Bu^n{}_4N^+/Pr^i/I$). Anions of this stoichiometry could be isolated from 3:5:4 molar ratios of HgX_2:$Hg(SR)_2$:$(Cat^+)X^-$ for $Cat^+/R/X = Ph_4P^+/Et/I$, Br or $Bu^n{}_4N^+/Pr^i/Cl$, as expected from eq 2.

$$3HgX_2 + 5Hg(SR)_2 + 4X^- \rightarrow 2[Hg_4(SR)_5X_5]^{2-} \quad (2)$$

In addition, recrystallization of $(Ph_4P)_2[Hg_4(SEt)_6Br_4]$ gave $(Ph_4P)_2[Hg_4(SEt)_5Br_5]$ in a form suitable for X-ray analysis, and the structure of this salt is described below. Under a different set of conditions, attempted recrystallization of $(Ph_4P)_2[Hg_4(SEt)_6Br_4]$ gave $(Ph_4P)_2[HgBr_4]$. An analogous result was obtained with the Et_4N^+ salt, and similarly, $(Et_4N)_2[Hg_4(SBu^n)_6I_4]$ yielded $(Et_4N)_2[HgI_4]$. These results lend support to the suggestion[6] that some $[(\mu\text{-SR})_6(HgX)_4]^{2-}$ complexes undergo dissocation to $Hg(SR)_2$ and $[HgX_4]^{2-}$.

The salts $(Ph_4P)_2[Hg_4(SBu^n)_4I_6]$ and $(Ph_4P)_2[Hg_4(SPr^i)_4Br_6]$ were isolated analytically and spectroscopically pure, respectively, from solutions containing $HgX_2/Hg(SR)_2/(Ph_4P^+)X^-$ in a 1:1:1 ratio (eq 3).

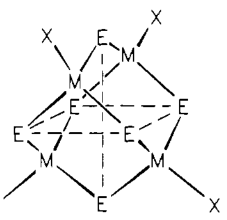
$$HgX_2 + Hg(SR)_2 + X^- \rightarrow {}^1/_2[Hg_4(SR)_4X_6]^{2-} \quad (3)$$

Attempts to produce anions containing more than six halides were unsuccessful. In mixtures with the appropriate HgX_2:$Hg(SR)_2$:X^- ratios, dissolution of the components was invariably incomplete.

An attempted recrystallization of crude $(Et_4N)_2[Hg_4(SPr^n)_6I_4]$ gave the novel salt $(Et_4N)_2[Hg_2(SPr^n)I_5]$ in a form suitable for X-ray analysis. The structure of the new anion is described below.

It is evident that at or near room temperature there is dissociation of $[Hg_4(SR)_6X_4]^{2-}$ to give a variety of possible products, the one isolated being that which is least soluble in the circumstances.

NMR. (i) **$[Hg_4(SR)_6X_4]^{2-}$.** At reduced temperature, the ^{199}Hg NMR spectra of $[Hg_4(SR)_6X_4]^{2-}$ added as a pure salt or prepared in situ is generally a single line, consistent with the formulation $[(\mu\text{-SR})_6(HgX)_4]^{2-}$ of skeleton I.[6,22] An exception is provided by complexes with R = Pr^i or Cy which show in addition a weaker two-line spectrum that is due to $[(\mu\text{-SR})_5(\mu\text{-X})(HgX)_4]^{2-}$ (see Figure 1a and discussion below). In these cases, addition of excess X^- produces the single-line spectrum of $[(\mu\text{-SR})_6(HgX)_4]^{2-}$. The exact equilibrium shift that produces this result is not clear.



I

To confirm that the single-line ^{199}Hg NMR spectra are indeed due to $[(\mu\text{-SR})_6(HgX)_4]^{2-}$, we have resorted to experiments involving mixing of metals. Mixtures of $[(\mu\text{-SR})_6(HgX)_4]^{2-}$ with the known[16] Zn_4 and Cd_4 analogues are expected to give a total of four Hg-containing complexes, $[(\mu\text{-Sr})_6(HgX)_{4-n}(MX)_n]^{2-}$ (n = 0–3). When M = Cd, a total of four $^{111/113}Cd$ NMR signals are observed also, corresponding to n = 1–4. Metal NMR data obtained at reduced temperature[22] for the various complexes $[(\mu\text{-SR})_6(HgX)_{4-n}(MX)_n]^{2-}$ are given in Table 4. For each system studied, the expected number of metal resonances is observed, and the formulation of $[(\mu\text{-SR})_6(HgX)_4]^{2-}$ is thus confirmed.

The values of δ_{Hg} for $[(\mu\text{-SR})_6(HgX)_4]^{2-}$ (Table 5, m = 0), combined with earlier data,[16] show that the ^{199}Hg chemical shift is influenced by the nature of both ER and X. The variations of δ_{Hg} are $SPr^i \approx SCy > SEt \approx SPr^n \approx SBu^n > SPh > SePh > TePh$ with ER and $Cl > Br > I$ with X. The variations with E of ER and with X are consistent with the ^{199}Hg NMR chemical shift showing the normal halogen dependence (NHD).[23]

The data in Table 4 show that increasing substitution of Zn for Hg in $[(\mu\text{-SR})_6(HgX)_4]^{2-}$ causes increasing shielding of the ^{199}Hg signal of the remaining mercury nuclei. On the other hand, increasing substitution of Cd for Hg produces increasing

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[22] Broad spectra are obtained at ambient probe temperature (see text).

[23] Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1980**, *10A*, 6.

Table 4. NMR Data for $[(\mu\text{-SR})_6(HgX)_{4-n}(MX)_n]^{2-}$ (M = Zn, Cd) in CH_2Cl_2[a]

R	X	M	*n*	δ_{Hg}[b]	δ_{Cd}[c]	$^2J(^{111}Cd-^{199}Hg)$[d] (Hz)
Et	I	Zn	0	−830		
			1	−844		
			2	−858		
			3	−873		
		Cd	0	−828		
			1	−811	571	142
			2	−794	575	140
			3	−776	579	*e*
			4		584	
	Br	Zn	0	−602		
			1	−610		
			2	−615		
			3	−618		
		Cd	0	−602		
			1	−592	594	
			2	−581	599	111[f]
			3	−570	603	113[f]
			4		607	
Pr^i	I	Zn	0	−904		
			1	−946		
			2	−984		
			3	−1005		
		Cd	0	−905		
			1	−889	534	146
			2	−869	538	139
			3	−848	543	119
			4		549	
	Br	Zn	0	−657		
			1	−678		
			2	−695		
			3	−714		
		Cd	0	−654		
			1	−647	572	96
			2	−638	575	104
			3	−627	579	116
			4		583	
Bu^n	I	Zn	0	−839		
			1	−855		
			2	−873		
			3	−892		
		Cd	0	−840		
			1	−823	566	153[b]
			2	−806	570	144
			3	−789	574	131
			4		578	

[a] Data measured at 213 K and concentration (at room temperature) = 0.05 mol/L of solvent, except as noted. [b] Relative to external pure $HgMe_2$ at 295 ± 1 K; reproducibility ±1 ppm. [c] Measured as ^{111}Cd relative to external $Cd(ClO_4)_2$ (0.1 M, aq) at 293 ± 1 K; reproducibility ±1 ppm. [d] Estimated error ±5 Hz. [e] Not well resolved. [f] At 193 K.

*de*shielding of ^{199}Hg, as well as the same effect for $^{111/113}Cd$. The effects observed[6] for $[(\mu\text{-SPr}^n)_6(HgI)_{4-n}(MI)_n]^{2-}$ are thus general. We find here that the magnitude of the substitution effects is affected by the nature of the ligands attached to the metal: the chemical shiftability at Hg is larger when X = I than when X = Br and also when R in SR is Pr^i rather than *n*-alkyl (Table 4 and ref 6).

In the spectra of many of the complexes containing both Cd and Hg, satellites due to two-bond $^{111/113}Cd-^{199}Hg$ coupling are observed, principally in the ^{111}Cd NMR spectra, where the signals are sharper. These couplings fall in the range 96–146 Hz (Table 4). For analogous complexes they are larger when X = I than when X = Br. Also, it is interesting that for $[(\mu\text{-SR})_6(HgX)_{4-n}(CdX)_n]^{2-}$ the values of ^2J decrease with increasing *n* when X = I but increase with increasing *n* when X = Br.

As the temperature is raised, the ^{199}Hg NMR spectra of all of the $[(\mu\text{-SR})_6(HgX)_4]^{2-}$ complexes become significantly deshielded and broaden, sometimes to the point that no signals can be observed.[10] Earlier, it was suggested that such a change is indicative of dissociation.[6] In the present work a range of products has been isolated at higher temperatures from solutions having

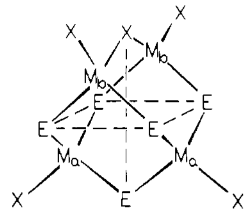
Table 5. ^{199}Hg NMR Data for $[(\mu\text{-SR})_{6-m}(\mu\text{-X})_m(HgX)_4]^{2-}$ in CH_2Cl_2 at 183 K[a]

		δ_{Hg}			
			$m = 1$		
R	X	$m = 0$	Hg_a[b]	Hg_b[b]	$m = 2$
Cy[c]	I	−880	−887	−1306	−1342
	Br	−642	−652	−858	−894[d,e]
	Cl	−527	−534[d]	−694[d]	*f*
Pr^i	I[g]	−887	−884	−1340	−1370
	Br[g]	−643	−649[h]	−863[h,i]	−896
	Cl[j]	−528	−534	−693	−722
Et	I[g]	−810	−842	−1240	−1320[d,k]
	Br[g]	−587	−618	−822	−904[d]
	Cl[j]	−482	−517[d]	−690[d]	*f*
Bu^n	I[g]	−821	−857	−1224	−1312

[a] Relative to external pure $HgMe_2$ at 295 ± 1 K; reproducibility ±1 ppm. Concentration (at room temperature) = 0.05 mol/L of solvent, except as noted. [b] See Structure II. [c] Cation: $Bu^n{}_4N^+$. [d] In a mixture with $HgX_2:Hg(SR)_2:X^- = 1:1:1$. Insoluble white material was present. [e] $[(\mu\text{-SCy})_5(\mu\text{-Br})(HgBr)_4]^{2-}$:*trans*-$[(\mu\text{-SCy})_4(\mu\text{-Br})_2(HgBr)_4]^{2-} \approx 1:1$. [f] Insufficient solubility for ^{199}Hg NMR. [g] Cation: Ph_4P^+ [h] $^2J(Hg_a-Hg_b) = 533 \pm 5$ Hz. [i] $^3J(Hg_b-S-C-H) \approx 102$ Hz. [j] Cation: Ph_4As^+. [k] $[(\mu\text{-SEt})_5(\mu\text{-I})(HgI)_4]^{2-}$:*trans*-$[(\mu\text{-SEt})_4(\mu\text{-I})_2(HgI)_4]^{2-} \approx 2:1$.

the correct stoichiometry for $[(\mu\text{-SR})_6(HgX)_4]^{2-}$, and this provides strong circumstantial evidence for dissociation.

(ii) $[Hg_4(SR)_{6-m}X_{4+m}]^{2-}$ (m = 1, 2). Metal NMR data have been obtained at reduced temperature[22] for several representative anions $[Hg_4(SR)_5X_5]^{2-}$, added as pure salts or produced in situ according to eq 2. The NMR spectroscopic results are summarized in Table 5. The spectra consist of two major signals of approximately equal intensities (e.g. Figure 1b; the spectra of the system $HgBr_2/Hg(SPr^i)_2/(Ph_4P)Br$ are particularly well resolved). Each of the lines has ^{199}Hg satellites, with $^2J(Hg-Hg) = 533 \pm 5$ Hz. Couplings of this magnitude have been found for $^2J(Hg-Hg)$ in the cations $[(\mu\text{-SR})_6(HgPR'_3)_4]^{2+}$.[4] One of the two signals occurs close to that of the $[(\mu\text{-SR})_6(HgX)_4]^{2-}$ parent, and the other is more shielded. This result is consistent with the formulation $[(\mu\text{-SR})_5(\mu\text{-X})(HgX)_4]^{2-}$ with the skeleton **II**, which



II

is of time-averaged C_{2v} symmetry when inversion at S is rapid, as is expected. Here two Hg atoms (Hg_a) have the kernel $(-RS)_3$-HgX while the other two (Hg_b) have the kernel $(-RS)_2(-X)$-HgX. The coordination kernels of Hg are identical in the site Hg_a and in $[(\mu\text{-SR})_6(HgX)_4]^{2-}$ and therefore their ^{199}Hg resonances are expected to occur in the same region. On this basis, the less shielded resonance of $[(\mu\text{-SR})_5(\mu\text{-X})(HgX)_4]^{2-}$ is assigned to Hg_a. By a process of elimination, the more shielded signal must then be assigned to Hg_b. This last assignment is confirmed by a spectrum obtained without ^1H decoupling, which shows only broadening for the resonance of Hg_a but a triplet splitting for the resonance of Hg_b. The coupling must be due to $^3J(Hg-S-C-H)$, and the triplet pattern indicates two attached $S(Pr^i)^-$ ligands.

When the halide is changed in $[(\mu\text{-SR})_5(\mu\text{-X})(HgX)_4]^{2-}$, both signals show the shielding pattern I > Br > Cl, as expected for a metal center showing the NHD. The separation of the two signals increases in the same order. In cadmium complexes the effect on σ_{Cd} of replacing *terminal* SPh by X varies in the order

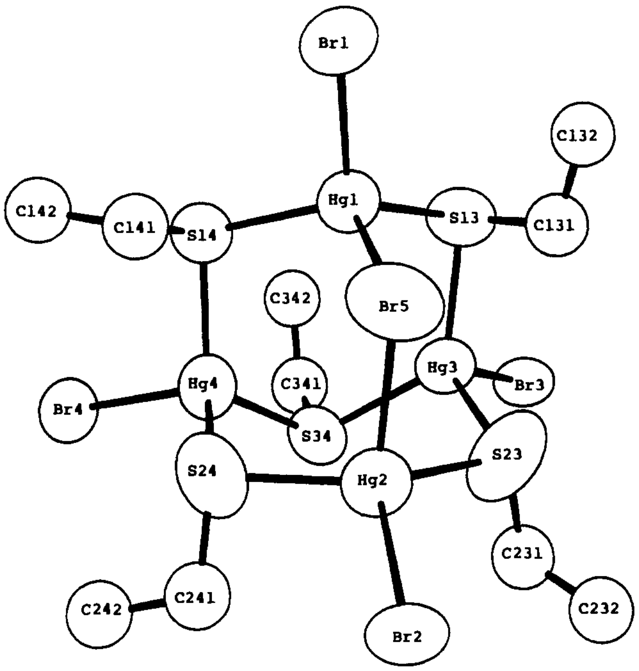
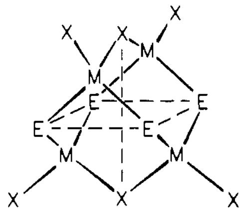


Figure 2. View of the anion in **1** (with 50% probability of the thermal ellipsoids). The carbon atoms were assigned arbitrary radii. The hydrogen atoms are omitted and only one disordered C(242) atom is shown for clarity.

I > Br > Cl,[24] and we presume that the same sequence occurs for σ_{Hg} when μ-SR is replaced by μ-X.

Reduced-temperature[22] ^{199}Hg NMR spectra of $[\text{Hg}_4(\text{SR})_4\text{X}_6]^{2-}$, added as pure salts or produced in situ (eq 3), consist of just one line (Table 5 and Figure 1c). This resonance is adjacent to that of Hg_b of $[(\mu\text{-SR})_5(\mu\text{-X})(\text{HgX})_4]^{2-}$ (Figure 1), indicating that same kernel. Accordingly, we assign it to *trans*-$[(\mu\text{-SR})_4(\mu\text{-X})_2(\text{HgX})_4]^{2-}$, of structure **III**.



III

Structure of $(\text{Ph}_4\text{P})_2[(\mu\text{-SEt})_5(\mu\text{-Br})(\text{HgBr})_4]$ (1). The accuracy and the precession in the matrix values were limited by disorder in the molecule and the quality of the single crystals. Nevertheless, the geometry of the anion, $[(\mu\text{-SEt})_5(\mu\text{-Br})(\text{HgBr})_4]^{2-}$, has been established beyond any doubt. The crystal structure has well-separated anions and cations, as indicated by the shortest anion–cation distances of 2.553 Å ($0.5 - x$, $0.5 + y$, $1.5 - z$) between C(142) and H(85) atoms. The shortest nonbonded contacts are H(63)···H(56) (2.413 Å; $0.5 - x$, $0.5 - y$, $2 - z$) and H(65)···H(75) (2.482 Å; $0.5 - x$, $0.5 + y$, $1.5 - z$). The Ph_4P^+ cations are unexceptional and will not be discussed further. The structure of the anion is shown in Figure 2 along with the numbering scheme. Selected bond distances and angles are shown in Table 6.

Table 6. Selected Bond Distances (Å) and Angles (deg) in $(\text{PPh}_4)_2[\text{Hg}_4\text{Br}_5(\text{SC}_2\text{H}_5)_5]$ (**1**)

Hg(1)–Br(1)	2.628(5)	Hg(1)–Br(5)	2.736(6)
Hg(2)–Br(2)	2.640(5)	Hg(2)–Br(5)	2.907(7)
Hg(3)–Br(3)	2.618(5)	Hg(4)–Br(4)	2.619(5)
Hg(1)–S(13)	2.472(11)	Hg(1)–S(14)	2.486(11)
Hg(2)–S(23)	2.408(15)	Hg(2)–S(24)	2.435(13)
Hg(3)–S(13)	2.518(12)	Hg(3)–S(23)	2.568(16)
Hg(3)–S(34)	2.505(12)	Hg(4)–S(14)	2.516(12)
Hg(4)–S(24)	2.612(14)	Hg(4)–S(34)	2.498(12)
S(13)–C(131)	1.802(10)	S(14)–C(141)	1.850(10)
S(23)–C(231)	1.796(10)	S(24)–C(241)	1.804(10)
S(34)–C(341)	1.803(10)		
Br(5)–Hg(1)–Br(1)	96.4(2)	S(13)–Hg(1)–Br(1)	115.7(3)
S(13)–Hg(1)–Br(5)	108.1(3)	S(14)–Hg(1)–Br(1)	105.0(3)
S(14)–Hg(1)–Br(5)	111.6(3)	S(14)–Hg(1)–S(13)	118.0(4)
Br(5)–Hg(2)–Br(2)	111.3(2)	S(23)–Hg(2)–Br(2)	108.4(4)
S(23)–Hg(2)–Br(5)	92.0(6)	S(24)–Hg(2)–Br(2)	101.6(3)
S(24)–Hg(2)–Br(5)	93.4(5)	S(24)–Hg(2)–S(23)	145.1(6)
S(13)–Hg(3)–Br(3)	107.1(3)	S(23)–Hg(3)–Br(3)	112.9(4)
S(23)–Hg(3)–S(13)	104.4(6)	S(34)–Hg(3)–Br(3)	102.3(3)
S(34)–Hg(3)–S(13)	126.4(4)	S(34)–Hg(3)–S(23)	103.9(5)
S(14)–Hg(4)–Br(4)	103.7(3)	S(24)–Hg(4)–Br(4)	111.4(3)
S(24)–Hg(4)–S(14)	103.0(5)	S(34)–Hg(4)–Br(4)	108.5(3)
S(34)–Hg(4)–S(14)	120.7(4)	S(34)–Hg(4)–S(24)	109.3(5)
Hg(2)–Br(5)–Hg(1)	99.8(2)	Hg(3)–S(13)–Hg(1)	100.3(4)
C(131)–S(13)–Hg(1)	101.6(16)	C(131)–S(13)–Hg(3)	98.3(11)
Hg(4)–S(14)–Hg(1)	103.4(4)	C(141)–S(14)–Hg(1)	100.1(12)
C(141)–S(14)–Hg(4)	104.7(19)	Hg(3)–S(23)–Hg(2)	101.7(5)
C(231)–S(23)–Hg(2)	104.8(22)	C(231)–S(23)–Hg(3)	101.4(16)
Hg(4)–S(24)–Hg(2)	97.9(5)	C(241)–S(24)–Hg(2)	94.9(17)
C(241)–S(24)–Hg(4)	109.5(20)	Hg(4)–S(34)–Hg(3)	105.5(5)
C(341)–S(34)–Hg(3)	101.0(17)	C(341)–S(34)–Hg(4)	106.3(16)

The anion has an adamantane-like structure in which four Hg atoms lie at the vertices of a distorted tetrahedraon. Five edges of the tetrahedron are bridged by sulfur atoms and one is bridged by a bromine atom, apparently a unique combination among adamantane-like structures that have been subjected to X-ray analysis. The bridging atoms occupy the corners of a highly distorted octahedron. The coordination of each Hg atom is completed by a terminal bromine atom. Thus the structure of the anion is a distorted version of structure **II**, described above. In it there are two types of coordination kernels, namely HgS_2Br_2 (Hg(1) and Hg(2)) and HgS_3Br (Hg(3) and Hg(4)).

The mean Hg–Br_t distance of 2.626(10) Å found in the anion is at the upper end of the range of terminal Br–Hg distances reported in the literature (2.47–2.65 Å).[25,26] The Hg–Br–Hg bridge is unsymmetrical, with Hg–Br_{br} distances of 2.736(6) and 2.907(7) Å. Thus the Hg–Br_{br} distances exceed the Hg–Br_t distance, a frequent observation.[27–31] Unsymmetrical Hg–Br–Hg bridges are a common phenomenon also.[27–31]

The Hg–S_{br} distances are in the range 2.408(15)–2.612(14) Å. Such variation is commonly observed for Hg–S_{br} distances of thiolate-bridged compounds of Hg(II).[32] However, the range of Hg–S_{br} distances found[5] for $[(\mu\text{-SPh})_6(\text{HgPPh}_3)_4]^{2+}$ is smaller, 2.534(3)–2.610(3) Å. Similarly, the ranges of the Hg···Hg distances and of the Hg–Hg–Hg angles are larger for $[(\mu\text{-SEt})_5(\mu\text{-Br})(\text{HgBr})_4]^{2-}$ than for $[(\mu\text{-SPh})_6(\text{HgPPh}_3)_4]^{2+}$, 3.808(3)–4.319(3) Å vs 4.276–4.392 Å for Hg···Hg distances and 54.77(6)–68.30(5)° vs 59.1–61.7° for the Hg–Hg–Hg angles. The greater deviation from the ideal adamantane-like skeleton that is found for the anion can be attributed to the introduction of dissimilar atoms into the adamantanoid core.

Configurational isomerism occurs in adamantane-like metal–thiolate complexes with the skeleton $[(\mu\text{-SR})_6\text{M}_4]$ due to the

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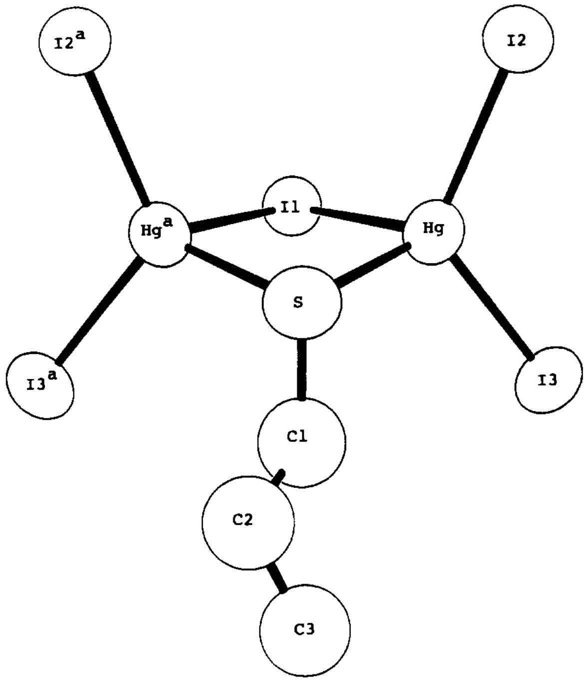

Figure 3. View of the anion in **2** (with 50% probability of the thermal ellipsoids). The hydrogen atoms are omitted and only one disordered C(2) atom is shown for clarity.

relative orientations of the R substituents at the pyramidal sulfur atoms.[1,33] These isomers are normally represented in terms of the number of axial (a) and equatorial (e) substituents in each of the cyclohexane-like chairs. Such isomerism is possible in $[(\mu\text{-Br})(\mu\text{-SEt})_5(\text{HgBr})_4)]^{2-}$ also. The configuration of the substituents on the sulfur atoms in this anion is [aae,aee,ae,ae]. Despite the distorted geometry of the $(\mu\text{-SR})_5(\mu\text{-Br})(\text{HgBr})_4$ skeleton, systematic variations of the S–Hg–S and S–Hg–Br and angles can be explained in terms of the interactions among a–a, a–e, and e–e substituents, as in earlier work.[5,34] The largest S–Hg–S angle is 145.1(5)° found for S(24)–Hg(2)–S(23). The large size of S(24)–Hg(2)–S(23) is due to a–a repulsive interaction between the Et groups attached to the S(24) and S(23) atoms. The S(23)–Hg(2)–Br(5) and S(24)–Hg(2)–Br(5) angles, 92.0(5) and 93.4(5)°, respectively, are found to be smaller than S(13)–Hg(1)–Br(5) (108.1°) and S(14)–Hg(1)–Br(5) (111.6°). The first two angles are associated with an interaction between Br(5) and an equatorial Et substituent and the last two with an interaction between Br(5) and an axial Et substituent.

Structure of $(\text{Et}_4\text{N})_2[(\mu\text{-I})(\mu\text{-SC}_3\text{H}_7)(\text{HgI})_2]$ (2). The crystal consists of discrete anion and cations. A view of the novel dimeric anion $[(\mu\text{-I})(\mu\text{-SC}_3\text{H}_7)(\text{HgI}_2)_2]^{2-}$ (with hydrogen atoms omitted) is shown in Figure 3. Selected bond distances and angles are given in Table 7. There is a crystallographically imposed mirror symmetry present in the dimer in which the bridging I, S, and α and γ carbon atoms sit on the mirror. Similarly, the mirror plane passes through both $[(\text{C}_2\text{H}_5)_4\text{N})_2]$ cations. The shortest nonbonded distance observed is H(2a)···H(12a) (2.178 Å; $x, -y, 0.5 + z$). The cations are unexceptional and warrant no further discussion.

Table 7. Selected Bond Distances (Å) and Angles (deg) in $(\text{Et}_4\text{N})_2[\text{Hg}_2\text{I}_5(\text{SC}_3\text{H}_7)]$ (**2**)

Hg–I(1)	2.944(2)	Hg–I(2)	2.712(2)
Hg–I(3)	2.743(2)	Hg–S	2.530(7)
S–C(1)	1.79(4)		
I(1)–Hg–I(2)	106.72(7)	I(1)–Hg–I(3)	102.82(7)
I(2)–Hg–I(3)	119.66(7)	I(1)–Hg–S	95.7(2)
I(2)–Hg–S	115.6(2)	I(3)–Hg–S	112.3(2)
Hg–I(1)–Hg^a	74.96(6)	Hg–S–Hg^a	90.2(3)
Hg–S–C(1)	100.8(10)	S–C(1)–C(2)	111(3)

^{a} The atoms are related by the symmetry operator $(-x, y, z)$.

In the dimer, each Hg is bonded to two terminal iodine atoms, a bridging iodine atom, and an *n*-propanethiolate ligand to complete an approximately tetrahedral HgI_3S kernel.[35] The four-membered ring $\text{Hg}_2\text{I}_{\text{br}}\text{S}_{\text{br}}$ has a "butterfly" conformation, with a dihedral angle of 159.2° between the $\text{HgI}_{\text{br}}\text{S}_{\text{br}}$ and $\text{Hg}^a\text{I}_{\text{br}}\text{S}_{\text{br}}$ planes. The Pr^n substituent occupies the endo (axial) position.[10] The Hg···Hg separation is 3.583(2) Å. The Hg–I$_t$ distances are 2.712(2) and 2.743(2) Å, which fall in the higher end of the range of analogous distances observed in various $[(\mu\text{-I})_2(\text{HgI}_2)_2]^{2-}$ ions.[36–40] The Hg–I$_{\text{br}}$ distance of 2.944(2) Å observed in the anion is comparable to values found for $[\text{Hg}_2\text{I}_6]^{2-}$ (range 2.864–2.962 Å).[36–40] However, the Hg–I–Hg angle (74.96(6)°) observed for the anion in **2** is smaller than comparable angles found for $[\text{Hg}_2\text{I}_6]^{2-}$ (83.8–88.0°).[36–40] On the other hand, the Hg–S–Hg angle of 90.2(3)° is larger than that observed for $[(\text{MeS})_2\text{Hg}(\text{SMe})_2\text{Hg}(\text{SMe})_2]^{2-}$ (85.73(5)°).[41] As the Hg–S$_{\text{br}}$ bond length of 2.530(7) Å is normal compared with analogous distances given in literature,[41–43] the angles at the bridging atoms in the four-membered ring $\text{HgSHg}^a\text{I}_{\text{br}}$ are expected to be a compromise forced by the disparity between the Hg–I$_{\text{br}}$ and Hg–S$_{\text{br}}$ bond lengths. A similar four-membered $\text{Hg}_2\text{S}Br$ ring is found in polymeric MeSHgBr.[28]

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Supplementary Material Available: Tables giving ^{1}H and ^{13}C NMR data for $(\text{Cat})_2[(\mu\text{-SR})_{6-m}(\mu\text{-X})_m(\text{HgX})_4]$, ^{199}Hg NMR data for $[(\mu\text{-SR})_6(\text{HgX})_4]^{2-}$, complete atomic and thermal parameters and bond distances and angles for **1**, and anisotropic thermal parameters and H atom positions for **1** and **2** and a view of the anion in **2** showing the orientation of ethyl group (13 pages). Ordering information is given on any current masthead page.

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