Inorg. Chem. **1990**, *29*, 2997–3002

Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario N6A 5B7, Canada

Synthesis and Multinuclear (^{13}C, ^{77}Se, ^{125}Te, ^{199}Hg) Magnetic Resonance Spectra of Adamantane-like Anions of Mercury(II), $[(\mu\text{-ER})_6(HgX)_4]^{2-}$ (E = S, Se, Te; X = Cl, Br, I)

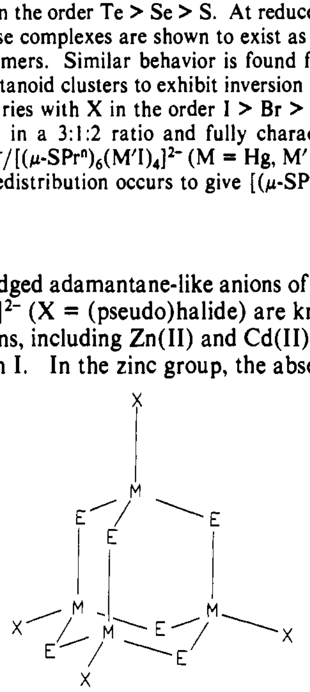
Philip A. W. Dean* and Veeragathy Manivannan

Received November 29, 1989

Multinuclear magnetic resonance has been used to characterize the new adamantane-like anions $[(\mu\text{-ER})_6(HgX)_4]^{2-}$ (ER = SPr^n, SPh, SePh, TePh; X = Cl, Br, I), which are formed in CH_2Cl_2 and (or) DMF from $Hg(ER)_2$, HgX_2 and $(R_4N)X$ in the correct stoichiometric ratio. The products $(Et_4N)_2[(\mu\text{-EPh})_6(HgCl)_4]$ (E = Se, Te) have been isolated analytically pure. At ambient probe temperature, only the complexes $[(\mu\text{-TePh})_6(HgX)_4]^{2-}$ are stable to dissociation of the $(\mu\text{-ER})_6Hg_4$ core. However, at 213 K, only the core of $[(\mu\text{-SPh})_6(HgCl)_4]^{2-}$ is measurably dissociated. Overall, the stability of the complexes to dissociation varies with E in the order Te > Se > S. At reduced temperature inversion at Te is slow on the NMR time scale in $[(\mu\text{-TePh})_6(HgX)_4]^{2-}$, and these complexes are shown to exist as one predominant configurational isomer or an equilibrium mixture of, probably, two such isomers. Similar behavior is found for $[(\mu\text{-SePh})_6(HgX)_4]^{2-}$ (X = Cl, Br), which are the first examples of SeR-bridged adamantanoid clusters to exhibit inversion at Se that is slow on the NMR time scale. In $[(\mu\text{-SePh})_6(HgX)_4]^{2-}$, the inversion rate at Se varies with X in the order I > Br > Cl. Pure $(Et_4N)_2[(\mu\text{-SPr}^n)_6(CdI)_4]$ has been synthesized from $Cd(SPr^n)_2$, CdI_2, and $(Et_4N)I$ in a 3:1:2 ratio and fully characterized by NMR spectroscopy. Metal (^{113}Cd, ^{199}Hg) NMR data for $[(\mu\text{-SPr}^n)_6(MI)_4]^{2-}/[(\mu\text{-SPr}^n)_6(M'I)_4]^{2-}$ (M = Hg, M' = Cd, Zn; M = Zn, M' = Cd) mixtures at 213 K show that an approximately statistical metal redistribution occurs to give $[(\mu\text{-SPr}^n)_6(MI)_{4-n}(M'I)_n]^{2-}$.

Introduction

Chalcogen-bridged adamantane-like anions of the general type $[(\mu\text{-ER})_6(MX)_4]^{2-}$ (X = (pseudo)halide) are known for several divalent metal ions, including Zn(II) and Cd(II).[1] These anions have the skeleton I. In the zinc group, the absence of this type of anion for Hg(II) is notable. The isolated product from a preliminary attempt to synthesize $[(\mu\text{-SPh})_6(HgCl)_4]^{2-}$ was $Hg(SPh)_2$.[2] Similarly, attempts to produce $[(\mu\text{-SPh})_6(HgSPh)_4]^{2-}$ in our own laboratories have been unsuccessful to date. Recently, we have established $(\mu\text{-ER})_6Hg_4$ cages in a series of adamantanoid *cations* $[(\mu\text{-ER})_6(HgL)_{3\text{ or }4}(Hg)_{1\text{ or }0}]^{2+}$ (E = S, Se, Te; L = PR'$_3$, E'PR'$_3$, etc.).[3] Therefore we felt that the anions $[(\mu\text{-ER})_6(HgX)_4]^{2-}$ deserved further investigation. This is particularly true since there is now some evidence[3c] that $(\mu\text{-ER})_6Hg_4$ cages may form more readily for ER = SePh or TePh than for ER = SPh and for ER = S–alkyl than for ER = SPh.



I

We report here the characterization of a variety of anions of the general type $[(\mu\text{-ER})_6(HgX)_4]^{2-}$ using the multinuclear magnetic resonance method. Carbon-13, ^{199}Hg, and ^{77}Se and ^{125}Te, when present, are all useful probe nuclei with spin $I = {}^1/_2$.[4] The isolation of some of the new anions is described. Our investigation has needed the study of some binary systems by NMR spectroscopy. Thus NMR evidence is presented for various series with mixed terminal halides, as well as for the series $[(\mu\text{-SPh})_{6-m}(\mu\text{-SePh})_m(HgI)_4]^{2-}$ with mixed bridging ligands and the series $[(\mu\text{-SPr}^n)_6(HgI)_{4-n}(M'I)_n]^{2-}$ (M' = Zn, Cd) with mixed metals. Metal NMR[4] data for the last series may be useful models for the study of the cysteinyl-bridged clusters of metallothionein containing Hg–Zn and Hg–Cd mixtures.[6] For the sake of completion we also provide ^{113}Cd NMR data for $[(\mu\text{-SPr}^n)_6(ZnI)_{4-n}(CdI)_n]^{2-}$.

Experimental Section

Materials and General Procedures. Literature methods were used to synthesize Ph_2Te_2,[3b,7] $Hg(EPh)_2$ (E = S,[8] Se,[9] Te[9]), $Hg(SPr^n)_2$,[10] and $[(Ph_3P)_2N]I$.[11] The compounds $M(SPr^n)_2$ (M = Zn, Cd) precipitated on mixing methanolic solutions of the metal nitrate and NaSPr^n (prepared in situ from NaOMe and Pr^{n}SH). All other chemicals were from commercial sources and were used as received.

All solvents for use in synthesis or in the preparation of NMR samples were dried over 3-Å molecular sieves and thoroughly deoxygenated by purging with Ar before use. All syntheses and preparations of NMR samples were carried out under an Ar or N_2 atmosphere.

Synthesis. Once isolated, the following compounds did not appear to be particularly air-sensitive. As a precaution, they were stored under an Ar atmosphere in a refrigerator.

$(Et_4N)_2[(\mu\text{-SePh})_6(HgCl)_4]$. Into a mixture of $HgCl_2$ (0.038 g, 0.14 mmol) and $Et_4NCl{\cdot}H_2O$ (0.050 g, 0.27 mmol) in CH_2Cl_2 (5 mL) at room temperature was stirred solid $Hg(SePh)_2$ (0.21 g, 0.40 mmol), producing a yellow solution. The solution was filtered; then the filtrate was layered with Et_2O (1 mL), and the mixture was left in the refrigerator overnight for crystallization to occur. The yellow crystalline product was separated by decantation, washed with Et_2O, and dried in vacuo. The yield was 0.24 g (75%). Anal. Calcd. for $C_{52}H_{70}Cl_4Hg_4N_2Se_6$ (mol. wt. 2141.07): C, 29.17; H, 3.30. Found: C, 28.71; H, 3.18.

$[(Ph_3P)_2N][Hg_4(SePh)_6I_3]$. The procedure for the preparation of $(Et_4N)_2[(\mu\text{-SePh})_6(HgCl)_4]$ was followed. A mixture of HgI_2 (0.048 g, 0.11 mmol), $[(Ph_3P)_2N]I$ (0.143 g, 0.22 mmol), and $Hg(SePh)_2$ (0.163 g, 0.32 mmol) in CH_2Cl_2 (3 mL) gave a clear yellow solution. This solution was layered with a mixture of Me_2CO (2 mL) and Et_2O (2 mL), and the mixture was left at 0–5 °C overnight for crystallization to occur.

---

(1) Coucouvanis, D.; Kanatzidis, M.; Simhon, E.; Baenziger, N. C. *J. Am. Chem. Soc.* **1982**, *104*, 1874. Fenske, D.; Meyer, J.; Merzweiler, K. *Z. Naturforsch., B* **1987**, *42*, 1207. Dean, P. A. W.; Vittal, J. J. *Can. J. Chem.* **1988**, *66*, 2443 and references therein.

(2) Christou, G.; Folting, K.; Huffman, J. C. *Polyhedron* **1984**, *3*, 1247.

(3) (a) Dean, P. A. W.; Vittal, J. J.; Trattner, M. H. *Inorg. Chem.* **1987**, *26*, 4245. (b) Dean, P. A. W.; Manivannan, V.; Vittal, J. J. *Inorg. Chem.* **1989**, *28*, 2360. (c) Dean, P. A. W.; Manivannan, V. *Can. J. Chem.* **1990**, *68*, 214.

(4) For the nuclei ^{199}Hg, ^{77}Se, ^{125}Te, ^{111}Cd, and ^{113}Cd, the percent natural abundances and receptivities relative to ^{13}C are 16.84 and 5.57, 7.58 and 3.01, 6.99 and 12.7, 12.75, and 6.97, and 12.26 and 7.67.[5]

(5) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983; p 230 ff.

(6) Stillman, M. J.; Law, A. Y. C.; Szymanska, J. A. In *Chemical Toxicology and Clinical Chemistry of Metals*; Brown, S. S., Savory, J., Eds; Academic: London, 1983; p 271 ff. Johnson, B. A.; Armitage, I. M. *Inorg. Chem.* **1987**, *26*, 3139.

(7) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.

(8) Peach, M. E. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1390.

(9) Okamoto, Y.; Yano, T. *J. Organomet. Chem.* **1971**, *29*, 99.

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

(11) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.

0020-1669/90/1329-2997$02.50/0 © 1990 American Chemical Society

The yellow crystalline product was separated by decantation, washed with $\mathrm{Et_2O}$, and dried in vacuo to yield 0.060 g (21%) of product. Anal. Calcd for $\mathrm{C_{72}H_{60}Hg_4I_3NP_2Se_6}$ (mol wt 2658.1): C, 32.53; H, 2.28; N, 0.53. Found: C, 32.61; H, 2.29; N, 0.42.

$(\mathrm{Et_4N})_2[(\mu\text{-TePh})_6(\mathrm{HgCl})_4]$. This compound was prepared from $\mathrm{HgCl_2}$ (0.052 g, 0.19 mmol), $\mathrm{Et_4NCl{\cdot}H_2O}$ (0.069 g, 0.38 mmol), and $\mathrm{Hg(TePh)_2}$ (0.34 g, 0.56 mmol) in $\mathrm{CH_2Cl_2}$ (4 mL) at room temperature in essentially the same way as the selenium analogue. On stirring, however, a clear solution was never obtained. Over about a 30-min period, the red color of solid $\mathrm{Hg(TePh)_2}$ was replaced by the yellow color of the solid product, and completion of the reaction was detected visually. The product was washed with $\mathrm{Et_2O}$ and dried in vacuo, to give a yield of 0.29 g (65%). Anal. Calcd for $\mathrm{C_{52}H_{70}Cl_4Hg_4N_2Te_6}$ (mol wt 2432.9): C, 25.67; H, 2.90. Found: C, 25.39; H, 2.42.

$(\mathrm{Et_4N})_2[(\mu\text{-SPr}^n)_6(\mathrm{CdI})_4]$. Starting with a stoichiometric mixture of $\mathrm{CdI_2}$, $\mathrm{Et_4NI}$, and $\mathrm{Cd(SPr^n)_2}$ in $\mathrm{CH_2Cl_2}$, the procedure paralleled that described for $(\mathrm{Et_4N})_2[(\mu\text{-SePh})_6(\mathrm{HgCl})_4]$. The colorless product obtained by refrigeration of the reaction mixture overnight was separated by filtration, washed with $\mathrm{Et_2O}$, and dried in vacuo. The yield was 75%. Anal. Calcd for $\mathrm{C_{34}H_{82}Cd_4I_4N_2S_6}$ (mol wt 1668.7): C, 24.47; H, 4.95; N, 1.68. Found: C, 24.48; H, 4.80; N, 1.73. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ_H 0.94 (t, $-\mathrm{SCH_2CH_2C}H_3$, $^3J(\mathrm{HH}) = 7.3$ Hz), 1.37 (m, $-\mathrm{NCH_2C}H_3$, $^3J(\mathrm{HH}) = 7.3$ Hz, $^3J(\mathrm{NH}) = 1.9$ Hz), 1.76 (septet, $-\mathrm{SCH_2C}H_2\mathrm{CH_3}$, $^3J(\mathrm{HH})_{\mathrm{av}} = 7.6$ Hz), 2.69 (br t, $-\mathrm{SC}H_2\mathrm{CH_2CH_3}$, $^3J(\mathrm{HH}) \approx 8$ Hz), 3.29 (q, $-\mathrm{NC}H_2\mathrm{CH_3}$, $^3\mathrm{J(HH)} = 7.3$ Hz). ^{13}C NMR ($\mathrm{CD_2Cl_2}$): δ_C 8.2 ($-\mathrm{NCH_2}C\mathrm{H_3}$), 14.1 ($-\mathrm{SCH_2CH_2}C\mathrm{H_3}$), 29.3 ($-\mathrm{SCH_2}C\mathrm{H_2CH_3}$), 31.6 ($-\mathrm{S}C\mathrm{H_2CH_2CH_3}$), 53.4 ($-\mathrm{N}C\mathrm{H_2CH_3}$, $^1J(\mathrm{NC}) = 3.0$ Hz).

$(\mathrm{Et_4N})_2[(\mu\text{-SPr}^n)_6(\mathrm{HgI})_4]$, prepared as for the cadmium analogue, was isolated as colorless plates in 55% yield. This compound was >99% pure by ^{1}H NMR spectroscopy ($\mathrm{CD_2Cl_2}$): δ_H 0.99 (t, $-\mathrm{SCH_2CH_2C}H_3$, $^3J(\mathrm{HH}) = 7.3$ Hz), 1.37 (m, $-\mathrm{NCH_2C}H_3$, $^3J(\mathrm{HH}) = 7.3$ Hz, $^3J(\mathrm{NH}) = 1.9$ Hz), 1.68 (septet, $-\mathrm{SCH_2C}H_2\mathrm{CH_3}$, $^3J(\mathrm{HH})_{\mathrm{av}} = 7.4$ Hz), 2.96 (t, $-\mathrm{SC}H_2\mathrm{CH_2CH_3}$, $^3J(\mathrm{HH}) = 7.4$ Hz), 3.32 (q, $-\mathrm{NC}H_2\mathrm{CH_3}$, $^3J(\mathrm{HH}) = 7.3$ Hz). ^{13}C NMR ($\mathrm{CD_2Cl_2}$): δ_C 8.3 ($-\mathrm{NCH_2}C\mathrm{H_3}$), 13.6 ($-\mathrm{SCH_2CH_2}C\mathrm{H_3}$), 30.3 ($-\mathrm{SCH_2}C\mathrm{H_2CH_3}$), 33.3 ($-\mathrm{S}C\mathrm{H_2CH_2CH_3}$), 53.4 ($-\mathrm{N}C\mathrm{H_2CH_3}$, $^1J(\mathrm{NC}) = 3.0$ Hz). However, elemental analyses were unsatisfactory. Anal. Calcd for $\mathrm{C_{34}H_{82}Hg_4I_4N_2S_6}$ (mol wt 2021.4): C, 20.20; H, 4.09; N, 1.39. Found: C, 21.60, 21.96; H, 4.28, 4.21; N, 1.31. We note that, probably fortuitously, the analyses are satisfactory for a monoetherate, but no $\mathrm{Et_2O}$ was detected by ^{1}H or ^{13}C NMR spectroscopy.

NMR Spectra. NMR spectra were obtained and referenced as described in previous publications from this laboratory.[3] Experimental errors in ^{13}C, ^{77}Se, ^{113}Cd, ^{125}Te, and ^{199}Hg chemical shifts are ±0.1, ±0.5, ±1, ±2, and ±1 ppm or less unless noted otherwise.

NMR samples were prepared in situ as the $\mathrm{Bu_4N^+}$ salts unless noted otherwise. They were formulated to give 0.03 mol of $[(\mu\text{-ER})_6(\mathrm{HgX})_4]^{2-}$/L of solvent at room temperature, except as noted.

Elemental Microanalyses. C, H, and N microanalyses were performed by Guelph Chemical Laboratories or Analytische Laboratorien, Gummersbach, West Germany.

Results and Discussion

Synthesis. NMR studies (see below) show that $\mathrm{R_4N^+}$ salts of the anions $[(\mu\text{-ER})_6(\mathrm{HgX})_4]^{2-}$ (ER = SPr^n, SPh, SePh, TePh; X = Cl, Br, I), formed according to eq 1,[12] exist in $\mathrm{CH_2Cl_2}$ and/or

$$3\mathrm{Hg(ER)_2} + \mathrm{HgX_2} + 2\mathrm{X^-} \rightleftharpoons [(\mu\text{-ER})_6(\mathrm{HgX})_4]^{2-} \rightleftharpoons \text{dissociation products} \quad (1)$$

DMF at reduced temperatures. At room temperature, all except the μ-TePh complexes are appreciably dissociated, though not necessarily back to $\mathrm{Hg(ER)_2}$. From $\mathrm{CH_2Cl_2}$ solutions at room temperature it proved possible to isolate pure salts of $[(\mu\text{-ER})_6(\mathrm{HgX})_4]^{2-}$ for X = Cl and ER = SePh or TePh. These salts were of lower solubility than the corresponding salts of the bromo and iodo complexes. For $[(\mu\text{-SePh})_6(\mathrm{HgCl})_4]^{2-}$, crystallization evidently leads to a reversal of the dissociation that appears to be occurring in solution (see below). An attempt to isolate the $[(\mu\text{-SePh})_6(\mathrm{HgI})_4]^{2-}$ anion as the $[(\mathrm{Ph_3P})_2\mathrm{N}]^+$ salt led to a poorly soluble product of composition $[(\mathrm{Ph_3P})_2\mathrm{N}][\mathrm{Hg_4(SePh)_6I_3}]$.[14] Addition of 1 mol equiv of $[(\mathrm{Ph_3P})_2\mathrm{N}]\mathrm{I}$ to a suspension of this product in DMF caused dissolution, and the reduced-temperature ^{77}Se NMR spectra of the resulting solution were characteristic of $[(\mu\text{-SePh})_6(\mathrm{HgI})_4]^{2-}$ (see below). This behavior parallels that found[3b] for $[(\mu\text{-TePh})_6(\mathrm{HgPR_3})_3(\mathrm{Hg})](\mathrm{ClO_4})_2$, which was isolated as a poorly soluble product from a solution of $[(\mu\text{-TePh})_6(\mathrm{PPh_3})_4](\mathrm{ClO_4})_2$ and which is reconverted to the latter on addition of 1 mol equiv of $\mathrm{PPh_3}$.

The new complex $[(\mu\text{-SPr}^n)_6(\mathrm{CdI})_4]^{2-}$, needed for mixing studies, was prepared by a self-assembly reaction of $(\mathrm{Bu_4N})\mathrm{I}$, $\mathrm{CdI_2}$, and $\mathrm{Cd(SPr^n)_2}$ in the correct stoichiometric ratio in $\mathrm{CH_2Cl_2}$. In $\mathrm{CH_2Cl_2}$ at 213 K, this species is characterized by a ^{113}Cd resonance with $\delta_{\mathrm{Cd}} = 578$ (0.1 M $\mathrm{Cd(ClO_4)_2(aq)}$ reference). The chemical shift is larger than that of $[(\mu\text{-SPh})_6(\mathrm{CdI})_4]^{2-}$,[15] as expected from the chemical shift sequence $[\mathrm{Cd(SPr^n)_4}]^{2-} > [\mathrm{Cd(SPh)_4}]^{2-}$.[16] The ^{1}H-decoupled spectrum is a singlet with ^{111}Cd satellites.[4] The coupling, $^2J(^{113}\mathrm{Cd{-}S{-}}^{111}\mathrm{Cd}) \approx 52$ Hz, is comparable to the 45–47 Hz found[17] for $[(\mu\text{-SPh})_6(\mathrm{CdSPh})_4]^{2-}$. The ^{1}H-coupled spectrum is a septet with $^3J(^{113}\mathrm{Cd{-}S{-}C{-}}^1\mathrm{H}) \approx 20$ Hz. Three-bond ^{113}Cd–^{1}H couplings of 13–20 Hz have been reported for $[\mathrm{Cd(SR)_4}]^{2-}$.[16]

NMR Studies of $[(\mu\text{-ER})_6(\mathrm{HgX})_4]^{2-}$. (i) ER = TePh; X = Cl, Br, I (1a–c). In DMF at 295 K,[18] **1a** is characterized by a singlet ($\Delta\nu_{1/2} \approx 450$ Hz) with ^{199}Hg satellites in the ^{125}Te NMR spectrum and a broader singlet ($\Delta\nu_{1/2} \approx 1000$ Hz) with incompletely resolved ^{125}Te satellites in the ^{199}Hg NMR spectrum (Table I). The satellite/center band ratio in the ^{125}Te NMR spectrum is ca. 0.19, close to the 0.198 expected statistically[3b] for the Hg–^{125}Te–Hg grouping with ^{199}Hg in natural abundance.[4] Also, the coupling $^1J(\mathrm{HgTe})$, 2700 ± 150 Hz, is similar to values measured[3b,3c] for other species containing a $(\mu\text{-TePh})_6\mathrm{Hg_4}$ cage. Evidently, a stable $(\mu\text{-TePh})_6\mathrm{Hg_4}$ cage is formed under the present conditions also. The cage is long-lived on the time scale of $^1J(\mathrm{HgTe})$, as has been found for earlier examples also.[3b,3c] This spectrum alone provides no information about coordination or otherwise of the halide, or about the lifetimes of any Hg–Cl linkage. Halide coordination is indicated by the different NMR spectroscopic properties of the μ-TePh complexes with different halides (Table I) and also by the NMR spectra of systems containing halide mixtures (see below). The latter systems also give information about the lifetime of the various Hg–X bonds.

Reducing the temperature causes the ^{125}Te and ^{199}Hg NMR spectra of **1a** in DMF to become more complex, as shown by the summary of the spectra in Table I.[18] At 213 K, the ^{125}Te NMR spectrum shows six approximately equally intense signals, while the ^{199}Hg NMR spectrum shows four approximately equally intense signals. Similar behavior has been found earlier and has been shown to result from a slowing of inversion at Te.[3b,3c] A total of four configurational isomers are possible for an adamantanoid cage $(\mu\text{-ER})_6\mathrm{M_4}$ (E = chalcogen), as a result of the possible different orientations of the R groups bound to the pyramidal E atoms.[15,19] Two of these isomers have C_1 symmetry and two have C_3 symmetry. In the slow-exchange limit, each of the C_1 isomers of $(\mu\text{-TePh})_6\mathrm{Hg_4}$ is expected to give six equally intense ^{125}Te resonances and four equally intense ^{199}Hg resonances. For each of the C_3 isomers, two equally intense resonances are expected for ^{125}Te and two resonances with relative intensities 1:3 for ^{199}Hg. Our results show that, at 213 K in DMF, **1a** occurs predominantly as one of the two C_1 isomers. On warming of the solution, inversion at Te becomes rapid on the time scales of $\Delta\delta_{\mathrm{Te}}$ and $\Delta\delta_{\mathrm{Hg}}$, and this rapid intramolecular exchange leads to the much simpler spectra observed at 295 K.

Except for the apparent overlap of two signals in the ^{199}Hg NMR spectrum at 213 K, the NMR spectroscopic behavior of the $[(\mu\text{-TePh})_6(\mathrm{HgBr})_4]^{2-}$ ion (**1b**) in DMF is generally similar

---

[12] In $\mathrm{CH_2Cl_2}$, $\mathrm{HgX_4}^{2-}$ is formed from $\mathrm{HgX_2}$ and 2 $\mathrm{X^-}$.[13]

[13] Colton, R.; Dakternieks, D. *Aust. J. Chem.* **1980**, *33*, 2405.

[14] At 213 K, a sample of composition $[\mathrm{Hg_4(SePh)_6I_3}]^-$, prepared in situ in DMF, gives two broad resonances by both ^{77}Se NMR ($\delta_{\mathrm{Se}} \approx 42, 54$; approximate relative intensities 1:1) and ^{199}Hg NMR spectroscopy ($\delta_{\mathrm{Hg}} \approx -1393, -1421$; approximate relative intensities 1:3). These observations are consistent with the structure $[(\mu\text{-SePh})_6(\mathrm{HgI})_3(\mathrm{Hg\{DMF\}}_x)]^-$.

[15] Dean, P. A. W.; Vittal, J. J.; Payne, N. C. *Inorg. Chem.* **1987**, *26*, 1683.

[16] Carson, G. K.; Dean, P. A. W.; Stillman, M. J. *Inorg. Chim. Acta* **1981**, *56*, 59.

[17] Dean, P. A. W.; Vittal, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 6436.

[18] The NMR spectra of **1a** in $\mathrm{CH_2Cl_2}$ at 295 K are very similar to those for DMF solutions, but the line widths are larger. As the $\mathrm{Bu_4N^+}$ salt, **1a** is poorly soluble in $\mathrm{CH_2Cl_2}$ at reduced temperature.

[19] Dance, I. G. *Polyhedron* **1986**, *5*, 1037 and references therein.

Table I. NMR Data for $[(\mu\text{-TePh})_6(HgX)_4]^{2-}$

X	solvent	T/K	$\delta_{Hg}{}^{a}$	$\delta_{Te}{}^{b}$	^{1}J(HgTe)/Hz^{c}
Cl	DMF	$213^{d,e}$	-1133^{f}	-136^{f}	
			-1148^{f}	-149^{f}	
			-1200^{f}	-153^{f}	
			-1235^{f}	-163^{f}	
				-184^{f}	
				-237^{f}	
		295^{f}	-1093^{g}	-146	2700
	CH_2Cl_2	$295^{d,h}$	$\approx -1230^{g}$	-142	2900^{i}
Br	DMF	213^{e}	-1282^{j}	-129^{f}	
			-1353^{f}	-148^{f}	
			-1382^{f}	-152^{f}	
				-166^{f}	
				-181^{f}	
				-227^{f}	
		295	$-1379^{g,k}$	-139	2860
Br	CH_2Cl_2	213^{l}	$-1253^{k,m}$	$-134^{m,n}$	2800
			$-1275^{k,m}$	$-140^{m,n}$	2860
			$-1336^{k,m}$	$-152^{m,n}$	*o*
			$-1368^{k,m}$	$-168^{m,n}$	3430
				$-173^{m,n}$	*o*
				$-228^{m,n}$	3100
			$1278^{p,q}$	$-139^{n,q}$	
			$\approx -1333^{g,q}$	$-146^{n,q}$	
		295	$-1357^{g,r}$	-134	2900^{s}
I	DMF	213^{e}	$-1628^{j,t}$	$-111^{f,g}$	
			$-1703^{f,t}$	$-137^{f,g}$	
			$-1735^{f,p}$	$-150^{f,g}$	
				$-165^{f,g}$	
				$-175^{f,g}$	
				$-202^{f,g}$	
		295	-1730^{g}	-127	3000
	CH_2Cl_2	$193^{d,l}$	$-1559^{f,m}$	$-119^{f,m}$	2820
			$-1571^{f,m}$	$-132^{f,m}$	2915
			$-1647^{f,m}$	$-148^{f,m}$	2890
			$-1672^{f,m}$	$-163^{f,m}$	2960
				$-178^{f,m}$	2890
				$-206^{f,m}$	3000
			$-1551^{f,q}$	$-149^{f,q}$	*o*
			$-1632^{q,u}$	$-162^{f,q}$	*o*
		295^{d}	*o*	-122^{g}	*o*

[a] Relative to external pure $HgMe_2$ at ambient probe temperature; estimated error ±1 ppm, except as noted. [b] Relative to external pure $TeMe_2$ at ambient probe temperature; estimated error ±2 ppm except as noted. [c] Measured in the ^{125}Te NMR spectrum; estimated error ±150 Hz or less, except as noted. [d] Saturated solution. [e] Probable C_1 isomer (see text). [f] Relative intensity ≈1. [g] Broad resonance. [h] Insufficiently soluble for measurements at reduced temperature. [i] Estimated error ±250 Hz. [j] Relative intensity ≈2. [k] Estimated error ±1.5 ppm. [l] Possible equilibrium mixture of a C_1 and C_3 isomer, with approximate relative populations 3 and 1 (see text). [m] Tentatively assigned to the C_1 isomer. [n] At 203 K. [o] Could not be observed with certainty. [p] Estimated error ±3 ppm. [q] Tentatively assigned to the C_3 isomer. [r] Estimated error ±5 ppm. [s] Estimated error ±200 Hz. [t] Estimated error ±2 ppm. [u] Unique Hg atom.

Table II. NMR Data for $[(\mu\text{-SePh})_6(HgX)_4]^{2-}$

X	solvent	T/K	$\delta_{Hg}{}^{a}$	$\delta_{Se}{}^{b}$	^{1}J(HgSe)/Hz^{c}
Cl	CH_2Cl_2	178^{d}	-876	32.1^{e}	
			≈ -883	26.3^{e}	
			-895	18.7^{e}	
			-924	15.8^{e}	
			-927	14.0^{e}	
				11.3^{e}	
				6.0^{e}	
				-8.1^{e}	
		233	-928	22.7	820
		295	≈ -1120	≈113	*f*
Br	CH_2Cl_2	178^{g}	-997^{h}	$36.0^{i,j}$	
			-1005^{h}	$\approx 24.3^{i-k}$	
			-1014^{l}	$21.4^{i,j}$	
			-1052^{l}	$16.8^{i,j}$	
				$9.3^{i,j}$	
		233	-1068	31.8	867^{m}
		295	≈ -1270	≈129	*f*
I	CH_2Cl_2	213	-1369	44.4	948
		295	≈ -1670	≈200	*f*
	DMF	213	-1394	43.3	948
		295	≈ -1577	≈177	*f*

[a] Relative to external pure $HgMe_2$ at ambient probe temperature; estimated error ±1 ppm, except as noted. [b] Relative to external pure Me_2Se at 295 K; estimated error ±0.5 ppm or less, except as noted. [c] Measured in the ^{77}Se NMR spectrum; estimated error ±15 Hz, except as noted. [d] Possible equilibrium mixture of a C_1 and C_3 isomer (see text). [e] Estimated error ±0.7 ppm. [f] Not observed. [g] Possible equilibrium mixture of two C_3 isomers (see text). [h] relative intensity ≈1. [i] See Figure 1. [j] Estimated error ±1 ppm. [k] Shoulder. [l] Relative intensity ≈3. [m] Estimated error ±20 Hz.

to that of **1a**, showing that **1b** is stable from 213 to 295 K. NMR data characterizing **1b** are given in Table I. Again, the data support the formation of a predominant C_1 isomer at 213 K, with rapid inversion at Te leading to much simpler spectra at 295 K.

When CH_2Cl_2 is used as the solvent for **1b**, the ^{199}Hg NMR spectrum of the solution at 213 K shows six lines, while the ^{125}Te NMR spectrum at 203 K (the temperature of best resolution) contains eight signals. These spectra cannot be accounted for in terms of the formation of any single configurational isomer. On the basis of the intensities, we tentatively attribute the spectra of an equilibrium mixture of a C_1 and a C_3 isomer, as shown in Table I. On warming of the sample to 295 K, the spectra once more become simplified as a result of exchange-averaging.

The general features of the ^{125}Te and ^{199}Hg NMR spectra of $[(\mu\text{-TePh})_6(HgI)_4]^{2-}$ (**1c**) are very similar to those of the spectra of **1b**, in both DMF and CH_2Cl_2 (Table I). Like **1a** and **1b**, **1c** is stable from 213 to 295 K. As is the case for **1b**, reduced-temperature spectra can be interpreted in terms of a C_1 isomer as the major species in DMF and a mixture of a C_1 and a C_3 isomer in CH_2Cl_2. Exchange-averaged spectra are observed at 295 K.

A 1:1 mixture of **1a** and **1c** in DMF at 213 K gives ^{199}Hg resonances in two well-separated groups centered at ca. −1180 and ca. −1630 ppm. The less and more shielded regions contain the chemical shifts found for **1a** and **1c** themselves and so can be assigned to the kernels $(\mu\text{-TePh})_3HgCl$ and $(\mu\text{-TePh})_3HgI$, respectively, in species of the type $[(\mu\text{-TePh})_6(HgCl)_{4-n}(HgI)_n]^{2-}$. Clearly, inter mercury halide exchange is slow on the time scale of $\Delta\delta_{Hg}$ under these conditions. The same conclusion can be reached from the spectra of a 1:1 mixture of **1b** and **1c** under the same conditions. Here broad ^{199}Hg resonances are found at −1290 and −1600 ppm, as expected for the kernels $(\mu\text{-TePh})_3HgBr$ and $(\mu\text{-TePh})_3HgI$ in $[(\mu\text{-TePh})_6(HgBr)_{4-n}(HgI)_n]^{2-}$. The rate of halide exchange for the anions $[(\mu\text{-TePh})_6(HgX)_4]^{2-}$ (and similar SePh- and SR-bridged species—see below) is significantly slower than for $HgX_4{}^{2-}$. In the monomeric halo complexes, halogen exchange in CH_2Cl_2 is slow on the NMR time scale only at 163 K.[13]

For the exchange-averaged spectra, the shielding of ^{199}Hg, σ_{Hg}, varies with X in the order Cl < Br < I, i.e. the normal halogen dependence.[20] The same order of shielding of the metal nucleus is found for other halo complexes of the divalent zinc-group elements, such as $MX_4{}^{2-}$ (M = Cd, Hg)[13] and $[(\mu\text{-EPh})_6(CdX)_4]^{2-}$.[15] Shielding of ^{125}Te in $[(\mu\text{-TePh})_6(HgX)_4]^{2-}$ shows inverse halogen dependence,[20] Cl > Br > I, and the magnitude of ^{1}J(HgTe) in these complexes varies with X in the order I > Br > Cl.

(ii) ER = SePh; X = Cl, Br, I (2a–c). Representative NMR data for **2a–c** are included in Table II. At 213 K in CH_2Cl_2, each of the complexes gives a ^{77}Se NMR spectrum consisting of a singlet center band with ^{199}Hg satellites. In each case, the satellite/center band intensity ratio is close to the 0.198 expected for an Hg–^{77}Se–Hg bridge with ^{199}Hg in natural abundance, e.g. ca. 0.18 for $[(\mu\text{-SePh})_6(HgCl)_4]^{2-}$. The halogen dependence of ^{1}J(HgSe) is in the same order as for ^{1}J(HgTe) in **1a–c**. The magnitude of ^{1}J, e.g. 770 ± 50, 860 ± 20, and 948 ± 15 Hz at 213 K for **2a–c**, respectively, puts this coupling in or close to the range of 860–1164 Hz established[3a,b] for the $(\mu\text{-SePh})_6Hg_4$ cage.

---

(20) Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1980**, *10a*, 6.

Clearly, the new halo complexes contain the same cage. The differing spectra of **2a–c** provide evidence for halogen coordination as in the proposed formulation.

For CH_2Cl_2 solutions, the ^{199}Hg NMR spectra of **2c** at 213 K and **2a** and **2b** at 233 K show singlet center bands with clear ^{77}Se satellites. The X-dependence of σ_{Hg} for **2a–c** is the same as for **1a–c** (see above). At 213 K, the ^{199}Hg NMR spectra of **2a** and **2b** are too broad for the observation of the satellites. This broadness does not result from intermolecular exchange, since ^1J is observed at 233 K. An intramolecular exchange process is indicated, the nature of which is clarified by measurements at lower temperatures. At 178 K, the ^{77}Se and ^{199}Hg NMR spectra of **2a** and **2b** in CH_2Cl_2 show multiple resonances. Thus **2a** gives rise to eight ^{77}Se signals and five ^{199}Hg signals, while the corresponding numbers for **2b** are 4 (at least) and 4 (Table II). The ^{77}Se NMR spectra of **2b** are broader than and not so well resolved as those of **2a**. For **2c**, there is broadening of the spectra at 178 K compared with those at 213 K, but no additional signals are resolved. The interpretation of these results parallels that given for **1a–c** (see above). At 178 K, inversion at Se has become slow on the time scales of $\Delta\delta_{Se}$ and $\Delta\delta_{Hg}$ for **2a** and **2b**, though the limiting spectra have probably not been reached. This is the first time such slow inversion has been documented for a $(\mu\text{-SeR})_6M_4$ cage. It appears that both **2a** and **2b** exist as a mixture of configurational isomers at 178 K, possibly a C_1 and a C_3 isomer for **2a** and two C_3 isomers, at least, for **2b**. For **2c** at 178 K, selenium inversion must be still occurring at an intermediate rate on the NMR time scale. The rates of inversion are thus **2a** < **2b** < **2c**. In the case of the $(\mu\text{-TePh})_6Hg_4$ cage, a dependence of the rate of Te inversion on the nature of the terminal ligand has already been noted.[3b,c]

Mixing experiments show that halide exchange is slow on the time scales of $\Delta\delta_{Hg}$ and $\Delta\delta_{Se}$ for **2a–c** and their redistributed products in CH_2Cl_2 at 213 K. A 1:1 mixture of **2a** and **2b** shows ^{77}Se signals in three regions centered at ca. 19, 23, and 28 ppm. From δ_{Se} for **2a** and **2b** and on the basis of earlier logic,[21] the regions can reasonably be assigned to the local environments Cl–Hg–^{77}Se–Hg–Cl, Cl–Hg–^{77}Se–Hg–Br, and Br–Hg–^{77}Se–Hg–Br, respectively, in the mixed complexes $[(\mu\text{-SePh})_6(HgCl)_{4-n}(HgBr)_n]^{2-}$. As expected then, ^{199}Hg resonances for the mixture are found in two regions, at ca. −906 and ca. −1041 ppm. These can be assigned to the kernels $(\mu\text{-SePh})_3HgCl$ and $(\mu\text{-SePh})_3HgBr$ occurring in the redistributed mixtures. Similarly, for a 1:1 mixture of **2b** and **2c**, six signals[22] occur in the range ca. 29.8–56.0 ppm, showing that redistribution occurs and that halogen exchange between different mercury sites is slow. The corresponding ^{199}Hg NMR spectra show two regions of resonance, centered on −1068 and −1357 ppm, assignable to the $(\mu\text{-SePh})_3HgBr$ and $(\mu\text{-SePh})_3HgI$ kernels, respectively.

When solutions of **2a–c** in CH_2Cl_2 are warmed toward ambient probe temperature, a series of reversible changes occurs. From 213 to ca. 273 K, gradual increases in the ^{77}Se and ^{199}Hg line widths occur, and in addition δ_{Se} increases gradually, while δ_{Hg} decreases gradually. The coupling ^1J(HgSe) collapses at ca. 253 K. After ca. 273 K, the lines remain broad and accelerated changes in chemical shift occur. For example, variable-temperature ^{77}Se NMR spectra of **2b** in CH_2Cl_2 are given in Figure 1.[23] We believe that the accelerated changes from ca. 273 to 295 K indicate the onset of significant dissociation and that the broad lines observed in this region are an exchange average of signals from $[(\mu\text{-SePh})_6(HgX)_4]^{2-}$ and dissociation products. As yet, we have been unable to pinpoint the latter. For **2c** at 295 K, the values of δ_{Hg} and δ_{Se} are close to those of $Hg(SePh)_2$, e.g. $\delta_{Hg} = -1521$ and $\delta_{Se} = 242$ for a saturated solution of $Hg(SePh)_2$ in CH_2Cl_2 at 295 K. However, the solubility of $Hg(SePh)_2$ in CH_2Cl_2 at 295 K is below 0.01 mol/L of CH_2Cl_2. Thus the complete solubility of a solution of **2c** (0.03 mol/L of CH_2Cl_2) at 295 K is inconsistent with extensive dissociation to $Hg(SePh)_2$ as the sole SePh-containing product.

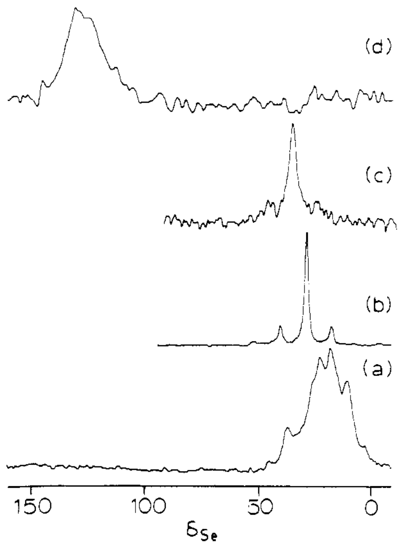


Figure 1. Selenium-77 NMR spectrum of $[(\mu\text{-SePh})_6(HgBr)_4]^{2-}$ in CH_2Cl_2 at (a) 188 K, (b) 213 K, (c) 253 K, and (d) 295 K. Spectra a and d were measured at 57.20 MHz; spectra b and c, at 38.15 MHz.

Table III. NMR Data for $[(\mu\text{-SR})_6(HgX)_4]^{2-\,a}$

R	X	solvent	T/K	$\delta_{Hg}{}^b$
Ph	Cl	DMF	213	−622 (−1009, −1082)[c]
			295	(−1091,[d] −1143[e])
		CH_2Cl_2	295[f]	(−945,[e] −1001[g])
Ph	Br	DMF	213	−777
			295	(−1116,[e] −1198,[h] −1208[e])
		CH_2Cl_2	213[i]	−759
			295	(−1121)
Ph	I	DMF	213	−1080
			295	(−1173,[e] −1276[e])
		CH_2Cl_2	213[j]	−1053[k]
			295	(−1504[l])
Pr^n	Cl	DMF[n]	213	−482
			295	(−693[k])
		CH_2Cl_2[m]	213	−479
			295	(−779)
Pr^n	Br	CH_2Cl_2[i]	213	−576
			295	(−843[k])
Pr^n	I	CH_2Cl_2	213	−820
			295	(≈−1085)

[a] Parenthesized data are believed to be those of dissociation products or of equilibrium mixtures containing dissociation products (see text). [b] Relative to external pure $HgMe_2$ at ambient probe temperature; estimated error ±1 ppm, except as noted. [c] Minor components. [d] Relative intensity ≈15. [e] Relative intensity ≈1. [f] Insufficiently soluble to obtain reduced temperature NMR data. [g] Relative intensity ≈10. [h] Relative intensity ≈3. [i] Saturated solution. [j] For a solution containing 0.01 mol of $[(\mu\text{-SPh})_6(HgI)_4]^{2-}$/L of solvent. [k] Estimated error ±2 ppm. [l] Estimated error ±3 ppm. [m] Saturated solution of the Et_4N^+ salt.

(iii) E = S. The thiolate-bridged complexes are more difficult to characterize in solution than their μ-TePh and μ-SePh analogues, due, in part, to the absence of a suitable probe nucleus at the chalcogen. Dissociation presents an additional complexity. Mercury-199 NMR data for solutions of $[(\mu\text{-SR})_6(HgX)_4]^{2-}$ under various conditions are summarized in Table III.

(a) R = Ph; X = Cl, Br, I (3a–c). These complexes have poor solubilities in CH_2Cl_2, particularly at reduced temperature. DMF was a more suitable solvent for most purposes. The complex **3c** occurs cleanly in DMF at 213 K and is characterized by a single line at −1080 ppm in the ^{199}Hg NMR spectrum. Single-line NMR spectra are notoriously unreliable, making confirmation of this

---

(21) Dean, P. A. W.; Vittal, J. J. *Inorg. Chem.* **1987**, *26*, 278.

(22) A maximum of nine signals is expected[21] for $[(\mu\text{-SeR})_6(MX)_{4-n}(MY)_n]^{2-}$.

(23) For **2b** in CH_2Cl_2, δ_{Se} and δ_{Hg} are 27.6 and −1053 at 213 K, 45 ± 3 and −1096 ± 8 at 273 K, and ca. 129 and ca. −1270 at 295 K. For **2a** in CH_2Cl_2, δ_{Se} and δ_{Hg} are 18.2 and −928 ± 2 at 213 K, ca. 47 and ca. −949 at 273 K, and ca. 113 and ca. −1120 at 295 K. For **2c** in DMF, δ_{Se} and δ_{Hg} are 43.3 and −1394, ca. 52 and ca. −1411, and ca. 177 and ca. −1577 at 213, 253, and 295 K, respectively. No ^{77}Se or ^{199}Hg resonance is seen for **2c** at 273 K. For $Hg(SePh)_2$ in DMF (0.05 mol/L of solvent) at 295 K, $\delta_{Hg} = -1563$ and $\delta_{Se} = 209.2$.

assignment essential. Confirmation was obtained by a mixing experiment. A 1:1 mixture of **2c** and **3c** in DMF at 213 K showed ^{199}Hg resonances in four regions centered at approximately −1079, −1188, −1295, and −1396 ppm.[24,25] From the chemical shift of **2c** and the proposed chemical shift of **3c**, together with earlier logic,[3b,15] the four regions can be assigned to the kernels (μ-SPh)$_3$HgI, (μ-SPh)$_2$(μ-SePh)HgI, (μ-SPh)(μ-SePh)$_2$HgI, and (μ-SePh)$_3$HgI, respectively, in the complexes $[(\mu\text{-SPh})_{6-m}(\mu\text{-SePh})_m(\text{HgI})_4]^{2-}$. Thus the ^{199}Hg NMR chemical shift and formulation of **3c** are confirmed. For the series $[(\mu\text{-EPh})_6(\text{HgI})_4]^{2-}$ (E = S, Se, Te) σ_{Hg} varies with E in the order Te > Se > S, as was found earlier[3a,b] for $[(\mu\text{-EPh})_6(\text{HgPR}_3)_4]^{2+}$ also.

Warming a solution of **3c** in DMF from 213 K causes significant reversible changes in the ^{199}Hg NMR spectrum. At 223 K, the spectrum still shows the signal of **3c** ($\delta_{\text{Hg}} = -1088$), but with this are two new signals, at −1149 and −1320 ppm. The approximate relative intensities are 2, 1, and 1, in order of increasing shielding. By 228 K, only the two new signals are evident ($\delta_{\text{Hg}} \approx -1155, -1315$), and they persist up to 298 K ($\delta_{\text{Hg}} \approx -1173, -1276$, with intensities ≈ 1:1). Apparently dissociation of $[(\mu\text{-SPh})_6(\text{HgI})_4]^{2-}$ occurs on warming. However, the exact identity of the dissociation products has so far eluded us. Their ^{199}Hg chemical shifts are in the same region as, but are not identical to, that of Hg(SPh)$_2$ in DMF, e.g. −1118 ppm at 295 K for a solution containing 0.1 mol of Hg(SPh)$_2$/L of solvent, with very small temperature and concentration sensitivities. The species HgI_4^{2-}, Hg(SPh)_4^{2-}, and HgI$_2$ can be ruled out on the basis of their ^{199}Hg chemical shifts.[13,26-28] Most likely, the dissociation products contain both SPh$^-$ and I$^-$, since different ^{199}Hg chemical shifts are shown by the dissociation products of $[(\mu\text{-SPh})_6(\text{HgBr})_4]^{2-}$ and $[(\mu\text{-SPh})_6(\text{HgCl})_4]^{2-}$ (see below).

Dissociation is also indicated for **3c** in CH$_2$Cl$_2$. At 213 K, a solution formulated to give 0.01 mol of **3c**/L of solvent[29] has $\delta_{\text{Hg}} = -1053$, while at 295 K a solution with 3 times this concentration has $\delta_{\text{Hg}} = -1536$. A saturated solution of Hg(SPh)$_2$ in CH$_2$Cl$_2$ at 295 K has $\delta_{\text{Hg}} = -1067$. This rules out complete dissociation to Hg(SPh)$_2$ at 295 K. However, the signal at −1536 ppm could be an exchange average of signals from undissociated **3c**, Hg(SPh)$_2$, and highly shielded[13,28] Hg(II)–I$^-$ species. Significant dissociation to poorly soluble HgI$_2$ can be excluded by the total solubility of the sample at 295 K.

The anion **3b** also occurs cleanly in DMF at 213 K, where it is characterized by $\delta_{\text{Hg}} = -777$, less shielded than **3c** as expected from the results for **1a–c**, and **2a–c**. Under the same conditions, a 1:1 mixture of **3b** and **3c** gives broad ^{199}Hg resonances at −778 and −1079 ppm. This result is consistent with the occurrence of just two different mercury kernels in the redistributed complexes $[(\mu\text{-SPh})_6(\text{HgBr})_{4-n}(\text{HgI})_n]^{2-}$, confirming the existence and chemical shift of $[(\mu\text{-SPh})_6(\text{HgBr})_4]^{2-}$ and also showing that halide exchange is slow on the time scale of $\Delta\delta_{\text{Hg}}$ under the experimental conditions.

When the sample of **3b** in DMF is warmed to 218 K, the ^{199}Hg NMR spectrum shows two minor signals at −1122 and −1282 ppm, in addition to the resonance of the tetranuclear anion. The more shielded signals grow in relative intensity on further warming until at ca. 233 K the signal of **3b** is no longer apparent. At 295 K, three signals from dissociation products are evident, at −1116, −1198, and −1208 ppm, with approximate relative intensities 1, 3, and 1. The least shielded resonance may indicate the presence of Hg(SPh)$_2$,[30] but the specific sources of the other two signals are not known at present, though HgBr_4^{2-}, Hg(SPh)_4^{2-}, and HgBr$_2$ can be eliminated by their ^{199}Hg NMR chemical shifts.[13,26-28]

A saturated solution of **3b** in CH$_2$Cl$_2$ at 213 K has $\delta_{\text{Hg}} = -759$, showing that the anion is intact. For a CH$_2$Cl$_2$ solution containing 0.03 mol of **3b**/L of solvent,[29] $\delta_{\text{Hg}} = -1121$ at 295 K, providing evidence for dissociation under these conditions. Extensive dissociation to Hg(SPh)$_2$ or HgBr$_2$ can be ruled out on the basis of ^{13}C NMR spectroscopy and solubility, respectively.

At 213 K, a solution formulated to give **3a** in DMF gives three ^{199}Hg NMR signals. A major signal at −622 ppm, is accompanied by two broad weak signals at ca. −1009 and ca. −1082 ppm. The least shielded resonance can be assigned to $[(\mu\text{-SPh})_6(\text{HgCl})_4]^{2-}$ by using the expected ^{199}Hg shielding pattern **3a** < **3b** < **3c**. This assignment is confirmed on the basis of a mixing experiment with **3c**. At 213 K, a 1:1 mixture of **3a** and **3c** gives a slow-exchange ^{199}Hg NMR spectrum consisting of four major resonances, at −624, −628, −1079, and −1102 ppm. The two more shielded signals are in the same region as that of **3c** itself and should be assigned to the local environment (μ-SPh)$_3$HgI, indicating the existence of $[(\mu\text{-SPh})_6(\text{HgCl})_{4-n}(\text{HgI})_n]^{2-}$. Correspondingly, the two less shielded resonances must be assigned to the kernel (μ-SPh)$_3$HgCl. The signal assigned to **3a** falls in the higher frequency region, at −622 ppm, and so is that of $[(\mu\text{-SPh})_6(\text{HgCl})_4]^{2-}$. The signals found at −1009 and −1082 ppm for the solution of **3a** must again be those of dissociation products. On warming of the sample, only the signals of the dissociation products are apparent from ca. 255 to 295 K, at which point the signals occur at −1091 and −1143 ppm with approximate relative intensities 15 and 1. The exact source of these signals remains unclear, though the species HgCl_4^{2-}, Hg(SPh)_4^{2-}, and HgCl$_2$ can be ruled out from ^{199}Hg NMR data,[13,26-28] as can Hg(SPh)$_2$ (see above). The extensive dissociation of **3a** at 295 K is in agreement with the observations of Christou et al.[2]

(b) R = Pr^n; X = Cl, Br, I (4a–c). At 213 K in CH$_2$Cl$_2$, **4c** gives a ^{199}Hg resonance with $\delta_{\text{Hg}} = -820$. This assignment was confirmed in a study of the corresponding complexes containing Cd(II)–Hg(II) and Zn(II)–Hg(II) mixtures (see below). At 233 K, the signal of **4c** is broader, with $\delta_{\text{Hg}} \approx -843$. However, at 253 K no signal is evident for this solution, suggesting that an exchange process is occurring. We believe that this exchange is between **4c** and its dissociation products, which must therefore have significant concentration at this temperature. At 295 K a broad ^{199}Hg resonance can be seen again, now with $\delta_{\text{Hg}} \approx -1085$. Presumably, this signal is the weighted average of that of that of any remaining $[(\mu\text{-SPr}^n)_6(\text{HgI})_4]^{2-}$ and those of its dissociation products. Significant dissociation of $[(\mu\text{-SPr}^n)_6(\text{HgI})_4]^{2-}$ to give HgI$_2$ as one product can be discarded on the basis of the total solubilty of the dissociated solution. HgI$_2$ is poorly soluble in CH$_2$Cl$_2$. An alternative dissociation to Hg(SPr^n)$_2$ and $[\text{HgI}_4]^{2-}$ is a possibility. When Hg(SPr^n)$_2$ is incorporated into an Hg$_4$(μ-SPr^n)$_6$ cage, $\delta_{\text{C}}(C_1)$ has been found[3a,c] to change most in the ^{13}C NMR spectrum. Solutions of **4c** in CH$_2$Cl$_2$ have $\delta_{\text{C}}(C_1) = 35.3$ and 34.0 at 213 and 295 K. For Hg(SPr^n)$_2$ in CH$_2$Cl$_2$ at 295 K, $\delta_{\text{C}}(C_1) = 31.0$.[31] Assuming that δ_{C} for the complex at 295 K is an exchange average, about 30% of the tetranuclear complex appears to be dissociated at 295 K. A dissociation of roughly 15% can be calculated from the weighted-average ^{199}Hg NMR chemical shift of ≈−1085 ppm together with the ^{199}Hg NMR chemical shifts of $[(\mu\text{-SPr}^n)_6(\text{HgI})_4]^{2-}$, $[\text{HgI}_4]^{2-}$ (−3380 ppm at 163 K in CH$_2$Cl$_2$,[13,32]), and Hg(SPr^n)$_2$ (−815 ppm at 295 K for a solution containing 0.03

---

(24) The ^{77}Se resonance of the mixture is a broad line at 44.1 ppm.

(25) In CH$_2$Cl$_2$ at 213 K, the corresponding values of δ_{Hg} are approximately −1102, −1168, −1273, and −1372 ppm. The ^{77}Se signal occurs at ≈45 ppm.

(26) Carson, G. K.; Dean, P. A. W. *Inorg. Chim. Acta* **1982**, *66*, 157.

(27) Peringer, P. P. *Inorg. Chim. Acta* **1980**, *39*, 67.

(28) In DMF at 295 K, with an HgX$_2$ concentration of 0.03 mol/L of solvent, $\delta_{\text{Hg}} = -1502, -2073$, and −3176 for X = Cl, Br, and I. With 2 mol equiv of Et$_4$NX (X = Cl) or Bu$_4$NX (X = Br, I) added, the chemical shifts become −1160, −1888, and −3145 ppm for X = Cl, Br, and I. (Peringer[27] has reported δ_{Hg} for 0.5 *m* HgX$_2$ in DMF at 308 K.) For saturated solutions of HgX$_2$ in CH$_2$Cl$_2$ at 295 K, $\delta_{\text{Hg}} = -1483$, −2245, and −3550, for X = Cl, Br, and I.

(29) The solubilities of **3b** and **3c** are reduced at 213 K.

(30) We were unable to confirm the presence of Hg(SPh)$_2$ using ^{13}C NMR spectroscopy. At 295 K, $\delta_{\text{C}} = 138.1$ (C$_1$), 132.5 (C$_{2,6}$), 128.8 ($C_{3,5}$), and 125.1 (C$_6$) in the aryl region of the ^{13}C NMR spectrum of the Bu$_4$N$^+$ salt of **3b** in DMF. For Hg(SPh)$_2$ under the same conditions, $\delta_{\text{C}} = 136.9$ (C$_1$), 132.7 (C$_{2,6}$), 129.9 (C$_{3,5}$), and 125.4 (C$_6$). The spectrum of **3b** is probably an exchange average.

(31) Hg(SPr^n)$_2$ is poorly soluble in CH$_2$Cl$_2$ at reduced temperature.

(32) Data from ref 13 have been converted to HgMe$_2$ as reference using $\delta_{\text{Hg}}(\text{HgMe}_2) = \delta_{\text{Hg}}(1\text{ M PhHgOAc in DMSO}) - 1437$ ppm.[33]

(33) Kidd, R. G.; Goodfellow, R. J. In *NMR and the Periodic Chart*; Harris, R. K., Mann, B. E., Eds.; Academic: London, 1978; Chapter 8, Table 8.33.

Table IV. Metal NMR Spectral Parameters for $[(\mu\text{-SPr}^n)_6(\text{MI})_{4-n}(\text{M'I})_n]^{2-}$ in CH_2Cl_2 at 213 K[a]

M	M′	*n*	δ_{Cd}[b]	δ_{Hg}[c]
Hg	Cd	0		−820
		1	565	−805
		2	569[d]	−788
		3	573[e]	−773
		4	578[f]	
Hg	Zn	1		−837
		2		−856
		3		−875
Zn	Cd	1	557	
		2	564	
		3	571	

[a] Concentration of tetranuclear anion is 0.03 mol/L of solvent at 295 K. [b] Relative to external 0.1 M $Cd(ClO_4)_2(aq)$ at 295 K; estimated error ±1 ppm or less. [c] Relative to external $HgMe_2$ at ambient probe temperature; estimated error ±1 ppm. [d] $^2J(^{113}\text{Cd–S–}^{199}\text{Hg}) = 160 \pm 10$ Hz. [e] $^2J(^{113}\text{Cd–S–}^{199}\text{Hg}) \approx 160$ Hz. [f] See text.

mol/L of solvent). These are only crude estimates, as they ignore any temperature sensitivity of the chemical shifts. However, they appear sufficiently close to support the suggestion that in CH_2Cl_2 the dissociation of $[(\mu\text{-SPr}^n)_6(\text{HgI})_4]^{2-}$ is to $\text{Hg(SPr}^n)_2$ and $[\text{HgI}_4]^{2-}$. In spite of the occurrence of dissociation, $(\text{Et}_4\text{N})_2[(\mu\text{-SPr}^n)_6(\text{HgI})_4]$, pure by ^{1}H NMR spectroscopy, can be isolated from CH_2Cl_2–Et_2O at 273–278 K (see Experimental Section).

The ^{199}Hg NMR spectroscopic behavior of solutions of **4a** and **4b** in CH_2Cl_2 parallels that of solutions of **4c**. At 213 K, a saturated solution of **4a** (as the Et_4N^+ salt) gives a resonance at −479 ppm,[34] attributed to the cluster $[(\mu\text{-SPr}^n)_6(\text{HgCl})_4]^{2-}$. At 253 K, no signal is observed for this solution, but at 295 K a broad resonance is found with $\delta_{Hg} \approx -779$. Similarly, the signals are −576 ppm, not observed, and ≈−843 ppm for a solution of **4b** at 213, 253, and 295 K, respectively. (The solutions at 213 and 253 K are saturated.) If dissociation to $\text{Hg(SPr}^n)_2$ and HgX_4^{2-} is assumed and if ^{13}C and ^{199}Hg NMR data are used as above,[35] the dissociations of **4a** and **4b** are estimated to be in the ranges 51–70% and 40–55%, respectively, in the solutions at 295 K.

(c) $[(\mu\text{-SPr}^n)_6(\text{MI})_{4-n}(\text{M'I})_n]^{2-}$ (M = Hg, M′ = Zn, Cd; M = Zn, M′ = Cd). Evidence for formation of mixed-metal complexes is obtained from both ^{113}Cd and ^{199}Hg NMR spectra of mixtures of **4c** and its cadmium analogue (see above) in CH_2Cl_2 at 213 K. As the Cd:Hg ratio is varied, the ^{199}Hg NMR spectra show a total of four signals, approximately equally spaced, with a range of −820 to −773 ppm. A total of four approximately equally spaced signals are found in the ^{113}Cd NMR spectra also, covering the range 565–578 ppm (0.1 M $Cd(ClO_4)_2(aq)$ reference). The number of signals shows that redistribution occurs in these mixtures to give $[(\mu\text{-SPr}^n)_6(\text{HgI})_{4-n}(\text{CdI})_n]^{2-}$, thus confirming the tetranuclearity of **4c** (and the Cd_4 analogue). Signal intensities show that the redistribution is approximately statistical in the equilibrium mixtures. From their order of appearance and on the basis of the metal NMR chemical shifts of the parent species, the various new signals can be assigned to individual members of the series. These assignments are given in Table IV. The data show that cadmium substitution into **4c** leads to deshielding of ^{199}Hg by 15 ppm/Cd. On the other hand, mercury substitution into $[(\mu\text{-SPr}^n)_6(\text{CdI})_4]^{2-}$ results in shielding of ^{113}Cd by 4–5 ppm/Hg. Mercury-199 satellites are observed by ^{113}Cd NMR spectroscopy for the complexes with $n = 2$ and 3. The broader lines of the ^{199}Hg NMR spectra preclude observation of $^{111/113}$Cd satellites. The values of $^2J(^{199}\text{Hg–S–}^{113}\text{Cd})$, 160 ± 10 and ≈160 Hz for $n = 2$ and 3, respectively, are intermediate between values of $^2J(^{113}\text{Cd–S–}^{111}\text{Cd})$ for the $(\mu\text{-SR})_6\text{Cd}_4$ cage[9b,17] and typical values of $^2J(^{199}\text{Hg–S–}^{199}\text{Hg})$ for the $(\mu\text{-SR})_6\text{Hg}_4$ cage.[3a]

Mercury-199 NMR spectra of mixtures of **4c** and its Zn_4 analogue[36] in CH_2Cl_2 at 213 K provide evidence for $[(\mu\text{-SPr}^n)_6(\text{HgI})_{4-n}(\text{ZnI})_n]^{2-}$, formed in approximately statistical amounts. Chemical shifts, assigned as above, are included in Table IV. From these, it can be seen that stepwise incorporation of Zn(II) into **4c** leads to an increase in the shielding of ^{199}Hg by 19 ppm/Zn. This is the reverse of the effect of Cd substitution discussed above.

To complete the series of binary clusters $[(\mu\text{-SPr}^n)_6(\text{MI})_{4-n}(\text{M'I})_n]^{2-}$ for the zinc-group elements, we have examined the ^{113}Cd NMR spectra of mixtures of $[(\mu\text{-SPr}^n)_6(\text{CdI})_4]^{2-}$ and its Zn_4 analogue,[36] again in CH_2Cl_2 at 213 K. As the Zn:Cd ratio is increased, starting from the parent Cd_4 complex, three new equally spaced ^{113}Cd NMR signals occur (Table IV). Evidently, the mixed-metal complexes $[(\mu\text{-SPr}^n)_6(\text{ZnI})_{4-n}(\text{CdI})_n]^{2-}$ are formed. The distribution of these species is approximately statistical, in contrast with earlier findings[37] that the series $[(\mu\text{-SPh})_6(\text{ZnSPh})_{4-n}(\text{CdSPh})_n]^{2-}$ shows markedly nonstatistical behavior. An additional point of contrast between these two series concerns the magnitude of the incremental changes in δ_{Cd} produced by Zn substitution. For $[(\mu\text{-SPr}^n)_6(\text{ZnI})_{4-n}(\text{CdI})_n]^{2-}$, ^{113}Cd is shielded by 7 ppm/Zn substituted into the parent Cd_4 species, while for $[(\mu\text{-SPh})_6(\text{ZnSPh})_{4-n}(\text{CdSPh})_n]^{2-}$ the analogous change is a shielding of 0.45 ppm.[37] At present, it is unclear whether the difference is due to the difference in bridging group, terminal group, or both, and our studies of this phenomenon are continuing.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of our work.

---

(34) For **4a** in DMF, $\delta_{Hg} = -482$ and −693 at 213 and 295 K, respectively.

(35) A saturated solution of the Et_4N^+ salt of **4a** in CH_2Cl_2 has $\delta_C(C_1) = 34.7$ and 32.1 at 213 and 295 K. For **4b** in CH_2Cl_2, $\delta_C(C_1) = 34.5$ and 33.1 at 213 and 295 K.

(36) $[(\mu\text{-SPr}^n)_6(\text{ZnI})_4]^{2-}$ was prepared in situ from a stoichiometric mixture of $\text{Zn(SPr}^n)_2$, ZnI_2, and $\text{Bu}_4\text{N}^+\text{I}^-$.

(37) Dean, P. A. W.; Vittal, J. J. *Inorg. Chem.* **1986**, *25*, 514. Dance, I. G. *Aust. J. Chem.* **1985**, *38*, 1745.