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New Adamantane-like Mercury–Chalcogen Cages. Synthetic and Multinuclear (^{31}P, ^{77}Se, ^{199}Hg) NMR Study of $[(\mu\text{-ER})_6(HgL)_4]^{2+}$ (E = S or Se; L = Tertiary Phosphine or Arsine) and Related Species with Mixed Ligands[1]

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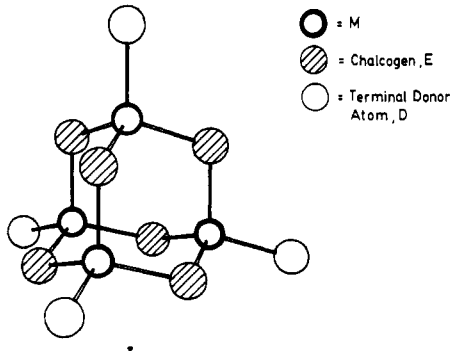
Reaction between $HgL_2(ClO_4)_2$, $Hg(ER)_2$, and L in a 1:3:2 ratio produces the isolable salts $[(\mu\text{-ER})_6(HgL)_4](ClO_4)_2$ (L = PPh_3, ER = SePh, SPh, SMe, or SEt; L = $AsPh_3$, ER = SPh; L = PEt_3, ER = SePh or SPh). Multinuclear (^{31}P, ^{77}Se, ^{199}Hg) NMR was used to demonstrate the adamantanoid structure of the cations in these salts as well as in those with L = PPh_3 and ER = S-*n*-Pr, S-*n*-Bu, or S-*n*-C_5H_{11}, which were studied in situ. To confirm that the new cations contain the hitherto unobserved $(\mu\text{-ER})_6Hg_4$ core, several series of clusters with mixed ligands were investigated (as ClO_4^- salts) by the multinuclear NMR technique also. The systems $[(\mu\text{-ER})_6(HgL)_4]^{2+}$–$[(\mu\text{-ER})_6(HgL')_4]^{2+}$ (ER = SePh, L = PPh_3, L′ = PEt_3; ER = SPh, L = PPh_3, L′ = PEt_3 or $AsPh_3$) give the series $[(\mu\text{-ER})_6(HgL)_{4-n}(HgL')_n]^{2+}$ (n = 0–4). The related species $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgSbPh_3)_n]^{2+}$ (n = 0–2 and possibly 3) were produced from $Hg(PPh_3)_2(ClO_4)_2$, $Hg(SPh)_2$, and $SbPh_3$. From the notably rich ^{31}P and ^{199}Hg NMR spectra of the system $[(\mu\text{-SPh})_6(HgPPh_3)_4]^{2+}$–$[(\mu\text{-SePh})_6(HgPPh_3)_4]^{2+}$ it was possible to demonstrate the existence of every possible mixed-chalcogen core in the series $[(\mu\text{-SPh})_{6-m}(\mu\text{-SePh})_m(HgPPh_3)_4]^{2+}$ (m = 0–6). The new $(\mu\text{-SR})_6Hg_4$ cages are possible models for the proposed $Hg_4(Cys)_{11}$ cluster in Hg_7-metallothionein.

Introduction

Recently, it was shown that Hg(II) displaces Zn and Cd from Zn,Cd-metallothionein II (Zn,Cd-MT), producing the Hg_7-MT protein.[2] As earlier optical spectroscopic studies[3,4] indicated that Hg-substituted MT contains Hg in cysteinyl binding sites, it was suggested[2] that Hg_7-MT contains thiolate-bridged $M_4(Cys)_{11}$ and $M_3(Cys)_9$ clusters similar to those that are known[5–7] to occur in Zn,Cd-MT. Simple models for the metal-binding sites of MT are highly desirable, and adamantanoid anions $[(\mu\text{-SPh})_6(MSPh)_4]^{2-}$ (M = Zn, Cd), which are possible models for the four-atom sites[8] of Zn,Cd-MT, have been well-established,[9–12] as have the selenium analogues.[11b,13,14] The anions have the skeleton I, with E and D = S or Se.[9,10,14] However, despite extensive interest in mercury thiolate chemistry,[15–20] no species containing the model $(\mu\text{-SR})_6Hg_4$ core have yet been reported; attempts to prepare $[(\mu\text{-SPh})_6(HgSPh)_4]^{2-}$ specifically have been unsuccessful to date.[19,21] Similarly, there has been no literature report of the $(\mu\text{-SeR})_6Hg_4$ core. These absences are somewhat surprising since chalcogen bridging is a feature of many Hg(II)–chalcogenate species (e.g. ref 15–18, 20, and 22).



I

In this paper we describe the isolation of several new compounds of the general formula $[Hg_4(ER)_6L_4](ClO_4)_2$ (E = S or Se; L = tertiary phosphine or arsine), as well as the synthesis in solution of various related complexes, some of which have mixed chalcogenates or mixed neutral ligands. This series contains a range of attractive probe nuclei, including ^{77}Se and ^{199}Hg in addition to the more common ^1H, ^{13}C, and ^{31}P, making the new species interesting candidates for multinuclear NMR spectroscopy.[23] Application of this technique has allowed us to demonstrate unambiguously that the tetranuclear cations are of adamantanoid structure and contain cages of the hitherto-unknown type $(\mu\text{-ER})_6Hg_4$.

Experimental Section

Materials and General Procedures. Literature syntheses without significant variation were followed for $Hg(O_2CCF_3)_2$,[25] $Hg(PPh_3)_2(ClO_4)_2$,[26,27] $Hg(AsPh_3)_2(ClO_4)_2$,[28] and mercury(II) thiolates[29,30] and

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benzeneselenolate.[30,31] The preparation of $Hg(PEt_3)_2(ClO_4)_2$ from $HgCl_2(PEt_3)_2$[32a] and $AgClO_4$ was carried out in the same way as the synthesis of $Hg(PPh_3)_2(ClO_4)_2$;[26] the purity and authenticity were confirmed by ^{31}P NMR. (For a 0.05 M solution in MeCN at 296 K, δ_P = 54.5 and $^1J(^{199}Hg-^{31}P)$ = 4539 ± 2 Hz (lit.[32b] $^1J(^{199}Hg-^{31}P)$ = 4457 Hz for $Hg(PEt_3)_2(BF_4)_2$ in Me_2CO)). Triphenylphosphine (Baker), -arsine (Aldrich), and -stibine (Eastman) were recrystallized from ethanol. All other chemicals were from commercial sources and were used as received.

Solvents were dried over 3A molecular sieves. Solvents used in synthesis or in preparation of NMR samples were thoroughly deoxygenated with Ar before use.

Synthesis. The following syntheses were performed under an argon atmosphere. Once isolated, the solid compounds were not particularly air sensitive and showed no obvious deterioration on standing in air for 1 or 2 days at 23 °C. According to ^{31}P NMR measurements, the compounds $[Hg_4(ER)_6L_4](ClO_4)_2$ were better than 95% pure when generated in situ in $CHCl_3$ or CH_2Cl_2. However, isolation of the individual compounds as pure solids required specific combinations of solvents and conditions, as described below.

$[Hg_4(SePh)_6(PPh_3)_4](ClO_4)_2$ (1). Solid PPh_3 (0.12 g, 0.46 mmol) was added to a solution containing 0.21 g (0.23 mmol) of $Hg(PPh_3)_2(ClO_4)_2$ in 10 mL of acetone precooled to 0 °C. The solid dissolved to give a clear solution. Into this was stirred 0.35 g (0.67 mmol) of $Hg(SePh)_2$ to produce, within a few minutes, a clear yellow solution. Cyclohexane was added carefully to form a layer. After the solution was kept at 5 °C for 24 h, the yellow flaky crystalline product was collected by filtration, washed with cyclohexane, and dried in vacuo; 0.59 g (90%) of pure product was obtained. Anal. Calcd for $C_{108}H_{90}Cl_2Hg_4O_8P_4Se_6$ (mol wt 2986.84): C, 43.43; H, 3.04. Found: C, 43.20; H, 3.14. ^1H NMR ($CDCl_3$): δ_H 6.7–7.8 (phenyl H).

$[Hg_4(SPh)_6(PPh_3)_4](ClO_4)_2 \cdot 1.5CHCl_3$ (2). To a solution of $Hg(PPh_3)_2(ClO_4)_2$ (0.28 g, 0.30 mmol) in 10 mL of $CHCl_3$ was added 0.16 g (0.60 mmol) of solid PPh_3, producing a clear solution. Into this was stirred 0.38 g (0.90 mmol) of solid $Hg(SPh)_2$ to give a yellow solution with traces of a suspended fine solid. The mixture was stirred for 10 min and then filtered. The filtrate was covered with a layer of diethyl ether and left undisturbed at 0–5 °C overnight. The resulting light yellow needlelike crystals were separated by decantation of the mother liquor, washed with diethyl ether, and dried in vacuo to yield 0.74 g (85%) of product. Anal. Calcd for $C_{108}H_{90}Cl_2Hg_4O_8P_4S_6 \cdot 1.5CHCl_3$ (mol wt 2884.53): C, 45.60; H, 3.19; Cl, 7.99. Found: C, 45.34 and 45.48; H, 3.17 and 3.07; Cl, 7.70. ^1H NMR (CD_2Cl_2): δ_H 7.32 ($CHCl_3$), 6.7–7.62 (phenyl H).

$[Hg_4(SMe)_6(PPh_3)_4](ClO_4)_2$ (3). A slurry of 0.27 g (0.90 mmol) of $Hg(SMe)_2$ in 10 mL of $CHCl_3$ was added with stirring to a solid mixture containing 0.28 g (0.30 mmol) of $Hg(PPh_3)_2(ClO_4)_2$ and 0.17 g (0.65 mmol) of PPh_3. After 10 min, most of the solids had dissolved to give a colorless solution. This was filtered and left to crystallize at 5 °C. The colorless transparent crystals obtained in ca. 12 h were separated by decantation, washed with diethyl ether, and dried in vacuo to obtain 0.49 g (69%) of the product. Anal. Calcd for $C_{78}H_{78}Cl_2Hg_4O_8P_4S_6$ (mol wt 2333.032): C, 40.16; H, 3.37. Found: C, 39.90; H, 3.67. ^1H NMR ($CDCl_3$): δ_H 1.85 (s, $-CH_3$), 7.24–7.57 (phenyl H).

$[Hg_4(SEt)_6(PPh_3)_4](ClO_4)_2 \cdot CH_2Cl_2$ (4). A solution of 0.48 g (1.5 mmol) of $Hg(SEt)_2$ in 5 mL of CH_2Cl_2 was added to a solution containing 0.46 g (0.50 mmol) of $Hg(PPh_3)_2(ClO_4)_2$ and 0.26 g (1.0 mmol) of PPh_3 in 10 mL of CH_2Cl_2. The mixture was stirred for 10 min and then filtered, saturated with diethyl ether, and left for crystallization at 5 °C. The white crystals were collected by filtration, washed with ether, and dried in vacuo to give 0.88 g (70%). Anal. Calcd for $C_{84}H_{90}Cl_2Hg_4O_8P_4S_6 \cdot CH_2Cl_2$ (mol wt 2502.13): C, 40.80; H, 3.71. Found: C, 40.64 and 40.83; H, 3.89 and 3.93. ^1H NMR ($CDCl_3$): δ_H 0.8 (t, $-CH_3$, ^3J(H–H) = 7.3 Hz), 2.48 (q, $-CH_2$, ^3J(H–H) = 7.3 Hz), 5.3 (CH_2Cl_2), 7.35–7.58 (phenyl H).

$[Hg_4(SPh)_6(AsPh_3)_4](ClO_4)_2 \cdot 1.5CHCl_3$ (5). This compound was prepared by a procedure analogous to that for **2**; yield 0.60 g (65%). Anal. Calcd for $C_{108}H_{90}As_4Cl_2Hg_4O_8S_6 \cdot 1.5CHCl_3$ (mol wt 3060.32): C, 42.98; H, 3.01. Found: C, 42.54 and 42.76; H, 3.14 and 2.94. ^1H NMR (CD_2Cl_2): δ_H 7.23 ($CHCl_3$), 6.75–7.51 (phenyl H).

$[Hg_4(SPh)_6(PEt_3)_4](ClO_4)_2$ (6). A 0.63-g (1.5-mmol) portion of solid $Hg(SPh)_2$ was stirred into a mixture of 0.32 g (0.50 mmol) of $Hg(PEt_3)_2(ClO_4)_2$ and 0.12 g (1.0 mmol) of PEt_3 in 10 mL of acetone, producing a clear colorless solution. This was saturated with diethyl ether and cooled to 5 °C for crystallization. The colorless crystals were separated by decantation, washed with cyclohexane, and dried in vacuo (0.84 g, 83%). Anal. Calcd for $C_{60}H_{90}Cl_2Hg_4O_8P_4S_6$ (mol wt 2128.93): C, 33.85; H, 4.26. Found: C, 33.66; H, 4.24. ^1H NMR ($(CD_3)_2CO$): δ_H 0.85 (d of t, $-CH_3$, ^3J(H–H) = 7.5 Hz, ^3J(P–H) = 19.8 Hz), 1.6 (t, $-CH_2$, ^3J(H–H) = 7.3 Hz), 7.23–7.80 (phenyl H).

$[Hg_4(SePh)_6(PEt_3)_4](ClO_4)_2$ (7). To a solution of $Hg(PEt_3)_2(ClO_4)_2$ (0.19 g, 0.30 mmol) and PEt_3 (0.071 g, 0.62 mmol) in 5 mL of $CHCl_3$ was added 0.46 g (0.90 mmol) of solid $Hg(SePh)_2$ with stirring. A clear yellow solution was obtained, from which the product separated as a thick yellow oil at the bottom. After 10 min the solvent was removed under a flow of argon gas. The viscous yellow product was dissolved in 5 mL of acetone. The acetone solution was filtered and cooled at 0 °C before addition of 10 mL of diethyl ether to form a layer over the top. The mixture was left overnight at 0 °C for crystallization to occur. The yellow crystalline solid product was separated by decantation of the mother liquor, washed with diethyl ether, and dried in vacuo to get 85% yield (0.62 g). Anal. Calcd for $C_{60}H_{90}Cl_2Hg_4O_8P_4Se_6$ (mol wt 2410.303): C, 29.90; H, 3.76. Found: C, 29.50; H, 3.52. ^1H NMR ($(CD_3)_2CO$: δ_H 0.84 (d of t, $-CH_3$, ^3J(H–H) = 7.6 Hz, ^3J(P–H) = 19.4 Hz), 1.63 (br s, CH_2), 7.30–7.86 (phenyl H).

The ^{13}C NMR spectra of all the new compounds are consistent with the formulations given.[33]

NMR Spectra. All NMR samples were prepared under Ar with concentrations on a mass of solute/volume of solvent basis. Proton and ^{13}C NMR spectra were obtained with Varian XL-200 and XL-300 spectrometer systems, respectively. Either spectrometer was used to obtain ^{31}P, ^{77}Se, and ^{199}Hg NMR spectra, the operating frequencies then being respectively 80.98 or 121.42, 38.15 or 57.20, and 35.75 or 53.60 MHz. Broad-band ^1H decoupling was used in collection of the ^{13}C, ^{31}P, and ^{199}Hg NMR data. The tube size was 5 mm o.d. for ^1H, ^{13}C, and most of the ^{31}P NMR spectroscopy, and in these cases the deuteriated solvent was the ^2D field/frequency lock substance. For the ^{77}Se, ^{199}Hg, and some of the ^{31}P NMR spectroscopy, the tubes were 10 mm o.d. With the samples of larger volume, protiated solvents were used and there was no field/frequency lock (field drift ≪1 Hz/day). The reference signals were those of the solvent for ^1H and ^{13}C, external 85% H_3PO_4 for ^{31}P, external neat Me_2Se for ^{77}Se, and external 0.1 M $Hg(ClO_4)_2$ in 5% v/v $HClO_4$ solution for ^{199}Hg. No corrections for diamagnetic susceptibility difference were made. The conversion of the ^{199}Hg chemical shifts to the more common $HgMe_2$ reference is $\delta_{Hg}(HgMe_2,ext) = \delta_{Hg}(Hg(ClO_4)_2,ext) - 2253$ ppm.[34] Probe temperatures were measured by means of a thermocouple probe in a stationary dummy sample of the appropriate solvent.

Simulation of NMR Spectra. Spectra were simulated by using a version of LAOCOON3[35] adapted locally[36] to run on a Victor 9000 computer. It was possible to simulate the appropriately weighted sum of all isotopomers with seven spins or less; these comprise 98% of the isotopomers present for a single complex.

Elemental Microanalyses. All C and H microanalyses were performed by Guelph Chemical Laboratories Ltd.

Results and Discussion

Synthesis. The compounds $[Hg_4(ER)_6L_4](ClO_4)_2$ (L = PPh_3, ER = SePh, SPh, SMe, SEt, S-*n*-Pr, S-*n*-Bu, or S-*n*-C_5H_{11}; L = $AsPh_3$, ER = SPh; L = PEt_3, ER = SePh or SPh) are produced quantitatively in solution (see the following section) from the appropriate mixture of $HgL_2(ClO_4)_2$,[37] $Hg(ER)_2$, and L in the molar ratio 1:3:2, according to eq 1. The same type of compounds

$$HgL_2(ClO_4)_2 + 3Hg(ER)_2 + 2L \rightarrow [Hg_4(ER)_6L_4](ClO_4)_2 \quad (1)$$

(30) The pure compounds $Hg(SR)_2$ give sharp ^{199}Hg NMR signals: $\Delta\nu \leq 10$ Hz. As solutions in $CHCl_3$ at 294 ± 1 K with concentration 0.1 mol/L of solvent (or saturated, as noted, for the less soluble compounds), δ_{Hg} = −871, −805, −807, −795, −801, −793, −801, −772, −889, and −1065 for R = Me (saturated), Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu (saturated), *n*-C_5H_{11}, c-C_6H_{12}, CH_2Ph, and Ph (saturated) respectively. For a saturated solution of $Hg(SePh)_2$ in $CHCl_3$ at 294 K, the ^{77}Se and ^{199}Hg NMR parameters are δ_{Hg} = −1512 ($\Delta\nu_{1/2} \approx 23$ Hz) and δ_{Se} = 248.3 ($\Delta\nu_{1/2} \approx 13$ Hz).

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(37) Use of $Hg(ClO_4)_2$ directly as a precursor leads to extensive formation of elemental Hg, as has been noted for formation of mononuclear phosphine complexes also.[26]

appear to form when L = PPh_3 and ER = SCH_2Ph or S-c-C_6H_{11} also. In all cases complete dissolution occurs in less than 5 min under the conditions used (room temperature, $[M_4]_{total} \approx (5–60) \times 10^{-3}$ M). The products were isolated in good to high yields for the following representative cases: L = PPh_3, ER = SePh (**1**), SPh (**2**), SMe (**3**), or SEt (**4**); L = $AsPh_3$, ER = SPh (**5**); L = PEt_3, ER = SPh (**6**) or SePh (**7**).

Before we turned to the potentially hazardous perchlorate salts, several preliminary experiments were carried out with $Hg(O_2C-CF_3)_2$ ($Hg(TFA)_2$) to form the clusters with PPh_3 as in eq 2.

$$Hg(TFA)_2 + 3Hg(ER)_2 + 4PPh_3 \rightarrow [Hg_4(ER)_6(PPh_3)_4](TFA)_2 \quad (2)$$

Study by ^{31}P and ^{199}Hg NMR studies confirms the existence of the indicated products at low temperatures for ER = SEt or S-*n*-Pr. However, ^{13}C NMR studies at ambient probe temperature show that the cations undergo partial dissociation to free $Hg(SR)_2$ under these conditions, so use of the TFA^- salts was discontinued. In contrast, the clusters as ClO_4^- salts do not appear to be dissociated at ambient probe temperature (see below). The difference in behavior is probably linked to the different coordination tendencies of the counteranions. The TFA^- anion is known[38,39] to compete with PPh_3 for sites on Hg(II), in contrast to ClO_4^-, which does not.[26,38]

NMR Studies. (i) $[Hg_4(ER)_6L_4](ClO_4)_2$. With ^{199}Hg in natural abundance,[23] an Hg_4 cluster exists in isotopomeric forms, $(^{199}Hg)_x(^0Hg)_{4-x}$. The expected[40] statistical fractional populations are 0.4783, 0.3874, 0.1177, 1.589×10^{-2}, and 8.042×10^{-4} for x = 0–4, respectively. In **1** and **7**, magnetically active ^{77}Se occurs also,[23] leading to isotopomeric chalcogen cores, $(^{77}Se)_y(^0Se)_{6-y}$, as well. The statistical[40] fractional populations of $(^{77}Se)_y(^0Se)_{6-y}$ are 0.623, 0.307, 6.29×10^{-2}, 6.88×10^{-3}, 4.23×10^{-4}, 1.39×10^{-5}, and 1.90×10^{-7} for y = 0–6, respectively. At reduced temperature, the $^{31}P\{^1H\}$, $^{199}Hg\{^1H\}$, and (where applicable) ^{77}Se NMR spectra of the various complexes $[Hg_4(ER)_6L_4]^{2+}$ are the expected composite. For example, the ^{31}P and ^{199}Hg NMR spectra of **1**, as a freshly prepared[41] 0.05 mol/L solution in $CHCl_3$ at 213 K, are shown in parts a and b, respectively, of Figure 1.

The ^{31}P NMR spectrum of **1** (Figure 1a) has features that taken together show the cation to have structure I, with E = Se (of SePh) and D = P (of PPh_3). First there is a singlet center band due to the $(^0Hg)_4$ isotopomer. Symmetrically displaced about this are the spectra of the isotopomers $(^{199}Hg)(^0Hg)_3$ and $(^{199}Hg)_2(^0Hg)_2$. The isotopomer $(^{199}Hg)(^0Hg)_3$ gives rise to an $A_3A'X$ (A = ^{31}P, X = ^{199}Hg) spin system, with one PPh_3 bound directly to ^{199}Hg and three PPh_3 ligands magnetically inequivalent to the first separated from ^{199}Hg by three bonds. The magnitudes of the coupling constants are in the order $^1J(^{199}Hg–^{31}P) \gg {}^3J(^{199}Hg–^{31}P) > {}^4J(^{31}P–^{31}P)$. Therefore, as shown in Figure 1a, the ^{31}P NMR spectrum of this isotopomer consists of parts: two quartets (relative intensity 1; partly overlapping the spectrum of the $(^{199}Hg)_2(^0Hg)_2$ isotopomer (see below)) separated by the large $^1J(^{199}Hg–^{31}P)$ and two doublets (relative intensity 3) adjacent to the center band separated by the smaller $^3J(^{199}Hg–^{31}P)$. The splitting within the quartets and the smaller splitting in the double doublet are both $^4J(^{31}P–^{31}P)$. Various other weak lines in Figure 1a arise from the isotopomer $(^{199}Hg)_2(^0Hg)_2$. The spectrum of this isotopomer is particularly obvious in the region of, and partly overlapping with, the quartets from the $(^{199}Hg)(^0Hg)_3$ isotopomer. A spectral simulation based on the expected $A_2A'A''XX'$ (A = ^{31}P, X = ^{199}Hg) spin system indicates that the spread of the weaker spectrum around each quartet of the $A_3A'X$ spectrum is $^2J(^{199}Hg–^{199}Hg)$, as shown in Figure 1a.

The ^{199}Hg NMR spectrum of **1** (Figure 1b) is also of the form expected for structure I and is consistent with the interpretation

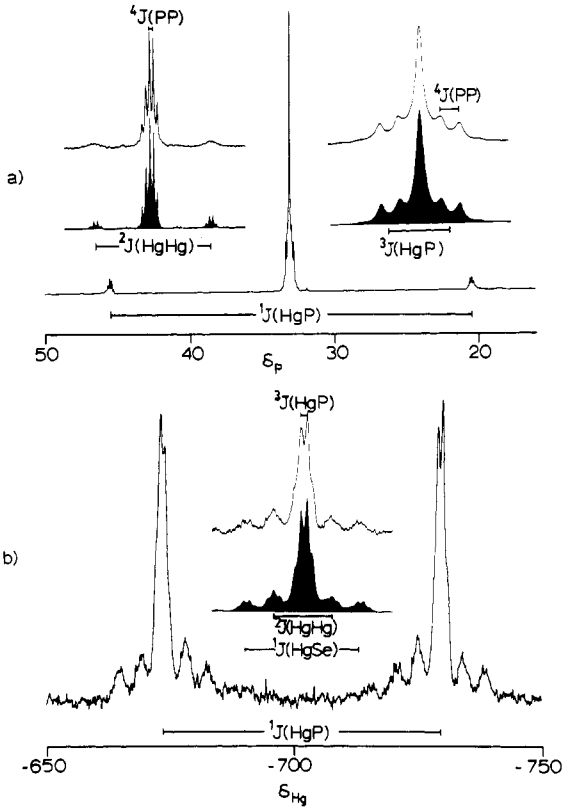

Figure 1. NMR spectra of $[(\mu\text{-SePh})_6(HgPPh_3)_4](ClO_4)_2$ in $CHCl_3$ at 213 K: (a) 121.42-MHz $^{31}P\{^1H\}$ NMR spectrum (left inset, 750 Hz wide expansion of the high-frequency satellite region with (below) a simulation; right inset, 150 Hz wide expansion of the center band with (below) a simulation); (b) 53.65-MHz $^{199}Hg\{^1H\}$ NMR spectrum (inset, 1500-Hz expansion of the low-frequency half of the spectrum with (below) a simulation).

of the ^{31}P NMR spectrum. The strongest feature of the ^{199}Hg NMR spectrum is a doublet of quartets, in which the large doublet splitting is $^1J(^{199}Hg–^{31}P)$ and the quartet splitting is $^3J(^{199}Hg–^{31}P)$, as indicated in the figure. This is the X part of the $A_3A'X$ spectrum of the isotopomer $(^{199}Hg)(^0Hg)_3$. Each quartet has two further satellite spectra. That with the larger separation is a result of one-bond coupling to ^{77}Se, as confirmed by the presence of the same 940-Hz coupling in the ^{77}Se NMR spectrum. The other, with the smaller 480-Hz coupling, is a result of $^2J(^{199}Hg–^{199}Hg)$ in the X part of the $A_2A'A''XX'$ spectrum of the isotopomer $(^{199}Hg)_2(^0Hg)_2$; the same coupling appears in the ^{31}P NMR spectrum (see above). Both these additional couplings are shown in Figure 1b. A spectral simulation using the parameters given in Table I and including statistical[40] contributions from the various isotopomers $^{31}P_4(^{199}Hg)_x(^0Hg)_{4-x}(^{77}Se)_y(^0Se)_{6-y}$ satisfactorily reproduce the ^{31}P and ^{199}Hg NMR spectra (Figure 1, insets).

In the ^{77}Se NMR spectrum of **1** (not shown), the intensity ratio (^{199}Hg satellites/center band) is ca. 0.18. This is close to the value 0.192 that can be calculated for structure I on statistical grounds by using the populations of the various isotopomers and the possible relative positions of ^{77}Se and ^{199}Hg. At 213 K, no additional fine structure is observed in the ^{77}Se NMR spectrum of **1**. However, at 237 K, the center band of the ^{77}Se NMR spectrum is a "filled in" triplet, as expected for the X part of the $A_2A'_2X$ spectrum of the $^{31}P_4(^0Hg)_4(^{77}Se)(^0Se)_5$ core. The splitting of the components, $(^4J(^{31}P–^{77}Se) + {}^2J(^{31}P–^{77}Se))_{av}$, is 28 Hz. It seems likely that the four-bond coupling will be near zero, so $^2J(^{31}P–^{77}Se) \approx$ 28 Hz.

Overall, the ^{31}P, ^{199}Hg, and ^{77}Se NMR spectra of **1** are consistent only with the skeleton $(\mu\text{-Se})_6(HgP)_4$, having structure I on a time average. Thus **1** must be formulated as $[(\mu\text{-SePh})_6(HgPPh_3)_4](ClO_4)_2$.

Table I also includes NMR data for all the other species $[Hg_4(ER)_6L_4]^{2+}$ that were obtained cleanly. The reduced-tem-

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(41) For all the complexes described here, samples that have been allowed to stand give NMR spectra that are less well-resolved than those of fresh samples.

Table I. NMR Spectral Parameters of $[(\mu\text{-ER})_6(HgL)_4](ClO_4)_2$ in $CHCl_3$[a]

ER	L	δ_P[b]	δ_{Hg}[c]	$^1J(^{199}Hg-^{31}P)$	$^3J(^{199}Hg-^{31}P)$	$^4J(^{31}P-^{31}P)$	$^2J(^{199}Hg-^{199}Hg)$
SePh[d]	PPh_3	32.9	−702	3025 ± 2	50 ± 2	15 ± 1	480 ± 25
SPh[e]	PPh_3	38.5	−443	4160 ± 2	33 ± 1	11 ± 1	445 ± 5[e]
SMe[f]	PPh_3	30.0	~−327[g,h]	3015 ± 3	48 ± 2	15 ± 1	500 ± 20
SEt	PPh_3	28.9	−329	2898 ± 2	48 ± 2	15 ± 2	505 ± 25
S-*n*-Pr[h]	PPh_3	26.3	−325	2982 ± 2	50 ± 2	15 ± 1	500 ± 20
S-*n*-Bu[h]	PPh_3	26.3	−326	2867 ± 2	51 ± 1	14 ± 1	500 ± 10
SPe[h,i]	PPh_3	26.7	−324	2840 ± 2	51 ± 1	14 ± 1	497 ± 3
SePh[j,l]	PEt_3	42.8	−638	3674 ± 3	24 ± 1	12 ± 1	443 ± 5
SPh[j,l]	PEt_3	49.2	−392	4550 ± 2	16 ± 1	9 ± 1	392 ± 5
SPh[f]	$AsPh_3$		−476				

[a] At 213 K for solutions with concentration 0.05 mol/L of $CHCl_3$ at room temperature, except where noted otherwise. All J values are in hertz. [b] Relative to external 85% H_3PO_4 at 296 K; estimated error ±0.1 ppm. [c] Relative to external $HgMe_2$; measured relative to 0.1 M $Hg(ClO_4)_2$(aq) at 296 K as external reference and converted by using $\delta_{Hg}(HgMe_2) = \delta_{Hg}(Hg(ClO_4)_2(aq)) - 2253$.[34] Estimated error ±1 ppm. [d] $^1J(^{199}Hg-^{77}Se) = 940 \pm 25$ Hz. δ_{Se} (relative to external pure Me_2Se at 298 K) = 6.6 ± 0.2. At 237 K for a 0.05 mol/L solution in $CHCl_3$, $^1J(^{199}Hg-^{77}Se) = 940 \pm 20$ Hz, $\delta_{Se} = 10.7$, and $(^4J(^{31}P-^{77}Se) + {}^2J(^{31}P-^{77}Se))_{av} = 28 \pm 1$ Hz $\approx {}^2J(^{31}P-^{77}Se)$. [e] At 296 K, $\delta_P = 39.4$, $\delta_{Hg} = -473$, $^1J(^{199}Hg-^{31}P) = 4109 \pm 5$ Hz, and $^2J(^{199}Hg-^{199}Hg) = 454 \pm 5$ Hz; neither $^3J(^{199}Hg-^{31}P)$ nor $^4J(^{31}P-^{31}P)$ is observed at this temperature. [f] Saturated solution in $CHCl_3$. [g] At ca. 233 K as the same was cooling; insufficiently soluble in $CHCl_3$ to obtain a ^{199}Hg NMR spectrum after thermal equilibration. [h] Prepared in situ. [i] Pe = *n*-C_5H_{11}. [j] At 237 K. [k] δ_{Se} (relative to external pure Me_2Se at 298 K) = 13.9 ± 0.1; neither $^1J(^{199}Hg-^{77}Se)$ nor $(^2J(^{31}P-^{77}Se) + {}^4J(^{31}P-^{77}Se))_{av}$ was observed. [l] For a solution with concentration 0.005 mol/L of $CHCl_3$ at room temperature.

perature ^{31}P NMR spectra of all of the other phosphine complexes show the same feature as the ^{31}P NMR spectrum of **1** and can be interpreted in a parallel manner. Apart from an absence of $^{77}Se-^{199}Hg$ coupling, the reduced-temperature ^{199}Hg NMR spectra for these species also resemble the corresponding spectrum of **1**. Evidently all these compounds contain cations having the adamantanoid structure $[(\mu\text{-ER})_6(HgPR_3)_4]^{2+}$. We have no good explanation for the absence of $^{31}P-^{77}Se$ and $^{77}Se-^{199}Hg$ couplings in the ^{77}Se and ^{199}Hg NMR spectra, respectively, of **7**.

The ^{199}Hg NMR spectrum of **5** consists of a single line (Table I) and does not in itself prove that the cation in this compound is the adamantanoid $[(\mu\text{-SPh})_6(HgAsPh_3)_4]^{2+}$. However, the spectra of all the other members of the series $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgAsPh_3)_n]^{2+}$ are consistent with such a structure (see below), and therefore it appears safe to assign **5** the same structure. We were unable to obtain any evidence for $[Hg_4(SPh)_6(SbPh_3)_4](ClO_4)_2$, but the adamantanoid species $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgSbPh_3)_n]^{2+}$ (n = 0–2 and perhaps 3) were characterized in equilibrium mixtures (see below). The parent $(SbPh_3)_4$ complex is probably capable of existence once a suitable preparative route is found.

Limiting slow-exchange spectra could not be obtained for $[Hg_4(S\text{-}c\text{-}C_6H_{11})_6(PPh_3)_4](ClO_4)_2$, which was prepared in situ. However, at 213 K, the ^{31}P and ^{199}Hg NMR spectra of a 0.05 mol/L solution in $CHCl_3$ gave sufficient detail ($\delta_P = 28.8$ ($\Delta\nu_{1/2} \approx 100$ Hz), $^1J(^{199}Hg-^{31}P) = 2805 \pm 20$ Hz, $^2J(^{199}Hg-^{199}Hg) \approx 500$ Hz, $\delta_{Hg} = -387$) to show the formation of the expected adamantanoid cation in this case.

Firm evidence was obtained for $[(\mu\text{-}SCH_2Ph)_6(HgPPh_3)_4]^{2+}$. This cation is produced in the appropriate mixture of $Hg(PPh_3)_2(ClO_4)_2$, $Hg(SCH_2Ph)_2$, and PPh_3 in $CHCl_3$, but in several attempts we found that this in situ reaction does not proceed cleanly. Nevertheless, the benzyl complex is a major product (the other products remain unidentified). The complex could be characterized on the basis of the expected NMR patterns. At 213 K in a solution of the correct composition to give $[Hg_4]_{total}$ = 0.05 mol/L of $CHCl_3$, $\delta_P = 30.3$, $\delta_{Hg} = -404$, $^1J(^{199}Hg-^{31}P) = 3686 \pm 6$ Hz, $^3J(^{199}Hg-^{31}P) = 41 \pm 2$ Hz, and $^4J(^{31}P-^{31}P) = 12 \pm 1$ Hz.

In contrast to the foregoing, we could obtain no evidence for PPh_3 complexes in which the S-*i*-Pr or S-*t*-Bu was the bridging ligand. The apparent absence of these two complexes is probably due to the steric bulk of the alkyl groups.

At ambient probe temperature, all fine structure is lost in the spectra of the alkane thiolate clusters: a single line with no ^{199}Hg satellites is found in the ^{31}P NMR spectrum and a very broad single line in the ^{199}Hg NMR spectrum. In the spectra of **1**, **6**, and **7**, $^1J(^{199}Hg-^{31}P)$ remains evident but other smaller couplings are lost in the general broadening. In the spectra of **2** the only noticeable losses are those of the two smallest couplings, $^4J(^{31}P-^{31}P)$ and $^3J(^{199}Hg-^{31}P)$. The complexes **1**, **6**, and **7** are evidently long-lived on the time scale of $^1J(^{199}Hg-^{31}P)$ but not on the time scale of smaller couplings, i.e. 3×10^{-4} s $\lesssim \tau \lesssim 3 \times 10^{-3}$ s. The complex **2** is more long-lived with a lifetime long on the time scale of $^2J(^{199}Hg-^{199}Hg)$, i.e. $\tau \lesssim 2 \times 10^{-3}$ s.

It is interesting to note that the relative values of δ_{Hg} found for the phosphine clusters are in the order predicted for the $(R_3P)Hg(ER)_3$ coordination sphere on the basis of additive substituent effects and the values of δ_{Hg} for $Hg(PR_3)_4^{2+}$ and $Hg(ER)_4^{2-}$. We find $\delta_{Hg} = -580$ for $Hg(PPh_3)_4^{2+}$ in $CHCl_3$ at 233 K. In combination with the values $\delta_{Hg} = -978$, −585, and −302 in $Hg(ER)_4^{2-}$ for ER = SePh, SPh, and SEt, respectively, at 297 K in D_2O-H_2O,[42] the order of δ_{Hg} then predicted is **1** < **2** < **4**, as is found. The predicted values themselves are not very close to those found: δ_{Hg} predicted for **1**, **2**, and **4** = −879, −584, and −373; δ_{Hg} found = −702, −443, and −329. These differences, for **1** and **2** at least, seem larger than could be expected[34] from the differences in solvent and temperature used to obtain the data for the Hg_4 clusters $Hg(PPh_3)_4^{2+}$ and $Hg(ER)_4^{2-}$. We conclude tentatively that the "local environment" effect[43] is only a first approximation for Hg(II), i.e. that δ_{Hg} is affected by more than just the atoms in the first coordination sphere. NMR data for $[Hg(ER)_3(PR_3)]^-$ would be useful for comparison with those for the Hg_4 clusters.

The data in Table I also show that all other things being equal the couplings $^2J(^{199}Hg-^{199}Hg)$, $^3J(^{199}Hg-^{31}P)$, and $^4J(^{31}P-^{31}P)$ are all larger in magnitudes when E = Se rather than S, L = PPh_3 rather than PEt_3, or R in RS = alkyl rather than Ph. The values of $^1J(^{31}P-^{199}Hg)$ show the inverse correlations. These relationships can be rationalized in terms of the "s" character of the hybrid orbitals of Hg. It has been suggested[44] that the Fermi contact mechanism makes the dominant contribution to $^1J(^{31}P-^{199}Hg)$ (which is known[45] to have an absolute positive sign). If so, a larger one-bond coupling can be attributed to a larger "s" character in the hybrid orbital of Hg that is involved in the Hg–P bond. The corresponding reduction in "s" character of the other bonds to Hg, those to the bridging chalcogen, would alone lead to reduction to couplings through the chalcogen atom if these are dominated by the Fermi contact mechanism as well. Similarly, changes at the chalcogen atom that promote an increase in the "s" character of the hybrid orbital of Hg that is used in the Hg–E bond should cause an increase in couplings through the chalcogen bridge. The Hg–P bond should show a complementary reduction in both Hg "s" character and $^1J(^{199}Hg-^{31}P)$.

The values obtained for $^2J(^{199}Hg-E-^{199}Hg)$ in $[(\mu\text{-ER})_6(HgPR'_3)_4]^{2+}$, 392–505 Hz for $^2J(^{199}Hg-S-^{199}Hg)$ and 438–480

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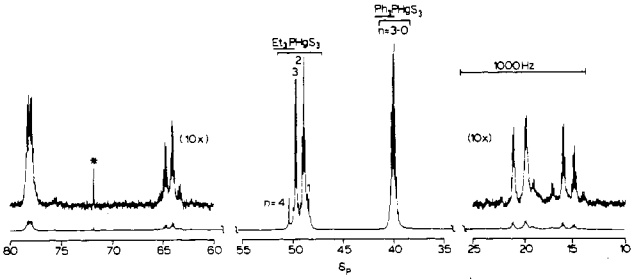

Figure 2. 80.98-MHz $^{31}P\{^1H\}$ NMR spectrum of a 1:3:2 $Hg(PEt_3)_2(ClO_4)_2$–$Hg(SPh)_2$–PPh_3 mixture in $CHCl_3$ at 237 K, showing the formation of $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgPEt_3)_n]^{2+}$. The ^{199}Hg satellites shown inset have the vertical scale expanded 10× (* = impurity).

Hz for $^2J(^{199}Hg–Se–^{199}Hg)$ (Table I), can be compared with the 2435–2959 Hz found[46] for $^2J(^{199}Hg–P–^{199}Hg)$ in anions containing eight-membered $(–Hg–P(c\text{-}C_6H_{11})_2–)_4$ rings.

(ii) $[(\mu\text{-ER})_6(HgL)_{4-n}(HgL')_n]^{2+}$. To confirm the tetrameric nature of the Hg_4 clusters and to learn more about them, NMR studies were made of several representative complexes with mixed terminal ligands (as the ClO_4^- salts). Two methods are available to prepare equilibrium mixtures of complexes. The first is the straightforward ligand redistribution reaction of $[(\mu\text{-ER})_6(HgL)_4]^{2+}$ with $[(\mu\text{-ER})_6(HgL')_4]^{2+}$ (eq 3). This method requires

$$[(\mu\text{-ER})_6(HgL)_4]^{2+} + [(\mu\text{-ER})_6(HgL')_4]^{2+} \rightleftharpoons \underset{\text{equilibrium mixture}}{[(\mu\text{-ER})_6(HgL)_{4-n}(HgL')_n]^{2+}} \quad (3)$$

that the two parent complexes be either isolable, the preferable situation, or, failing that, preparable in situ. A second method is to generate the mixed-ligand complexes in situ from HgL_2^{2+},[37] $Hg(ER)_2$, and L′ (eq 4). This is the only method that can be

$$HgL_2^{2+} + 3Hg(ER)_2 + 2L' \rightleftharpoons \underset{\text{equilibrium mixture}}{[(\mu\text{-ER})_6(HgL)_{4-n}(HgL')_n]^{2+}} \quad (4)$$

used to produce the desired species if one of the parent complexes cannot be prepared, as is the case for L′ = $SbPh_3$ (see above). By this method, complete coverage of the L-rich part of the series can be obtained by substituting L′–L mixtures for L′ or by adding $[(\mu\text{-ER})_6(HgL)_4]^{2+}$ to the HgL_2^{2+}–L′–$Hg(ER)_2$ mixture; however, the L′-rich part of the series is inaccessible.

(a) $[(\mu\text{-EPh})_6(HgPPh_3)_{4-n}(HgPEt_3)_n]^{2+}$ (E = S or Se). Equilibrium mixtures containing these complexes (as the ClO_4^- salts) can be obtained according to either eq 3 or eq 4. For both benzenechalcogenates, the parent tetranuclear complexes and the complexes $Hg(PR_3)_2^{2+}$ are available for both phosphines.

Figure 2 shows the slow-exchange ^{31}P NMR spectrum of a mixture of average composition $[(\mu\text{-SPh})_6(HgPPh_3)_2(HgPEt_3)_2]^{2+}$ in $CHCl_3$[47] at 237 K. At ambient probe temperature the spectrum is collapsed to two broad signals, each with ^{199}Hg satellites. The sample in this case was prepared according to eq 4, but identical results are obtained from a mixture in which 2:6 = 1:1, as expected from eq 3.

In Figure 2 the center-band resonances fall into two regions. By comparison with the ^{31}P NMR spectra of **2** and **6** (Table I), the less shielded region can be assigned to PEt_3 on Hg and the more shielded to PPh_3 on Hg. Within the PEt_3-on-Hg region the center bands that can be seen are a singlet, a doublet, a triplet, and a quartet. These can be assigned straightforwardly to PEt_3 in $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgPEt_3)_n]^{2+}$ with n = 4, 3, 2, and 1, respectively. The splitting of the multiplets is due to four-bond $^{31}P–^{31}P$ coupling over the pathway $Ph_3{}^{31}P–Hg–S–Hg–{}^{31}PEt_3$, and the maximum observed multiplicity of four confirms the tetranuclear nature of the clusters. In the PPh_3-on-Hg region there occur the corresponding quartet, triplet, doublet, and singlet from the mixed-ligand clusters with n = 3, 2, 1, and 0, respectively. There is considerable signal overlap in this region, but the separate components can be identified by increasing the frequency of measurement from 80.98 to 121.42 MHz, from the centroids of the ^{199}Hg satellite spectra (see below), and from the spectra of mixtures with different PPh_3:PEt_3 ratios. In the last case, confirmation of all the assignments is also obtained.

Every center band in Figure 2 has a ^{199}Hg satellite spectrum. The satellite spectra of **2** and **6** have been discussed in (i) above. When n = 1–3, each complex has two isotopomers containing one ^{199}Hg: one with ^{199}Hg bound to PPh_3, the other with ^{199}Hg bound to PEt_3. The isotopomers $[(\mu\text{-SPh})_6(^{199}HgPPh_3)(^0HgPPh_3)_{3-n}(^0HgPEt_3)_n]^{2+}$ give rise to $A_{3-n}A'M_nX$ spectra (A, M = ^{31}P; X = ^{199}Hg) that are of first-order appearance because $^1J(^{199}Hg–^{31}P) \gg {}^3J(^{199}Hg–^{31}P)$, $^4J(^{31}P–^{31}P)$ and so can be analyzed straightforwardly. Similarly, the isotopomers $[(\mu\text{-SPh})_6(^0HgPPh_3)_{4-n}(^{199}HgPEt_3)(^0HgPEt_3)_{n-1}]^{2+}$ produce $A_{4-n}M_{n-1}M'X$ spectra that can be analyzed readily. In all cases the satellite spectra appear as pairs of quartets. This quartet fine structure is further confirmation of the tetranuclear nature of the cations with mixed ligands.

Evidence for isotopomers containing two ^{199}Hg nuclei was observed in the PPh_3-on-Hg region of the complex with n = 1 and in the PEt_3-on-Hg region of the complex with n = 3. In these cases the quartet satellites due to the $(^{199}Hg)(^0Hg)_3$ isotopomer are flanked by additional weaker signals. The value of $^2J(^{199}Hg–^{199}Hg)$ is obtained from the separation of these minor signals as described in (i) above. In the complex with n = 1, the probability of forming $[(\mu\text{-SPh})_6(^{199}HgPPh_3)_2(^0HgPPh_3)(^0HgPEt_3)]^{2+}$ is twice that of forming $[(\mu\text{-SPh})_6(^{199}HgPPh_3)(^0HgPPh_3)_2(^{199}HgPEt_3)]^{2+}$. Therefore, the two-bond coupling observed in the PPh_3-on-^{199}Hg region of the complex with n = 1 is probably $^2J(Ph_3P^{199}Hg–S–^{199}HgPPh_3)$ rather than $^2J(Ph_3P^{199}Hg–S–^{199}HgPEt_3)$. An analogous argument suggests that the two-bond coupling observed in the PEt_3-on-^{199}Hg region of the species with n = 3 is $^2J(Et_3P^{199}Hg–S–^{199}HgPEt_3)$ rather than $^2J(Et_3P^{199}Hg–S–^{199}HgPPh_3)$. As expected, the values of ^2J are of the same magnitude as the corresponding couplings in the parent complexes.

Details of the ^{31}P NMR spectra of $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgPEt_3)_n]^{2+}$ are given in Table II. From these data it can be seen that each individual complex can be characterized by its value(s) of $^1J(^{199}Hg–^{31}P)$. This feature makes analysis of the ^{199}Hg NMR spectra of the complexes straightforward, since the spectra consist of doublets, with splitting $^1J(^{199}Hg–^{31}P)$ (some with additional fine structure due to $^3J(^{199}Hg–^{31}P)$. Table II contains the ^{199}Hg NMR chemical shifts found by using this correlation between the ^{31}P and ^{199}Hg NMR spectra.

The complexes $[(\mu\text{-SePh})_6(HgPPh_3)_{4-n}(HgPEt_3)_n]^{2+}$ give reduced-temperature ^{31}P NMR spectra that are very similar to those of the sulfur analogues and can be assigned and analyzed in an identical manner. Again the values of $^1J(^{199}Hg–^{31}P)$ allow a correlation of the ^{199}Hg and ^{31}P NMR spectra. Most of the ^{199}Hg NMR signals for the complexes with mixed terminal ligands showed ^{77}Se satellites, like the spectrum of **1** but unlike that of **7** (see above). In the ^{77}Se NMR spectra of this series, a total of nine lines is expected if δ_{Se} is sensitive to the nature of all the terminal ligands.[13] Seven or possibly eight signals are observed, in the region δ_{Se} = −1.5 to +20.7.[33] We conclude that δ_{Se} is sensitive to the nature of all ligands present but that some signal overlap occurs. Full details of the ^{31}P, ^{199}Hg, and ^{77}Se NMR spectra of $[(\mu\text{-SePh})_6(HgPPh_3)_{4-n}(HgPEt_3)_n]^{2+}$ have been deposited as supplementary material.

For the two series with mixed terminal phosphines we find the following changes as n increases: (a) both $\delta_P(PPh_3)$ and $\delta_P(PEt_3)$ show slight monotonic increases; (b) $\delta_{Hg}(^{199}Hg$ on $PPh_3)$ changes irregularly and $\delta_{Hg}(^{199}Hg$ on $PEt_3)$ decreases monotonically; (c) both $^1J(^{199}Hg–^{31}PPh_3)$ and $^1J(^{199}Hg–^{31}PEt_3)$ decrease. We also note again (see above) that for comparable complexes the values of $^1J(^{199}Hg–^{31}P)$ are smaller in the SePh complexes than in the SPh complexes, while those of $^3J(^{199}Hg–^{31}P)$ and $^4J(^{31}P–^{31}P)$ are

(46) Eichbichler, J.; Peringer, P. *Chem. Ber.* **1984**, *117*, 1215.
(47) Similar but less well-resolved spectra are observed when Me_2CO is used as solvent.

Table II. NMR Spectra (^{31}P and ^{199}Hg) of $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgPEt_3)_n]^{2+}$ in $CHCl_3$ at 237 K[a]

Chemical Shifts

	PPh_3		PEt_3			PPh_3		PEt_3	
n	δ_P[b]	δ_{Hg}[c]	δ_P[b]	δ_{Hg}[c]	n	δ_P[b]	δ_{Hg}[c]	δ_P[b]	δ_{Hg}[c]
0[d]	38.5	−450[e]			3	39.1	−434[f]	48.5	−390
1	38.7	−455[e]	47.3	−365	4[g]			49.2	−392
2	38.9	−452[f]	47.7	−378					

Nuclear Spin–Spin Coupling Constants (Hz)

	PPh_3		PEt_3			
n	$^1J(^{199}Hg-^{31}P)$[h]	$^3J(^{199}Hg-^{31}P)$[h]	$^1J(^{199}Hg-^{31}P)$[h]	$^3J(^{199}Hg-^{31}P)$[i]	$^4J(^{31}P-^{31}P)$[j]	$^2J(^{199}Hg-^{199}Hg)$
0[d]	4147	33[e,j]			11	450 ± 10[e]
1	4027	31[e,j]	4763	16[k]	10	410 ± 10[e,l]
2	3883	*m*	4713	15[k]	10	*m*
3	3741	*m*	4638	16,[k] 15[o]	10	~420[f,n]
4[g]			4550	16[o]	9	392 ± 5

[a] As an equilibrium mixture of ClO_4^- salts in a solution where $[Hg_4]_{total}$ = 0.05 mol/L of solvent, and PEt_3:PPh_3 = 1:1 unless noted otherwise. [b] Relative to external 85% H_3PO_4; estimated error ±0.1 ppm. [c] Relative to external pure $HgMe_2$; measured relative to external 0.1 M $Hg(ClO_4)_2$(aq) and converted to $HgMe_2$ as reference by using $\delta_{Hg}(HgMe_2) = \delta_{Hg}(0.1\ M\ Hg(ClO_4)_2(aq)) - 2253$.[34] Estimated error ±1 ppm. [d] In a solution of $[Hg_4(SPh)_6(PPh_3)_4](ClO_4)_2$ where $[Hg_4]$ = 0.05 mol/L of solvent, δ_P = 38.4, δ_{Hg} = −450, $^1J(^{199}Hg-^{31}P)$ = 4138 ± 2 Hz, $^4J(^{31}P-^{31}P)$ = 11 ± 1 Hz, $^2J(^{199}Hg-^{199}Hg)$ = 448 ± 2 Hz, and $^3J(^{199}Hg-^{31}P)$ = 35 ± 1 Hz. [e] In a solution where $[Hg_4]_{total}$ = 0.05 mol/L of solvent and PEt_3:PPh_3 = 1:3. [f] In the supernatant of a saturated mixture ($[Hg_4]_{total}$ < 0.02 mol/L of $CHCl_3$) where PEt_3:PPh_3 = 3:1. [g] In a solution of $[Hg_4(SPh)_6(PEt_3)_4](ClO_4)_2$ where $[Hg_4]_{total}$ = 0.005 mol/L of solvent. [h] Estimated error ±3 Hz. [i] Estimated error ±1 Hz. [j] In the quartet fine structure of the ^{199}Hg NMR spectrum. [k] $Ph_3P^{199}Hg-S-Hg^{31}PEt_3$ coupling, observed in ^{31}P NMR spectrum (PEt_3 region). [l] In the ^{199}Hg satellites of the PPh_3 region of the ^{31}P NMR spectrum. [m] Could not be observed with certainty. [n] In the ^{199}Hg satellites of the PEt_3 region of the ^{31}P NMR spectrum. [o] $Et_3P^{199}Hg-S-Hg^{31}PEt_3$ coupling, observed in the ^{31}P NMR spectrum (PEt_3 region).

larger. An interesting observation for the SePh complexes is that $^3J(Ph_3P^{199}Hg-Se-Hg-^{31}PEt_3)$ (44–49 Hz[33]) and $^3J(Ph_3P^{199}Hg-Se-Hg-^{31}PPh_3)$ (50 Hz, Table I) are about twice as large as $^3J(Et_3P^{199}Hg-Se-Hg-^{31}PEt_3)$ (23–24 Hz, Table I and supplementary material).

(b) $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgL')_n]^{2+}$ (L' = $AsPh_3$ or $SbPh_3$). For L' = $AsPh_3$, equilibrium mixtures of these mixed-ligand complexes were made according to either eq 3 or eq 4. Analysis of the ^{31}P and ^{199}Hg NMR spectra[33] of this system as described above allowed characterization of the full series $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgAsPh_3)_n]^{2+}$.

Solutions of the $SbPh_3$-containing clusters were prepared as in eq 4 only. The reduced-temperature ^{31}P NMR spectra[33] of $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(SbPh_3)_n]^{2+}$ are very similar to those of the $AsPh_3$ analogues for n = 1 and 2 and can be analyzed in the same way. These two complexes were also characterized by ^{199}Hg NMR.[33] However, we have no good explanation for the appearance in the ^{31}P NMR spectra of two approximately equally intense signals, both with ^{199}Hg satellites, at the position expected for the complex with n = 3. Unfortunately, the lack of $[(\mu\text{-SPh})_6(HgSbPh_3)_4]^{2+}$ precludes a detailed study of the $SbPh_3$-rich part of this series by either ^{31}P or ^{199}Hg NMR.

At ambient probe temperature much of the fine structure found in the reduced-temperature ^{31}P and ^{199}Hg NMR spectra of mixtures of $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgL')_n]^{2+}$ (L' = $AsPh_3$ or $SbPh_3$) is lost. Exchange averaging of the ^{31}P NMR spectra of the species with n = 1–3 produces a center band that is a single line, but this has ^{199}Hg satellites. Thus the $^{199}Hg^{31}PPh_3$ fragment is long-lived on the time scale of ^1J under conditions where averaging of its environment is rapid on the ^{31}P NMR chemical shift time scale, i.e. $2 \times 10^{-4}\ s \lesssim \tau \lesssim 4 \times 10^{-3}\ s$. A separate but broadened ^{31}P NMR spectrum is found for **2**, when present. Evidently **2** is longer lived as a cluster than the complexes with mixed terminal ligands.

Considering all the series $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgL)_n]^{2+}$ (L = PEt_3, PPh_3, $AsPh_3$ or $SbPh_3$), the increases in $\delta_P(PPh_3)$ caused by remote terminal substitution, i.e. by an increase in n, are in the order $PPh_3 < PEt_3 < AsPh_3 < SbPh_3$. The corresponding increases in $\delta_{Hg}(HgPPh_3)$ are in the order $PPh_3 < AsPh_3 < SbPh_3$. (In the series $[(\mu\text{-EPh})_6(HgPPh_3)_{4-n}(HgPEt_3)_n]^{2+}$ $\delta_{Hg}(HgPPh_3)$ varies irregularly (Tables II and (supplementary material) S2).)

(iii) $[(\mu\text{-SPh})_{6-m}(\mu\text{-SePh})_m(HgPPh_3)_4]^{2+}$. Mixtures of **1** and **2** give very complicated reduced-temperature ^{31}P and ^{199}Hg NMR spectra, as exemplified by parts a and b and part c of Figure 3, respectively. The spectra can be understood in terms of redistribution to form adamantanoid complexes with mixed-chalcogen cores according to eq 5.

$$\mathbf{1} + \mathbf{2} \rightleftharpoons [(\mu\text{-SPh})_{6-m}(\mu\text{-SePh})_m(HgPPh_3)_4]^{2+} \quad (5)$$

In the ^{31}P NMR spectrum shown in Figure 3a,b, the center bands fall into four regions. The most shielded region includes the signal due to **1** while the least shielded region includes the signal of **2**. Therefore, it seems that from high to low frequency the four regions should be associated with the four possible combinations of geminal atoms S_3, S_2Se, SSe_2, and Se_3, respectively.[48] The additional complexity observed within each region has two sources: sensitivity of δ_P to the nature of the chalcogens four bonds away from phosphorus and non-zero four-bond $^{31}P-^{31}P$ coupling in those clusters containing more than one environment for ^{31}P.

It is straightforward to show that a total of 20 different environments can occur for ^{31}P and ^{199}Hg in the full series $[(\mu\text{-SPh})_{6-m}(\mu\text{-SePh})_m(HgPPh_3)_4]^{2+}$ and to deduce the relative populations of the different environments in each complex.[33] Also, it is known (Table I) that $^4J(^{31}P-Hg-Se-Hg-^{31}P) > {}^4J(^{31}P-Hg-S-Hg-^{31}P)$. Then proceeding as discussed above, using the signal multiplicities and intensity changes as the **1**:**2** ratio is changed, it is possible to assign the ^{31}P NMR spectra of the series $[(\mu\text{-SPh})_{6-m}(SePh)_m(HgPPh_3)_4]^{2+}$ completely. Detailed assignments have been deposited as supplementary material. It was helpful to find that δ_P increases according to the nature of the distant chalcogen atoms in the same order as for the geminal chalcogen atoms, $S_3 > S_2Se > SSe_2 > Se_3$. The change caused by the change of a distant atom is around 1 order of magnitude smaller than the result of a geminal change, however. A second useful generalization also evolves. There is only a small range of values of $^1J(^{199}Hg-^{31}P)$ associated with a given combination of geminal chalcogen atoms: ~4160 to 4180 Hz for S_3, ~3720 to 3780 Hz for S_2Se, 3356 to ~3480 Hz for SSe_2, and ~2990 to ~3040 Hz for Se_3.[33]

All the $S_{6-m}Se_m$ cores that are possible for tetranuclear clusters are found to occur, including isomeric forms when m = 2–4. Thus the nuclearity and integrity of the clusters are confirmed.

In the ^{199}Hg NMR spectra, there are apparently five groups of signals, as shown in Figure 3c. However, each chemically different $^{199}Hg^{31}PPh_3$ grouping should give rise to a *doublet*, as a result of $^1J(^{199}Hg-^{31}P)$. As confirmed by the ^{199}Hg NMR

(48) The alternative possibility that δ_P is most sensitive to the chalcogens four bonds distant does not seem plausible and so has been disregarded.

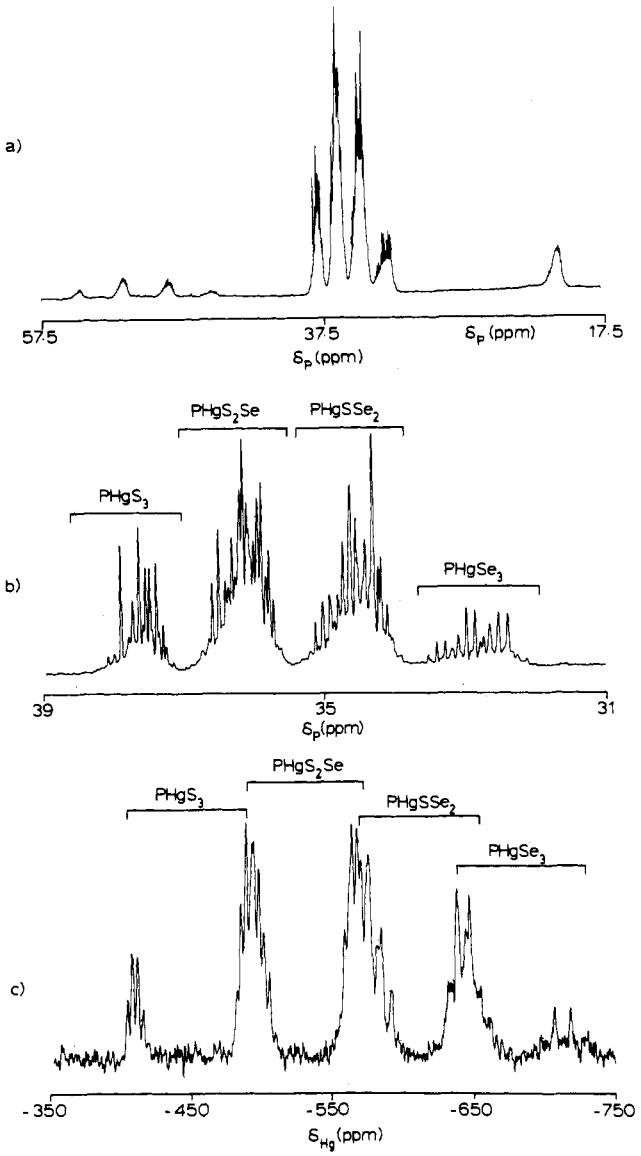

Figure 3. NMR spectra of a 1.1:1 $[(\mu\text{-SPh})_6(HgPPh_3)_4](ClO_4)_2$–$[(\mu\text{-SePh})_6(HgPPh_3)_4](ClO_4)_2$ mixture in $CHCl_3$ at 213 K, showing the formation of $[(\mu\text{-SPh})_{6-m}(\mu\text{-SePh})_m(HgPPh_3)_4]^{2+}$: (a) 121.42-MHz $^{31}P\{^1H\}$ NMR spectrum; (b) expansion of the center band region of the ^{31}P NMR spectrum (with resolution enhancement); (c) 53.65-MHz $^{199}Hg\{^1H\}$ NMR spectrum. In (b) and (c) the regions associated with the four different coordination kernels of mercury are indicated.

spectrum at 35.75 MHz, the spectrum results from four overlapping groups of doublets. The lowest frequency group contains the spectrum of **1** and the highest frequency group that of **2**. Accordingly the groups can be assigned to the kernels $Ph_3{}^{31}P^{199}HgSe_3$, $Ph_3{}^{31}P^{199}HgSe_2S$, $Ph_3{}^{31}P^{199}HgSeS_2$, and $Ph_3{}^{31}P^{199}HgS_3$ from low to high frequency. These assignments are confirmed by the values of $^1J(^{199}Hg–^{31}P)$ within the groups, which decrease with increasing Se substitution as found in the ^{31}P NMR spectra (see above).

It is evident that the δ_{Hg} is influenced mainly by the atoms bound directly to ^{199}Hg. The complexity of each grouping in the ^{199}Hg NMR spectrum shows that there is, in addition, an effect of the chalcogens three bonds distant. Again, a consideration of the number and relative intensities of the doublets (from $^1J(^{199}Hg–^{31}P)$) that can be expected for each possible $S_{6-m}Se_m$ core allows satisfactory assignment.[33] The effect on δ_{Hg} of changing distant chalcogens is a shielding for each Se-for-S substitution. This effect is in the same direction as, and approximately 4–13 % of, the effect of changing geminal chalcogen atoms. As a whole, the ^{199}Hg NMR results lead to the same overall conclusion as the ^{31}P NMR data.

In contrast to the well-resolved ^{31}P and ^{199}Hg NMR spectra obtained for mixtures of **1** and **2** at 213 K, the corresponding ^{77}Se NMR spectra (at 57.20 MHz) were poorly resolved with relatively small chemical shift dispersion. In addition to the signal from **1** at $\delta_{Se} = 6.7$, a broad resonance was found with $\delta_{Se} \simeq 9.1$ ($\Delta\nu_{1/2} \approx 100$ Hz) and an incompletely resolved group of signals in the region $\delta_{Se} \approx 12$–15, with the signals of higher chemical shift occurring at higher S:Se ratios. All the new signals have ^{199}Hg satellites, with $^1J(^{199}Hg–^{31}P) \approx 850$–900 Hz. Following ref 13, we tentatively attribute the different signal positions to different combinations of the four chalcogen atoms geminal to ^{77}Se. It seems that replacement of a geminal Se by S causes a deshielding of ^{77}Se, which is opposite to the effect found[13] for $[(\mu\text{-SPh})_{6-m}(\mu\text{-SePh})_m(ZnI)_4]^{2-}$.

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Registry No. **1**, 110903-73-6; **2**, 110903-75-8; **3**, 110903-77-0; **4**, 110903-79-2; **5**, 110934-43-5; **6**, 110903-81-6; **7**, 110903-83-8; $[(\mu\text{-S-}n\text{-Pr})_6(HgPPh_3)_4](ClO_4)_2$, 110934-45-7; $[(\mu\text{-S-}n\text{-Bu})_6(HgPPh_3)_4](ClO_4)_2$, 110903-85-0; $[(\mu\text{-SPe})_6(HgPPh_3)_4](ClO_4)_2$, 110903-87-2; $[(\mu\text{-SPh})_6(HgPPh_3)_3(HgPEt_3)](ClO_4)_2$, 110903-89-4; $[(\mu\text{-SPh})_6(HgPPh_3)_2(HgPEt_3)_2](ClO_4)_2$, 110903-91-8; $[(\mu\text{-SPh})_6(HgPPh_3)(HgPEt_3)_3](ClO_4)_2$, 110903-93-0; $[(\mu\text{-SePh})_6(HgPPh_3)_3(HgPEt_3)](ClO_4)_2$, 110903-95-2; $[(\mu\text{-SePh})_6(HgPPh_3)_2(HgPEt_3)_2](ClO_4)_2$, 110903-97-4; $[(\mu\text{-SePh})_6(HgPPh_3)(HgPEt_3)_3](ClO_4)_2$, 110903-99-6; $[(\mu\text{-SPh})_6(HgPPh_3)_3(HgAsPh_3)](ClO_4)_2$, 110904-01-3; $[(\mu\text{-SPh})_6(HgPPh_3)_2(HgAsPh_3)_2](ClO_4)_2$, 110904-03-5; $[(\mu\text{-SPh})_6(HgPPh_3)(HgAsPh_3)_3](ClO_4)_2$, 110904-05-7; $[(\mu\text{-SPh})_6(HgPPh_3)_3(HgSbPh_3)](ClO_4)_2$, 110904-07-9; $[(\mu\text{-SPh})_6(HgPPh_3)_2(HgSbPh_3)_2](ClO_4)_2$, 110904-09-1; $[(\mu\text{-SPh})_6(HgPPh_3)(HgSbPh_3)_3](ClO_4)_2$, 110904-11-5; $[(\mu\text{-SPh})_6(\mu\text{-SePh})(HgPPh_3)_4](ClO_4)_2$, 110904-13-7; *cis*-$[(\mu\text{-SPh})_4(\mu\text{-SePh})_2(HgPPh_3)_4](ClO_4)_2$, 110904-15-9; *trans*-$[(\mu\text{-SPh})_4(\mu\text{-SePh})_2(HgPPh_3)_4](ClO_4)_2$, 110904-17-1; *fac*(1)-$[(\mu\text{-SPh})_3(\mu\text{-SePh})_3(HgPPh_3)_4](ClO_4)_2$, 110904-19-3; *mer*-$[(\mu\text{-SPh})_3(\mu\text{-SePh})_3(HgPPh_3)_4](ClO_4)_2$, 110904-21-7; *fac*(2)-$[(\mu\text{-SPh})_3(\mu\text{-SePh})_3(HgPPh_3)_4](ClO_4)_2$, 110904-23-9; *trans*-$[(\mu\text{-SPh})_2(\mu\text{-SePh})_4(HgPPh_3)_4](ClO_4)_2$, 110904-25-1; *cis*-$[(\mu\text{-SPh})_2(\mu\text{-SePh})_4(HgPPh_3)_4](ClO_4)_2$, 110904-27-3; $[(\mu\text{-SPh})(\mu\text{-SePh})_5(HgPPh_3)_4](ClO_4)_2$, 110904-29-5; $Hg(AsPh_3)_2(ClO_4)_2$, 21393-75-9; $Hg(PEt_3)_2(ClO_4)_2$, 110904-30-8; $Hg(SMe)_2$, 21094-80-4; $Hg(SEt)_2$, 811-50-7; $Hg(S\text{-}n\text{-}Pr)_2$, 4080-28-8; $Hg(S\text{-}i\text{-}Pr)_2$, 54760-87-1; $Hg(S\text{-}n\text{-}Bu)_2$, 23601-34-5; $Hg(S\text{-}t\text{-}Bu)_2$, 3374-16-1; $Hg(S\text{-}n\text{-}C_5H_{11})_2$, 4080-30-2; $Hg(S\text{-}c\text{-}C_6H_{11})_2$, 110904-31-9; $Hg(SCH_2Ph)_2$, 110874-75-4; $Hg(SPh)_2$, 21514-24-9; $Hg(SePh)_2$, 21514-25-0; ^{77}Se, 14681-72-2; ^{199}Hg, 14191-87-8; $Hg(PPh_3)_2(ClO_4)_2$, 21393-72-6.

Supplementary Material Available: Tables of assigned ^{13}C NMR data for $[(\mu\text{-ER})_6(HgL)_4]^{2+}$, assigned ^{31}P, ^{199}Hg, and ^{77}Se NMR data for $[(\mu\text{-SePh})_6(HgPPh_3)_{4-n}(HgPEt_3)_n]^{2+}$, assigned ^{31}P and ^{199}Hg NMR data for $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgL')_n]^{2+}$ (L = $AsPh_3$, $SbPh_3$) and $[(\mu\text{-SPh})_{6-m}(\mu\text{-SePh})_m(HgPPh_3)_4]^{2+}$, and the different environments possible in $[(\mu\text{-SPh})_{6-m}(\mu\text{-SePh})_m(^{199}HgPPh_3)(^0HgPPh_3)_3]^{2+}$ (8 pages). Ordering information is given on any current masthead page.