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

# New Adamantane-like Mercury-Chalcogen Cages. 2.[1] Synthetic and Multinuclear ($^{31}$P, $^{77}$Se, $^{125}$Te, $^{199}$Hg) Magnetic Resonance Study of Tellurolate-Bridged Mercury(II) Clusters $[(\mu\text{-TeR})_6(HgPR'_3)_4]^{2+}$ and $[(\mu\text{-TeR})_6(Hg)(HgPR'_3)_3]^{2+}$ and Related Species with Mixed-Bridging Chalcogenates

Philip A. W. Dean,* Veeragathy Manivannan, and Jagadese J. Vittal

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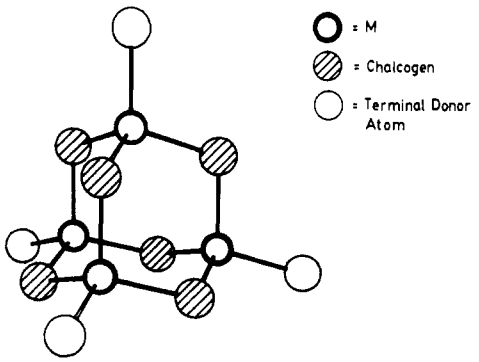
The salts $[(\mu\text{-TePh})_6(HgPR'_3)_3(Hg)](ClO_4)_2$ (R' = Ph, 4-$C_6H_4$Me, 4-$C_6H_4$Cl) are preparable from $Hg(TePh)_2$, $Hg(PR'_3)_2(ClO_4)_2$, and $PR'_3$ in a 3:1:1 ratio in $CH_2Cl_2$ or $CHCl_3$. The new cations have been characterized in $CH_2Cl_2$ and DMF by multinuclear ($^{31}$P, $^{125}$Te, $^{199}$Hg) magnetic resonance and shown to be of adamantanoid structure with novel tellurolate bridging. These spectra provide clear evidence for preferential formation of one (R' = Ph) or a mixture of both (R' = 4-$C_6H_4$Cl, in DMF solution) of the two $C_3$ isomers that are possible for adamantane-like $(\mu\text{-TeR})_6M_4$ as a result of inversion at the pyramidal Te atoms. Such preferential isomer formation has not been demonstrated previously for any adamantanoid chalcogenate-bridged $(\mu\text{-ER})_6M_4$ in solution. Mixtures of $Hg(TeR)_2$, $Hg(PR'_3)_2(ClO_4)_2$, and $PR'_3$ in a 3:1:2 ratio, or $[(\mu\text{-TePh})_6(HgPR'_3)_3(Hg)](ClO_4)_2$ and $PR'_3$ in a 1:1 ratio, lead to $[(\mu\text{-TeR})_6(HgPR'_3)_4](ClO_4)_2$ in $CH_2Cl_2$ solution. The salts were isolated for R = Me, R' = Ph and R = Ph, R' = Et, but for R = Ph, R' = Ph, 4-$C_6H_4$Me, or 4-$C_6H_4$Cl, attempted isolation gave the cations with three $PR'_3$ ligands. Multinuclear magnetic resonance spectra show that $[(\mu\text{-TeR})_6(HgPR'_3)_4]^{2+}$ (R = Ph, R' = Et, *n*-Bu, Ph, 4-$C_6H_4$Me, 4-$C_6H_4$Cl; R = Me, R' = *n*-Bu, Ph) again have the adamantanoid structure. At reduced temperature one $C_3$ isomer exists for R = Ph, R' = 4-$C_6H_4$Cl. However, both $C_3$ isomers occur in equilibrium for R = Ph, R' = Ph or 4-$C_6H_4$Me, and for R = Me, R' = Ph the equilibrium mixture contains at least one $C_1$ isomer and probably at least one $C_3$ isomer. At ambient probe temperature the $(\mu\text{-TeR})_6Hg_4$ core is long-lived on the NMR time scale for all $[(\mu\text{-TeR})_6(HgPR'_3)_4]^{2+}$ complexes though rapid inversion at Te leads to time-averaged tetrahedral symmetry. Time averaging persists to reduced temperature when R' = alkyl. For the cations with R = Ph, the rate of inversion at Te varies with R' in the order alkyl > 4-$C_6H_4$Me > Ph > 4-$C_6H_4$Cl. When R = Ph, R' = 4-$C_6H_4$Me, NMR spectra ($^{31}$P, $^{77}$Se, $^{125}$Te, $^{199}$Hg) of mixtures of $[(TeR)_6(HgPR'_3)_4]^{2+}$ and $[(\mu\text{-ER})_6(HgPR'_3)_4]^{2+}$ (E = S, Se) provide evidence for the formation of the mixed-chalcogen cores $(\mu\text{-Te})_{6-m}(\mu\text{-E})_mHg_4$.

## Introduction

An earlier paper from these laboratories[1] dealt with the cations $[(\mu\text{-ER})_6(HgL)_4]^{2+}$ (E = S, Se; L = tertiary phosphine or arsine). By means of multinuclear magnetic resonance spectroscopy, these new species and some related mixed-ligand complexes were shown to have the adamantanoid skeleton I. Thus, the cations provided




I

the first examples of the $(\mu\text{-ER})_6Hg_4$ (E = S, Se) cages. More recently, X-ray analysis has been used[2] to confirm the existence of the $(\mu\text{-SR})_6Hg_4$ core in $[(\mu\text{-SPh})_6(HgPPh_3)_4](ClO_4)_2$.

With the existence of the $(\mu\text{-ER})_6Hg_4$ cages proven for E = S and Se, we thought it of interest to attempt to extend the series to the analogous previously unknown Te-containing cage. Ultimately it should then be possible to assess the chemical, spectroscopic, and structural changes associated with variation of the chalcogen in the adamantane-like cage system. To our knowledge, the $(\mu\text{-TeR})_6M_4$ skeleton has not been established[3] to date for any metal. However, bridging tellurolate ligands are well-established[4] and a $^{113}$Cd NMR study[5] of $Ph_2Te_2$:$[(\mu\text{-EPh})_6(CdEPh)_4]^{2-}$ (E = S, Se) mixtures provided good evidence for partial $PhTe^-$ substitution of the adamantanoid $Cd_4$ clusters.

We report here the synthesis of two groups of complexes containing the $(\mu\text{-TeR})_6Hg_4$ core. The first group contains cations of the general formula $[(\mu\text{-TeR})_6(HgPR'_3)_4]^{2+}$, exact analogues of $[(\mu\text{-ER})_6(HgL)_4]^{2+}$ (E = S, Se), discussed above. The second group, of general formula $[(\mu\text{-TeR})_6(Hg)(HgPR'_3)_3]^{2+}$, represents a new type of adamantanoid cluster in which only three of the four metal atoms have strongly bound terminal ligands. Both groups, as well as the mixed-ligand complexes $[(\mu\text{-TePh})_{6-m}(EPh)_m(HgP\{4\text{-}C_6H_4Me\}_3)_4]^{2+}$ (E = S, Se), have been characterized in solution by $^{31}$P, $^{125}$Te, $^{199}$Hg, and (where appropriate) $^{77}$Se NMR.[6] The NMR spectra of several of the new complexes exhibit interesting temperature dependence, providing evidence for slow exchange between invertomers.

## Experimental Section

**Materials and General Procedures.** Literature methods were used to synthesize $Hg(EPh)_2$ (E = S,[8a] Se,[8b] Te[8b]), $Hg(PR'_3)_2(ClO_4)_2$ (R = Ph, 4-$C_6H_4$Me),[9] $[HgCl_2(P(4\text{-}C_6H_4Cl)_3)]_2$,[10] $Hg(PEt_3)_2(ClO_4)_2$,[1] and $HgCl_2(P\{n\text{-}Bu\}_3)_2$.[11] Following ref 9, treatment of the appropriate $HgCl_2$ adducts (plus an added 1 mol of phosphine for the 1:1 adduct) with $AgClO_4$ in $CH_2Cl_2$ gave $Hg(PR'_3)_2(ClO_4)_2$ (R = *n*-Bu, 4-$C_6H_4$Cl). Comparison of $^{31}$P NMR spectra with literature spectra[1,9,12] confirmed

(1) Part 1: Dean, P. A. W.; Vittal, J. J.; Trattner, M. H. *Inorg. Chem.* **1987**, *26*, 4245.
(2) Dean, P. A. W.; Vittal, J. J.; Payne, N. C. To be submitted for publication.
(3) Since the completion of our work, we have received a personal communication from Dr. A. K. Singh (Indian Institute of Technology, Delhi, India) regarding the synthesis of compounds thought to be $[(\mu\text{-TeAr})_4(HgPPh_3)_4](ClO_4)_2$.
(4) Berry, F. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. G., McCleverty, J., Eds.; Pergamon: Oxford, 1987; Vol. 2, Chapter 17, p 669 ff. and references therein.
(5) Dean, P. A. W.; Vittal, J. J. *Inorg. Chem.* **1986**, *25*, 514.
(6) The nuclei $^{31}$P, $^{125}$Te, $^{199}$Hg, and $^{77}$Se all have spin $I = {}^1/_2$. Their % natural abundances and receptivities relative to $^{13}$C are respectively 100 and 3.77 × $10^2$, 6.99 and 12.7, 16.84 and 5.57, and 7.58 and 3.01.[7]
(7) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983; p 230 ff.
(8) (a) Peach, M. E. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1390. (b) Okamoto, Y.; Yano, T. *J. Organomet. Chem.* **1971**, *29*, 99.
(9) Allman, T.; Goel, R. G. *Can. J. Chem.* **1984**, *62*, 621.
(10) Allman, T.; Goel, R. G. *Can. J. Chem.* **1984**, *62*, 615.
(11) Bell, N. A.; Dee, T. D.; Goggin, P. L.; Goldstein, M.; Goodfellow, R. J.; Jones, T.; Kessler, K.; McEwan, D. M.; Nowell, I. W. *J. Chem. Res., Miniprint* **1981**, 201; *J. Chem. Res., Synop.* **1981**, 2.

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the purity and authenticity of the various $Hg(PR'_3)_2(ClO_4)_2$.

In the initial part of our study, commercial $Ph_2Te_2$ (Strem Chemicals) was used in the synthesis of $Hg(TePh)_2$. After the loss of this commercial source, $Ph_2Te_2$ was prepared by a literature method.[13] In our hands, this synthesis gave orange-red $Ph_2Te_2$ contaminated with a poorly soluble black impurity, probably Te powder. This impurity was removed from a $CHCl_3$ slurry of the crude product on a column of Kieselgel 60 (Merck). After the solvent was stripped from the eluate, the orange-red product was recrystallized from EtOH.

Triphenyl- and tri-4-tolylphosphines (from BDH and Aldrich, respectively) were recrystallized from EtOH before use. Tris(4-chlorophenyl)phosphine (Digital Specialty Chemicals) showed no phosphorus-containing impurities but was pumped overnight to remove residual solvent. All other chemicals were from commercial sources and were used as received.

HPLC grade DMF (Aldrich, with Sure Seal) was used directly under Ar. All other solvents were dried over 3-Å molecular sieves and thoroughly deoxygenated with Ar before use in synthesis or preparation of NMR samples.

**Synthesis.** The following syntheses were carried out under an argon atmosphere. The isolated solid compounds did not appear to be very air-sensitive. However, as a precaution, they were stored in a refrigerator under Ar.

**$[Hg_4(TePh)_6(PPh_3)_3](ClO_4)_2$ (1).** Into a solution of $Hg(PPh_3)_2(ClO_4)_2$ (0.12 g, 0.13 mmol) in 5 mL of $CH_2Cl_2$ at room temperature was stirred solid $PPh_3$ (0.030 g, 0.13 mmol) and then solid $Hg(TePh)_2$ (0.24 g, 0.39 mmol). After 10 min the mixture was filtered and $Et_2O$ was layered onto the yellow filtrate. Crystallization began within 10 min at room temperature and was completed by cooling to 0–5 °C in the refrigerator for ca. 18 h. The yellow crystals were separated by decantation of the mother liquor, washed with $Et_2O$, and dried in vacuo to yield 0.28 g (72%). Crystallinity was lost during the drying process. Anal. Calcd for $C_{90}H_{75}Cl_2Hg_4O_8P_3Te_6$ (mol wt 3016.37): C, 35.84; H, 2.51. Found: C, 35.88; H, 2.72.

An attempt to isolate $[Hg_4(TePh)_6(PPh_3)_4](ClO_4)_2$ (see below) from $CHCl_3$ solution by addition of $Et_2O$ followed by refrigeration also resulted in pure **1**. Found: C, 35.93, 36.04; H, 2.60, 2.69. Similarly, addition of $Et_2O$ to a $CH_2Cl_2$ solution of $[Hg_4(TePh)_6(PPh_3)_4](ClO_4)_2$ resulted in solid **1** (identified by $^{31}P$ NMR spectroscopy). A sample of **1**, as a fine yellow powder, was obtained without addition of an inert diluent when a solution of $[Hg_4(TePh)_6(PPh_3)_4](ClO_4)_2$ in $CHCl_3$ was allowed to stand for several weeks at room temperature in a capped vessel. We presume that adventitious oxidation of one $PPh_3$ occurred in this case, giving the 4:3 Hg:$PPh_3$ ratio required to produce poorly soluble **1**.

**$[Hg_4(TePh)_6(P\{4\text{-}C_6H_4Me\}_3)_3](ClO_4)_2$ (2).** This compound was synthesized in essentially the same manner as **1**, but by using $CHCl_3$ as the initial solvent and with crystallization induced by cooling the filtrate to 0–5 °C overnight without the addition of $Et_2O$. The yield of the yellowish orange product was 72%. Anal. Calcd for $C_{99}H_{93}Cl_2Hg_4O_8P_3Te_6$ (mol wt 3142.58): C, 37.83; H, 2.98; Cl, 2.26. Found: C, 37.05; H, 2.88; Cl, 2.16, 1.92. $^1H$ NMR ($CD_2Cl_2$): $\delta_H$ 2.32 (s, $CH_3$), 6.66–7.32 (phenyl H).

More or less pure **2** (judged from $^{31}P$ NMR spectroscopy) also resulted from an attempt to isolate $[Hg_4(TePh)_6(P\{4\text{-}C_6H_4Me\}_3)_4](ClO_4)_2$ from $CH_2Cl_2$ by addition of $Et_2O$.

**$[Hg_4(TePh)_6(P\{4\text{-}C_6H_4Cl\}_3)_3](ClO_4)_2$ (3).** This salt was prepared in the same manner as **1**, except that it was unnecessary to add $Et_2O$ to induce crystallization. The yellow product that formed when all the $Hg(TePh)_2$ had reacted was separated from the mother liquor by decantation, washed with $Et_2O$, and dried in vacuo. The yield was 49%. Anal. Calcd for $C_{90}H_{66}Cl_{11}Hg_4O_8P_3Te_6$ (mol wt 3326.36): C, 32.50; H, 2.00. Found: C, 32.09; H, 1.81. $^1H$ NMR ($CD_2Cl_2$): $\delta_H$ 6.78–7.39 (phenyl H).

This same compound was formed as an immediate yellow precipitate when $Et_2O$ was layered onto a solution of $[Hg_4(TePh)_6(P\{C_6H_4Cl\}_3)_4](ClO_4)_2$ in $CH_2Cl_2$.

**$[Hg_4(TePh)_6(PEt_3)_4](ClO_4)_2$ (4).** Solid $Hg(TePh)_2$ (0.93 g, 1.5 mmol) was added with stirring to a mixture of $Hg(PEt_3)_2(ClO_4)_2$ (0.32 g, 0.51 mmol) and $PEt_3$ (0.12 g, 1.0 mmol) in 7 mL of acetone. After ca. 30 min, most of the $Hg(TePh)_2$ had dissolved to give a reddish orange solution. The small amount of solid that remained was removed by filtration. After $Et_2O$ (6 mL) was layered onto the filtrate, crystallization occurred on keeping the mixture at 0 °C overnight. The yellowish orange product was separated by decantation of the mother liquor, washed with $Et_2O$, and dried in vacuo, to give a yield of 0.70 g (51%). Anal. Calcd for $C_{60}H_{90}Cl_2Hg_4O_8P_4Te_6$ (mol wt 2702.13): C, 26.67; H, 3.36. Found: C, 26.72; H, 3.57. $^1H$ NMR ($CD_2Cl_2$): $\delta_H$ 1.0 (br s, $CH_3$), 1.7 (br s, $CH_2$), 7.14–7.78 (phenyl H).

**$[Hg_4(TeMe)_6(PPh_3)_4](ClO_4)_2$ (5).** Following the synthetic route for $Hg(TePh)_2$,[8b] crude $Hg(TeMe)_2$[14] was obtained as a brownish yellow powder by stirring an equimolar mixture of Hg and $Me_2Te_2$ in $C_6H_6$ for 2 days at room temperature. Anal. Calcd for $C_2H_6HgTe_2$ (mol wt 485.86): C, 4.94; H, 1.24. Found: C, 4.69; H, 0.88. The crude $Hg(TeMe)_2$ was added incrementally with stirring to a mixture of $Hg(PPh_3)_2(ClO_4)_2$ (0.103 g, 0.111 mmol) and $PPh_3$ (0.060 g, 0.22 mmol) in 6 mL of $CHCl_3$ at room temperature, until the $^{31}P$ NMR spectrum of the supernatant liquid at −60 °C showed no evidence for $[Hg(PPh_3)_4]^{2+}$. At this point the heterogeneous mixture was filtered. The yellow filtrate was covered with a layer of $Et_2O$ (1 mL) and left undisturbed at 0–5 °C overnight. The resultant yellow crystalline solid was separated by decantation of the mother liquor, washed with $Et_2O$, and dried in vacuo to yield 0.20 g (63%) of yellow powder. Anal. Calcd for $C_{78}H_{78}Cl_2Hg_4O_8P_4Te_6$ (mol wt 2906.25): C, 32.24; H, 2.71. Found: C, 32.48; H, 2.93. $^1H$ NMR ($CD_2Cl_2$): $\delta_H$ 1.65 (br, $CH_3$), 7.42–7.52 (phenyl H).

**Measurement and Simulation of NMR Spectra.** NMR samples were prepared and $^1H$, $^{31}P$, $^{77}Se$, and $^{199}Hg$ NMR spectra obtained and simulated as described in part 1.[1] For $^{31}P$ and $^{77}Se$ NMR spectra, the primary references were 85% $H_3PO_4$ and neat $Me_2Se$ at 294 K, respectively. External 0.1 M $Hg(ClO_4)_2$ in 5% v/v $HClO_4$ solution at 294 K was used as the primary reference for $^{199}Hg$ NMR spectra and converted to the more usual $HgMe_2$ reference by using $\delta_{Hg}(HgMe_2, \text{external}) = \delta_{Hg}(Hg(ClO_4)_2, \text{external}) - 2253$ ppm.[15a] Tin-119 and $^{125}Te$ NMR spectra were obtained as reported in a previous publication from these laboratories.[16] Chemical shifts for $^{125}Te$ are quoted relative to the usual standard, external pure $Me_2Te$. During our initial measurements, external 0.5 M $Ph_2Te_2$ in $CH_2Cl_2$ was used as a primary standard. For this, $\delta_{Te}(Me_2Te, \text{external}) = \delta(Ph_2Te_2 \text{ in } CH_2Cl_2, \text{external}) + 422$.[15b] Since the $Ph_2Te_2$ standard deteriorates on standing for long periods, a more stable standard is desirable. We found it convenient to use the $^{119}Sn\{^1H\}$ NMR resonance of pure $SnMe_4$ as a reference signal. With fresh solutions of $Ph_2Te_2$ and with the field preshimmed but unlocked, $\nu(^{125}Te \text{ in } Ph_2Te_2 \text{ in } CH_2Cl_2)/\nu(^{119}Sn \text{ in pure } SnMe_4)$ was found to be 0.846 409 ± 0.000 002 at 295 ± 2 K. (The error range reflects mainly the reproducibility in $\nu(^{125}Te \text{ in } Ph_2Te_2)$.) Thus $\delta_{Te}$ is quoted with an estimated error of ±2 ppm.

## Results and Discussion

**Synthesis.** The procedure used previously[1] to obtain $[Hg_4(ER)_6(PR'_3)_4](ClO_4)_2$ (E = S, Se) is readily extended to produce the tellurium analogues in $CHCl_3$ or $CH_2Cl_2$ (eq 1, $n = 2$). NMR

$$Hg(PR'_3)_2(ClO_4)_2 + 3Hg(TeR)_2 + nPR'_3 \rightarrow [Hg_4(TeR)_6(PR'_3)_{2+n}](ClO_4)_2 \quad (1)$$

experiments (see below) show that the cations with $n = 2$ form cleanly in solution for R = Ph, R′ = Ph, 4-$C_6H_4Me$, 4-$C_6H_4Cl$, or *n*-Bu, for R = Me, R′ = Ph, and in ca. 90% yield for R = Ph, R′ = Et. The products were isolated with reasonable yield in analytically pure form for R = Me, R′ = Ph and for R = Ph, R′ = Et. However, when R = Ph and R′ = Ph, 4-$C_6H_4Me$, or 4-$C_6H_4Cl$, attempts to isolate $[Hg_4(TeR)_6(PR'_3)_4]^{2+}$ led to the isolation of $[Hg_4(TeR)_6(PR'_3)_3](ClO_4)_2$ instead. These compounds are preparable directly in solution according to eq 1, $n = 1$. They are characterizable by NMR spectroscopy and could be isolated in reasonable to good yields. In contrast, no NMR evidence for the cations with $n = 1$ could be found even during attempted in situ preparations for R = Ph, R′ = Et or *n*-Bu.

**NMR Studies. (i) Isotopomers of the $(\mu\text{-Te})_6Hg_4$ Core.** Both Hg and Te are polyisotopic. Therefore, an adamantane-like $(\mu\text{-Te})_6Hg_4$ core will exist in isotopomeric forms. For our multinuclear NMR studies, the distributions of the spin-active (spin $I = {}^1/_2$) nuclei $^{199}Hg$ and $^{125}Te$ are of interest. We have given the expected statistical fractional populations of $(^{199}Hg)_x(^0Hg)_{4-x}$

(12) Colton, R.; Dakternieks, D. *Aust. J. Chem.* **1981**, *34*, 323.
(13) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.
(14) In several attempts we were unable to obtain analytically pure $Hg(TeMe)_2$.
(15) (a) Kidd, R. G.; Goodfellow, R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic: London, 1978; Chapter 8, Table 8.31 and references therein. (b) Rodger, C.; Sheppard, N.; McFarlane, H. C. E.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic: London, 1978; Chapter 12, Table 12.11 and references therein.
(16) Dean, P. A. W.; Srivastava, R. S. *Inorg. Chim. Acta* **1985**, *105*, 1.

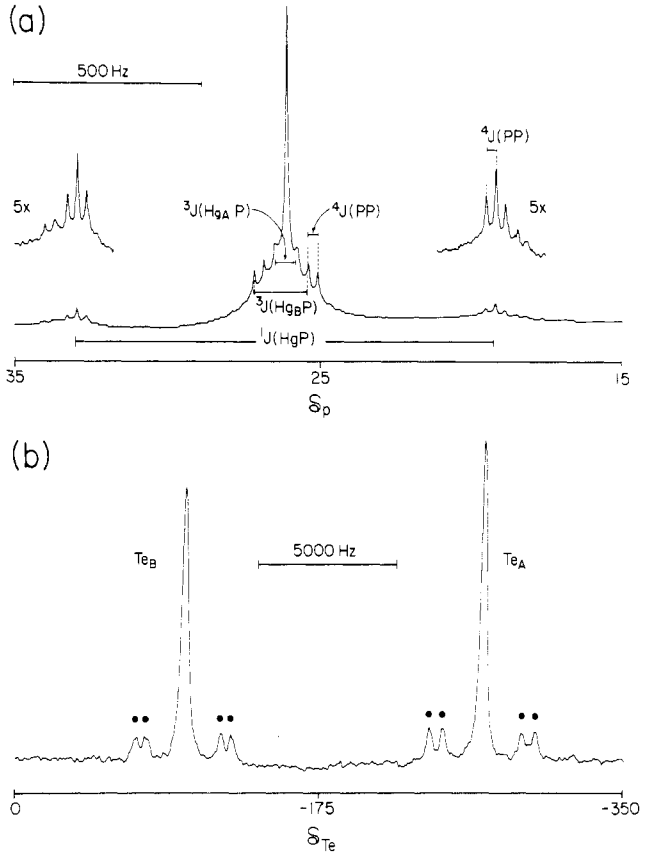


**Figure 1.** NMR spectra of $[(\mu\text{-TePh})_6(HgPPh_3)_3(Hg)](ClO_4)_2$ in DMF at 214 K: (a) 80.98 MHz $^{31}P\{^1H\}$ NMR spectrum; (b) 63.14 MHz $^{125}Te\{^1H\}$ NMR spectrum (● = $^{199}Hg$ satellite).

previously:[1] these are 0.4783, 0.3874, 0.1177, $1.589 \times 10^{-2}$, and $8.042 \times 10^{-4}$ for $x = 0$–4, respectively. From counting statistics[17] the expected fractional populations of $(^{125}Te)_y(^0Te)_{6-y}$ are 0.647, 0.293, $5.48 \times 10^{-2}$, $5.50 \times 10^{-3}$, $3.10 \times 10^{-4}$, $9.31 \times 10^{-6}$, and $1.17 \times 10^{-7}$ for $y = 0$–6, respectively. When chemically different sites are available for the nuclei of interest, as they are for $^{199}Hg$ and $^{125}Te$ in $[(\mu\text{-TeR})_6(HgL)_3(HgL')]^{2+}$ (see below), more than one isotopic isomer occurs for a given value of $x$ and $y$.

**(ii) $[Hg_4(TePh)_6(PR'_3)_3]^{2+}$.** Perchlorate salts of these cations are formed for all the triarylphosphines that were studied ($PPh_3$, $P(4\text{-}C_6H_4Me)_3$, $P(4\text{-}C_6H_4Cl)_3$). The salt of the $P(4\text{-}C_6H_4Me)_3$ complex is sufficiently soluble in $CH_2Cl_2$ that NMR studies could be carried out on the isolated material. However, the salts of the $PPh_3$ and $P(4\text{-}C_6H_4Cl)_3$ complexes have poor solubilities in $CH_2Cl_2$ once isolated. Accordingly, NMR studies in these two cases were made on supersaturated samples prepared in situ according to eq 1, $n = 1$. DMF was found to be a useful alternative solvent for our NMR study. All three compounds have solubilities in DMF of at least 0.05 mol/L of solvent. We presume that enhanced solubility in DMF is caused by solvent coordination at the unique mercury with either entry into a vacant site or displacement of a weakly bound $ClO_4^-$ anion.

**(a) R′ = Ph.** Figure 1a shows the $^{31}P$ NMR spectrum of **1** in DMF at 214 K. This spectrum is just that expected for the cation $[(\mu\text{-TePh})_6(HgPPh_3)_3(Hg\{DMF\}_z)]^{2+}$ (**1′**) having 3-fold symmetry. Table Ia lists the $^{199}Hg$ distribution in the major isotopomers expected to contribute to the spectrum, with the corresponding fractional populations and NMR patterns. No $^{31}P$–$^{125}Te$ coupling is observed in the $^{31}P$ (or $^{125}Te$) NMR spectrum, and a satisfactory simulation is obtained by using the appropriate composite with the $^{31}P$–$^{31}P$, $^{31}P$–$^{199}Hg$, and $^{199}Hg$–$^{199}Hg$ coupling constants given in Table II.

The $^{125}Te$ NMR spectrum of **1** in DMF at 214 K is presented in Figure 1b and summarized in Table II. This spectrum shows

(17) Calingaert, G.; Beatty, H. A. *J. Am. Chem. Soc.* **1939**, *61*, 2748.

**Table I.** Distribution of $^{199}Hg$ Nuclei in the Major Isotopomers of $[(\mu\text{-TeR})_6(HgPR'_3)_3(HgL)]^{2+}$ with $C_{3v}$ Symmetry

| isotopomer[a] | fractional abund | $^{31}P$ NMR pattern[b,c] (a) L = solv | (b) L = $PR'_3$ |
|---|---|---|---|
| $(^0HgPR'_3)_3(^0HgL)$ | 0.4783 | $A_3$ | $A_3F$ |
| $(^0HgPR'_3)_2(^{199}HgPR'_3)(^0HgL)$ | 0.2906 | $A_2A'X$ | $A_2A'FX$ |
| $(^0HgPR'_3)_3(^{199}HgL)$ | 0.0969 | $A_3X$ | $A_3FX$ |
| $(^0HgPR'_3)(^{199}HgPR'_3)_2(^0HgL)$ | 0.0589 | $AA'A''XX'$ | $AA'A''FXX'$ |
| $(^0HgPR'_3)_2(^{199}HgPR'_3)(^{199}HgL)$ | 0.0589 | $A_2A'MX$ | $A_2A'FMX$ |

[a] $^0Hg$ represents spin-inactive Hg. [b] A and F represent $^{31}P$; M and X represent $^{199}Hg$. [c] Coupling to $^{125}Te$ is not observed in the $^{31}P$ NMR spectrum.

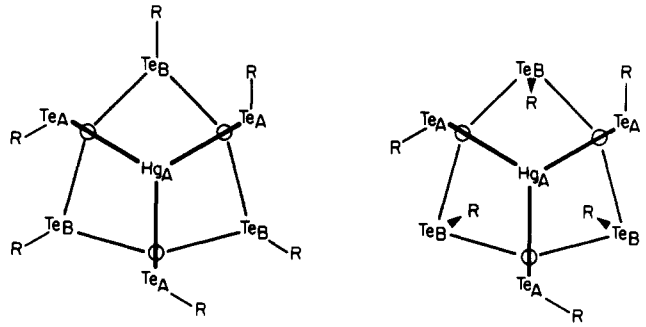


**Figure 2.** Two $C_3$ isomers of $(\mu\text{-TeR})_6Hg_4$, viewed down their $C_3$ axes: (left) isomer II; (right) isomer IV (O = $Hg_B$). One enantiomer of each isomer is shown.

two approximately equally intense signals consistent with the 3-fold symmetry indicated by the $^{31}P$ NMR spectrum. By comparison with the $^{125}Te$ NMR spectra of $[(\mu\text{-TePh})_6(HgPPh_3)_4]^{2+}$ and $[(\mu\text{-TePh})_6(HgP\{4\text{-}C_6H_4Cl\}_3)_3(Hg\{DMF\}_z)]^{2+}$, described and discussed below, we tentatively assign the more and less shielded resonances to $^{125}Te$ in the environments $Ar_3PHgTe(Ph)Hg(DMF)_z$ (A) and $Ar_3PHgTe(Ph)HgPAr_3$ (B), respectively. The presence of two pairs of $^{199}Hg$ satellites about each of the two $^{125}Te$ lines is quite evident in Figure 1b. Different one-bond couplings to the two chemically distinct $^{199}Hg$ nuclei are expected for $Te_A$. The occurrence of two one-bond $^{199}Hg$–$^{125}Te_B$ couplings can be accounted for if the cation has static or time-averaged $C_3$ symmetry but is inconsistent with time-averaged $C_{3v}$ symmetry. As has been discussed earlier,[18] a total of four isomers are expected for the adamantanoid metal–chalcogenate cage, $M_4(\mu\text{-ER})_6$, as a result of inversion at the pyramidal E atoms of the six $\mu$-ER groups. In isomer I the axial/equatorial (a/e) dispositions of the R groups in the four six-membered rings are aaa,aae,aee,eee and the point-group symmetry is $C_1$. The other isomers are as follows: II (aae,aae,aae,eee; point-group symmetry $C_3$), III (aae,aae,-aee,aee; point-group symmetry $C_1$), and IV (aaa,aee,aee,aee; point-group symmetry $C_3$). The two $C_3$ isomers are represented in Figure 2. The $^{125}Te$ NMR spectral results can be accounted for in terms of the occurrence of either isomer II or isomer IV alone, provided that inversion at Te is slow. Alternatively, *time-averaged* $C_3$ symmetry could occur if there were rapid inversion at $Te_B$ but not at $Te_A$, i.e. rapid intramolecular II $\rightleftharpoons$ IV exchange without racemization. (Racemization would lead to time-averaged $C_{3v}$ symmetry, which can be ruled from the observation of two values for $^1J(^{125}Te_B$–$^{199}Hg)$ as discussed above.) These conclusions are not altered if the assignments in the $^{125}Te$ NMR spectrum are reversed. To our knowledge, this is the first concrete evidence for the preferential occurrence of specific isomers of an adamantane-like $M_4(ER)_6$ cage in solution. It is worth

(18) Dean, P. A. W.; Vittal, J. J.; Payne, N. C. *Inorg. Chem.* **1987**, *26*, 1683 and references therein.

(19) A less appealing possibility is that $C_3$ symmetry results from an *SSSS/RRRR* or *RSSS/SRRR* arrangement of chiral $PAr_3$ ligands occurring when the aryl groups of each ligand adopt a fixed propeller-like conformation. No NMR evidence for fixed conformations of the phosphine was found previously[1] for $[(\mu\text{-ER})_6(HgPPh_3)_4]^{2+}$ (E = S, Se). (In solid $[(\mu\text{-SPh})_6(HgPPh_3)_4](ClO_4)_2\cdot 1.5CHCl_3$ all the $PPh_3$ ligands have the same chirality, however.[2])

**Table II.** NMR Data for $[(\mu\text{-TePh})_6(HgPR'_3)_3(Hg)](ClO_4)_2$[a,b]

| R′ (isomer)[b] | solvent | T, K | concn[c] | $\delta_P$[d] | $\delta_{Te}$[e] | $\delta_{Hg}$[f] | $^1J$(P–Hg), Hz[g] | $^1J$(Te–Hg),[h] Hz[i] | $^2J$(Hg–Hg), Hz | $^3J$(P–Hg), Hz[g] | $^4J$(P–P), Hz[j] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ph | DMF | 214 | 0.03 | 26.1 | −268 (A)<br>−97 (B) | −1098 (A)<br>−875 (B) | 1110 | 3780 (AA)[k]<br>2830 (AB)[k]<br>2710 (BB)<br>3470 (BB′) | ≈300 (BB′)[l] | 143 (BB)<br>57 (BA) | 25 |
| | $CH_2Cl_2$ | 214 | 0.05 | 26.6 | −232 (A)<br>−95 (B) | −898 (A)<br>−839 (B) | 1330<br>2800 (AB)[k] | 4320 (AA)[k]<br>2730 (BB)<br>3670 (BB′) | ≈560 (AB)[m] | 144 (BB)<br>*n* | 28 |
| 4-$C_6H_4Me$ | DMF | 214 | 0.03 | 25.4 | −264 (A)<br>≈−99 (B)[o] | −1087 (A)<br>−857 (B) | 1343 | 3810 (AA)[k]<br>2790 (AB)[k]<br>≈2800 (BB)<br>3380 (BB′) | ≈450 (AB)[m] | 138 (BB)<br>59 BA) | 25 |
| | $CH_2Cl_2$ | 214 | 0.05 | 26.3 | −229 (A)<br>≈−121 (B)[o] | *p*<br>−851 (B) | | 4230 (AA)[k]<br>2890 (AB)[k] | | 133 (BB)<br>≈30 (BA) | 27 |
| 4-$C_6H_4Cl$ ($C_3$(1))[b,s] | DMF | 214 | 0.05[q] | 21.0 | −275 (A)<br>−125 (B) | ≈−1128 (A)<br>−857 (B) | 800 | ≈3350[r]<br>≈3580[t] | | 130 (BB)<br>52 (BA) | 27 |
| 4-$C_6H_4Cl$ ($C_3$(2))[b] | DMF | 214 | | 21.4 | −275 (A)<br>−111 (B) | ≈−1128 (A)<br>−904 (B) | 735 | ≈3350[r]<br>≈3100[t] | | 140 (BB)<br>48 (BA) | 25 |
| 4-$C_6H_4Cl$ ($C_3$(1))[b,u] | DMF | 253 | | 21.0 | −258 (A)<br>−114 (B) | −1117 (A)<br>−883 (B) | 780 | 3520 (AA)[k]<br>2670 (AB)[k]<br>2910 (BB)<br>3890 (BB′) | ≈575 (AB)[m] | 146 (BB)<br>*n* | 25 |
| 4-$C_6H_4Cl$ | $CH_2Cl_2$ | 214 | 0.05 | 20.1 | −250 (A)<br>−105 (B) | −936 (A)<br>−858 (B) | 720 | 4080 (AA)[k]<br>2930 (AB)[k]<br>2840 (BB)<br>3570 (BB′) | | ≈136 (BB)<br>*n* | 22 |

[a] Labeling: $[(\mu\text{-Te}_A\text{Ph})_3(\mu\text{-Te}_B\text{Ph})_3(Hg_A\{solv\})(Hg_BP_BR'_3)_3]^{2+}$, with $Te_A$ bound to $Hg_A$. In the parenthetic assignments atoms are labeled in the order they occur in the column headings. [b] See text. [c] Units of mol/L of solvent at ambient temperature. [d] Relative to external 85% $H_3PO_4$ at 296 K; estimated error ±0.1 ppm. [e] Relative to external pure $Me_2Te$ as secondary reference (see Experimental Section); estimated error ±2 ppm, unless noted otherwise. [f] Relative to external pure $Me_2Hg$ as secondary reference (see Experimental Section); estimated error ±1 ppm, unless noted otherwise. [g] Estimated error ±2 Hz, unless noted otherwise. [h] Coupling to $^{125}Te$. [i] Measured in the $^{125}Te$ NMR spectrum; estimated error ±50 Hz, unless noted otherwise. [j] Estimated error ±1 Hz, unless noted otherwise. [k] These assignments are tentative and may be reversed. [l] From the $^{31}P$ NMR spectrum. [m] From the resonance of $Hg_A$ in the $^{199}Hg$ NMR spectrum. [n] $^3J(P_B–Hg_A)$ is not observed. [o] Broad signal. [p] The signal from $Hg_A$ could not be located with certainty. [q] Total concentration of both isomers. [r] Average coupling to $Te_A$. [s] Major isomer. [t] Average coupling to $Te_B$. [u] Only the $C_3$(1) isomer is present at this temperature.

noting that more information about the invertomeric composition of **1′** is available from its $^{125}Te$ NMR spectrum than from its $^{31}P$ NMR spectrum.

The $^{199}Hg$ NMR spectrum of **1** at 214 K in DMF (not shown) is that expected for a cation of static or time-averaged $C_3$ symmetry. The $^{199}Hg$ resonances of **1′** fall into regions (Table II). Less shielded and of relative intensity approximately 3 is a doublet of triplets in which the larger doublet splitting is $^1J(^{31}P–^{199}Hg)$ and the smaller triplet splitting is $^3J(^{31}P–^{199}Hg)$. This is the X part of the $A_2A'X$ spectrum of the second isotopomer in Table Ia. More shielded and of relative intensity approximately 1 is a broad signal that is apparently an incompletely resolved quartet. This is the X part of the $A_3X$ spectrum of the third isotopomer in Table Ia. This signal has $^{199}Hg$ satellites due to $^2J(M–X)$ in the $A_2A'MX$ spectrum of the last isotopomer in Table Ia. We could not observe the $^{199}Hg$ satellites in the less shielded region.

As the temperature of the DMF solution of **1** is raised, the various NMR spectra broaden. At ambient probe temperature, the $^{31}P$ NMR spectrum is a single broad line consistent with relatively rapid intermolecular exchange of phosphine. No $^{125}Te$ or $^{199}Hg$ NMR signals could be observed under these conditions. The $^{125}Te$ and $^{199}Hg$ resonances are evidently exceedingly broad, indicating an exchange process with a rate intermediate on the $\delta_{Te}$ and $\delta_{Hg}$ time scales.

The $^{31}P$, $^{125}Te$, and $^{199}Hg$ NMR spectra of **1** in $CH_2Cl_2$ at reduced temperature are not quite so well resolved as, but otherwise very similar to, the spectra obtained by using a DMF solution. They can be analyzed and interpreted in terms of static or time-averaged $C_3$ symmetry as described above. In this case the unique Hg center may be three-coordinate or have a coordinated counterion. The reduced-temperature NMR data are presented in Table II. Once again, the various spectra broaden with increase in temperature. The interpretation of these spectra is essentially identical with that for the corresponding solutions in DMF.

**(b) R′ = 4-$C_6H_4Me$.** The $^{31}P$, $^{125}Te$, and $^{199}Hg$ NMR spectra of **2** in DMF at 214 K are very similar to the corresponding spectra of **1**, showing the existence of $[(\mu\text{-TePh})_6(HgP\{4\text{-}C_6H_4Me\}_3)_3(Hg\{DMF\}_z)]^{2+}$ (**2′**). The spectra can be analyzed and interpreted in the same way as for **1′**. The NMR parameters are given in Table II. The $^{31}P$ NMR spectrum of **2** in $CH_2Cl_2$ at reduced temperature also resembles that of **1**. In this solvent the $^{199}Hg$ NMR spectrum of **2** is not so well-resolved as that of **1**, however, and the resonance of the unique Hg nucleus could not be located with certainty. Possibly residual intramolecular exchange is still occurring under these conditions with a rate intermediate on the $\delta_{Hg}$ time scale but rapid on the $\delta_P$ time scale. This would be consistent with the quite different line widths of the two signals found in the $^{125}Te$ NMR spectrum also. At 214 K, $\Delta\nu_{1/2} \approx 370$ and $\approx 690$ Hz for the $^{125}Te$ signals at −229 and ≈−121 ppm, respectively. Details of these spectra are included in Table II. The various NMR spectra of **2** in both DMF and $CH_2Cl_2$ are collapsed or considerably broadened at ambient probe temperature. Overall, the spectra of the DMF and $CH_2Cl_2$ solutions of **2** again point to preferential formation of one or the other or a rapidly exchanging mixture of both $C_3$ isomers.

**(c) R′ = 4-$C_6H_4Cl$.** The $^{31}P$, $^{125}Te$, and $^{199}Hg$ NMR spectra of **3** prepared in situ in $CH_2Cl_2$ (Table II) were generally similar at all temperatures to those of **1** and can be interpreted in the same manner.

Samples of **3** in DMF show more complicated behavior than the corresponding solutions of **1** or **2**. Parts a and b of Figure 3 show the $^{31}P$ and $^{125}Te$ NMR spectra, respectively, of this salt in DMF at 214 K. In Figure 3a separate $^{31}P$ NMR spectra are observed for the two possible $C_3$ isomers of the $P(4\text{-}C_6H_4Cl)_3$ complex. The molar ratio of the two isomers is approximately 2:3. In the absence of a method to correlate spectra and isomers, we arbitrarily label the more abundant isomer $C_3$(1) and the less abundant $C_3$(2). The $^{125}Te$ spectrum (Figure 3b) is also consistent with the occurrence of two isomers. By comparison with the spectra of the $PPh_3$ and $P(4\text{-}C_6H_4Cl)_3$ complexes discussed above, both $C_3$ isomers are expected to produce a more shielded $^{125}Te$ resonance due to $Te_A$ (in the environment $Ar_3PHgTe(Ph)Hg(DMF)_z$) and a less shielded $^{125}Te$ resonance due to $Te_B$ (in the environment $Ar_3PHgTe(Ph)HgPAr_3$). The apparent three-line spectrum shown in Figure 3b results from accidental coincidence of the $Te_A$ lines of $C_3$(1) and $C_3$(2). The isomers $C_3$(1) and $C_3$(2)

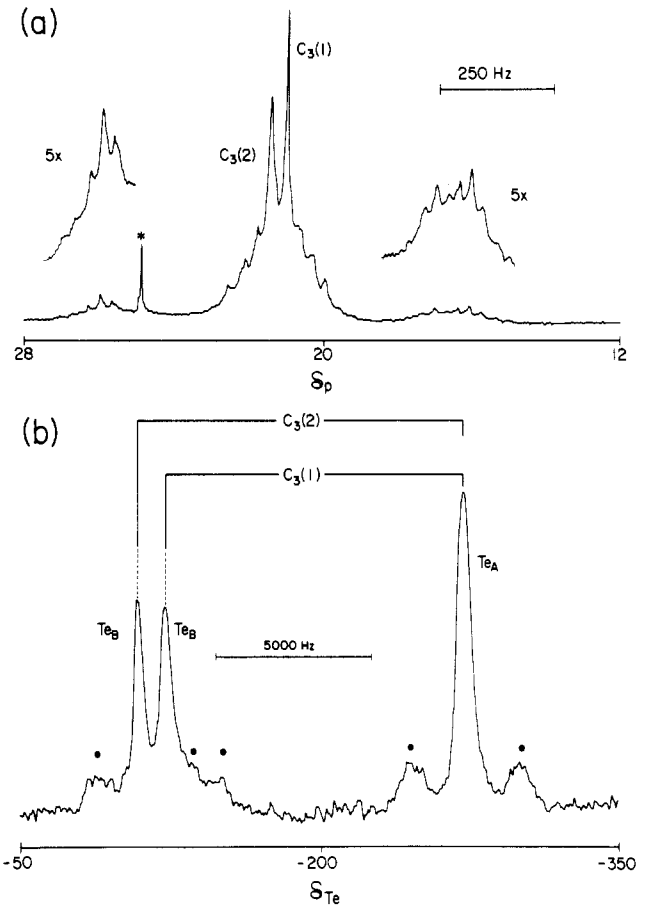


**Figure 3.** NMR spectra of $[(\mu\text{-TePh})_6(HgP\{4\text{-}C_6H_4Cl\}_3)_3(Hg)](ClO_4)_2$ in DMF at 214 K: (a) 80.98 MHz $^{31}P\{^1H\}$ NMR spectrum; (b) $^{125}Te\{^1H\}$ NMR spectrum (✱ = impurity; ● = $^{199}Hg$ satellite).

differ in the position of the Ph group on $Te_B$. Change in this position is expected to produce a major effect on $\delta_{Te_B}$ but only a minor effect on $\delta_{Te_A}$, as is observed.

The $^{199}Hg$ NMR spectrum (not shown) of **3** in DMF at 214 K is consistent with the interpretation of the $^{31}P$ and $^{125}Te$ NMR spectra. Two sets of resonances are found in the region now expected for the $Ar_3PHg(\mu\text{-Te})_3$ moiety, each set a doublet (from $^1J(^{31}P\text{–}^{199}Hg)$) of triplets (from $^3J(^{31}P\text{–}^{199}Hg)$). Overlap apparently occurs in the region expected for the kernel $(DMF)_xHg(\mu\text{-Te})_3$, and only a single broad line with $^{199}Hg$ satellites is found. Again, it can be argued that this chemical shift should be insensitive to changes in the position of the Ph group on $Te_B$, as is found.

When the temperature of the DMF solution is raised from 214 K, the $^{31}P$ NMR spectrum of $C_3(1)$ becomes predominant so that only its "$C_3$" pattern is evident at ca. 238 K. This pattern persists until ca. 263 K. Thereafter, this spectrum broadens and a new broad signal grows, with $\delta_P \approx 17$ and $\Delta\nu_{1/2} \approx 250$ Hz at 271 K. This signal, which is not due to free $P(4\text{-}C_6H_4Cl)_3$, becomes the major one at ambient probe temperature. These changes are reversible, although slow decomposition of the sample seems to occur at 294 K. In the $^{125}Te$ NMR spectrum, there is a gradual reduction in the $C_3(2)$:$C_3(1)$ intensity ratio on warming, until at ca. 271 K only the spectrum of the $C_3(1)$ isomer is evident. Parallel changes occur in the $^{199}Hg$ NMR spectrum from 214 to 271 K. Finally, at 294 K, the $^{125}Te$ NMR spectrum shows the spectrum of the $C_3(1)$ isomer as a minor component and six new resonances ($\delta_{Te} \approx +15, -12, -164, -217, -231, -301$). The samples decompose too rapidly at 294 K for collection of a useful $^{199}Hg$ NMR spectrum. A definitive explanation of the changes occurring in the $^{31}P$ and $^{125}Te$ NMR spectra from 263 to 294 K is not possible, but we hypothesize that they indicate conversion of the $C_3(1)$ isomer into one (or both) of the possible $C_1$ isomers (see above).

**(iii) $[Hg_4(TeR)_6(HgPR'_3)_4]^{2+}$.** These cations can be produced more or less cleanly in $CH_2Cl_2$ solution according to eq 1 ($n$ = 2). For R = Ph, R' = aryl they are also formed quantitatively in $CH_2Cl_2$ from equimolar mixtures of $[Hg_4(TeR)_6(PR'_3)_3]^{2+}$ and $PR'_3$. The characterization of the complexes by multinuclear magnetic resonance is described below.

Mixtures with the correct stoichiometry to produce $[(\mu\text{-TePh})_6(HgPAr_3)_4]^{2+}$ in DMF give low-temperature NMR spectra showing $[(\mu\text{-TePh})_6(HgPAr_3)_3(Hg\{DMF\}_z)]^{2+}$ (see above) as the major species present. Clearly, there is extensive solvolysis of $[(\mu\text{-TePh})_6(HgPAr_3)_4]^{2+}$ under these conditions. Similar DMF complexes could not be detected for R' ≠ Ar. Instead we obtained evidence for decomposition.

**(a) R = Ph or Me, R' = *n*-Bu.** The cation with R = Ph, R' = *n*-Bu (**6'**) is produced quantitatively in $CH_2Cl_2$ according to eq 1, $n$ = 2. The $^{31}P$ NMR spectrum of a sample of this species at 214 K[20,21] is very like that reported[1] for the thiolate congener. By analogy it can be analyzed in terms of time-averaged tetrahedral symmetry,[22] to give the NMR parameters included in Table III. At 174 K, the $^{31}P$ NMR spectrum is slightly broadened but otherwise unchanged. On warming of the sample from 214 K, the smaller $^4J(^{31}P\text{–}^{31}P)$ and $^3J(^{31}P\text{–}^{199}Hg)$ couplings are lost by ca. 275 K, but $^1J(^{31}P\text{–}^{199}Hg)$ and $^2J(^{199}Hg\text{–}^{199}Hg)$ persist in the $^{31}P$ NMR spectrum up to 294 K. The lifetime of the cluster at 294 K must be in the approximate range $0.02 > \tau > 0.002$ s.

None of the four individual invertomers of tetracyclic $(\mu\text{-TePh})_6Hg_4$ have $T_d$ symmetry. Therefore, inversion at Te must be rapid on the $^{31}P$ NMR time scale for **6'** down to 174 K. Consistent with such rapid inversion, the $^{125}Te$ NMR spectrum of **6'** at 219 K shows a single line with one pair of $^{199}Hg$ satellites. The intensity ratio $^{199}Hg$ satellite:center band is ca. 0.19. This is close to the value of 0.198[23] expected for the fragment Hg–Te–Hg on statistical grounds[17] when $^{199}Hg$ is in natural abundance. At 174 K, when the $^{31}P$ NMR spectrum is still sharp enough to detect the 19-Hz $^{31}P\text{–}^{31}P$ coupling, the $^{125}Te$ NMR spectrum of **6'** is a very broad line with $\delta_{Te} \approx -247$ and $\Delta\nu_{1/2} \approx 2000$ Hz. This result suggests that at 174 K the rate of Te inversion is becoming noticeably slower on the $\delta_{Te}$ time scale. When the temperature is raised from 214 K, the $^{199}Hg$ satellites in the $^{125}Te$ NMR spectrum broaden until, at temperatures above ca. 271 K, they are no longer evident. The observation of $^2J(^{199}Hg\text{–}^{199}Hg)$ in the $^{31}P$ NMR spectrum at temperatures above 271 K confirms the integrity of the $(\mu\text{-Te})_6Hg_4$ cage under these conditions. The loss of $^{125}Te\text{–}^{199}Hg$ coupling may indicate the onset of an intramolecular exchange process that effectively allows the movement of the tetrahedral $Hg_4$ relative to the octahedral $Te_6$ of the $(\mu\text{-Te})_6Hg_4$ cage. In the limit of fast intramolecular exchange this should lead to a reduction of $^1J(^{125}Te\text{–}^{199}Hg)$ by 50%, as is observed for $[(\mu\text{-TePh})_6(HgPEt_3)_4]^{2+}$ (see below). At intermediate rates, such a process could lead to "smearing out" of the $^{199}Hg$ satellites to the point where they become unobservable.

As expected from the results of $^{31}P$ and $^{125}Te$ NMR spectroscopy, the $^{199}Hg$ NMR spectrum of **6'** is a doublet, due to $^1J(^{31}P\text{–}^{199}Hg)$, at temperatures 214–294 K. The $^{199}Hg$ satellites resulting from the isotopomer $(^0Hg)_2(^{199}Hg)_2$ are evident in the $^{199}Hg$ NMR spectra (cf. ref 1), but $^3J(^{31}P\text{–}^{199}Hg)$ was not resolved.

When crude $Hg(TeMe)_2$ (see Experimental Section) is added to a 1:2 mixture of $Hg(P\{n\text{-Bu}\}_3)_2(ClO_4)_2$ and $P\{n\text{-Bu}\}_3$ in $CH_2Cl_2$, the $^{31}P$, $^{199}Hg$, and $^{125}Te$ NMR spectra of the supernatant mixture at 214 K show the patterns expected for the cation $[(\mu\text{-TeMe})_6(HgP\{n\text{-Bu}\}_3)_4]^{2+}$ with time-averaged tetrahedral symmetry. Unfortunately, we were unable to produce this cation cleanly, perhaps because we could not obtain pure $Hg(TeMe)_2$. The solutions always contained $[Hg(P\{n\text{-Bu}\}_3)_3]^{2+}$ and several unidentified species as well. At 214 K, the tetranuclear complex

(20) Supplementary material.
(21) Apart from slight temperature dependence of $^1J(^{31}P\text{–}^{199}Hg)$, the spectrum varies little over the range 181–276 K.
(22) It should be noted that no information about the isomer(s) present can be obtained from this spectrum.
(23) As a result of a typographical error, this ratio is given as 0.192 in ref 1.

**Table III.** NMR Data for $[(\mu\text{-TeR})_6(HgPR'_3)_4](ClO_4)_2$ in $CH_2Cl_2$[a-c]

| R, R′ (isomer)[b] | T, K | $\delta_P$[d] | $\delta_{Te}$[e] | $\delta_{Hg}$[f] | $^1J$(P–Hg), Hz[g] | $^1J$(Te–Hg),[h] Hz[i] | $^2J$(Hg–Hg), Hz | $^3J$(P–Hg), Hz[g] | $^4J$(P–P), Hz[j] |
|---|---|---|---|---|---|---|---|---|---|
| Ph, *n*-Bu[k] | 214 | 14.5 | −263 | −981 | 2237 | 2720 | 446 ± 3 | 56 | 19 |
| | 294 | 15.3 | −225 | −1050 | 2267[l] | *m* | ≈480 | | |
| Ph, Et[k] | 214 | 23.9 | −258 | −1004 | 2197 | 2770 | 460 ± 5 | 57 | 18 |
| | 294 | 23.8 | −225 | −1066 | 2287[l] | 1330 | | | |
| Ph, 4-$C_6H_4Cl$ ($C_3$) | 181 | −5.3 (A) | −271 (A) | −1067 (A) | 1480 (AA) | 3130[n] | | 70 (AB) | 21 (AB) |
| | | 17.1 (B) | −109 (B) | −1005 (B) | 600 (BB) | ≈3080[o,p] | | 84 (BA) | 21 (BB′) |
| | | | | | | | | 120 (BB) | |
| | 294 | | 13.5 | −152 | −1073 | | ≈3275 | | |
| Ph, Ph ($C_3$(1))[q] | 181 | −6.5 (A) | −253 (A) | −1005 (A) | ≈1350 (AA) | ≈3050[n] | | | |
| | | 22.9 (B) | −201 (B) | −976 (B) | ≈900 (BB) | ≈3220[o] | | | |
| Ph, Ph ($C_3$(2)) | 181 | −8.8 (A) | −253 (A) | −1005 (A) | ≈1040 (AA) | ≈3050[n] | | | |
| | | 23.4 (B) | −106 (B) | −916 (B) | ≈855 (BB) | ≈2950[o,r] | | | |
| Ph, Ph[k,s] | 294 | 20.0 | −191 | −1051 | | 2979 | | | |
| Ph, 4-$C_6H_4Me$ ($C_3$(1))[q] | 181 | *t* | ≈−261 (A) | ≈−1025?[t] | | ≈3130[n] | | | |
| | | | −207 (B) | | | | | | |
| Ph, 4-$C_4H_6Me$ ($C_3$(2)) | 181 | −2.7 (A) | ≈−261 (A) | −988? (B) | 2006 (AA) | | | | |
| | | 22.4 (B) | −182 (B) | | 1300 (BB) | | | | |
| Ph, 4-$C_6H_4Me$[k] | 234 | 18.9 | −216 | −1012 | 1570[u] | 2860 | | | |
| Ph, 4-$C_6H_4Me$[k] | 294 | 19.7 | −192 | −1074 | | ≈2940 | | | |
| Me, Ph[k] | 294[v] | 0.2 | −572 | −1190 | | 3055 | | | |

[a] Concentration: 0.05 mol/L of $CH_2Cl_2$ at ambient temperature. [b] See text. [c] Labeling used for $C_3$ isomers: $[(\mu\text{-Te}_A\text{R})_3(\mu\text{-Te}_B\text{R})_3(Hg_AP_AR'_3)(Hg_BP_BR'_3)_3]^{2+}$, with $Te_A$ bound to $Hg_A$. In the parenthetic assignments atoms are labeled in the order they occur in the column headings. [d] Relative to external 85% $H_3PO_4$ at 296 K; estimated error ±0.1 ppm. [e] Relative to external pure $Me_2Te$ as secondary reference (see Experimental Section); estimated error ±2 ppm. [f] Relative to external pure $Me_2Hg$ as secondary reference (see Experimental Section); estimated error ±1 ppm. [g] Estimated error ±2 Hz, unless noted otherwise. [h] Coupling to $^{125}Te$. [i] In the $^{125}Te$ NMR spectrum; estimated error ±50 Hz, unless noted otherwise. [j] Estimated error ±1 Hz. [k] Time-averaged tetrahedral symmetry. [l] Estimated error ±25 Hz. [m] $^{199}Hg$ satellites are too broad to observe. [n] Average coupling to $Te_A$. [o] Average coupling to $Te_B$. [p] Two incompletely resolved pairs of satellites. [q] Major isomer (tentative for R′ = 4-$C_6H_4Me$). [r] At 214 K, two couplings to $Te_B$ are resolved: 2650 ± 100 and 3590 ± 100 Hz. [s] Probably $C_3$(1) isomer only (see text). [t] Broad resonance(s). [u] Estimated error ±10 Hz. [v] Complicated behavior at reduced temperature (see text).

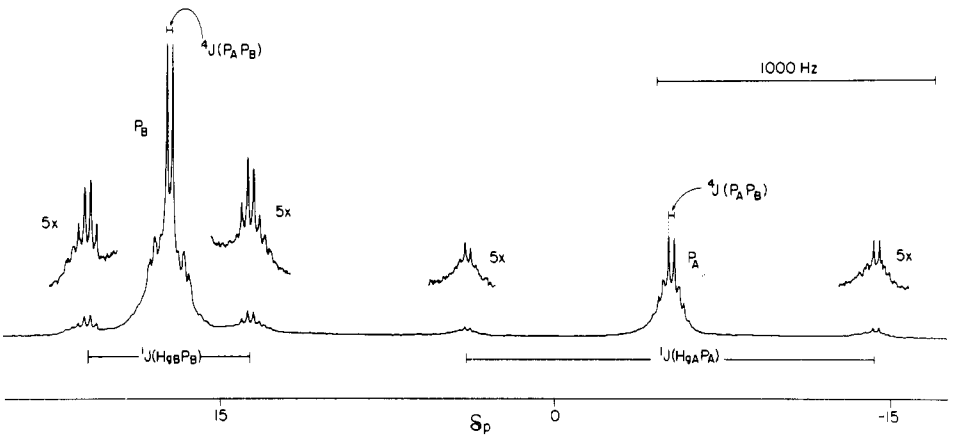


**Figure 4.** 80.98-MHz $^{31}P\{^1H\}$ NMR spectrum of $[(\mu\text{-TePh})_6(HgP\{4\text{-}C_6H_4Cl\}_3)_4](ClO_4)_2$ in $CH_2Cl_2$ at 214 K. For clarity, the three-bond $^{31}P$–$^{199}Hg$ couplings are not indicated.

is characterized by the NMR spectral parameters $\delta_P$ = 4.2, $\delta_{Hg}$ = −1030 ± 1, $^1J(^{31}P\text{–}^{199}Hg)$ = 1623 ± 5 Hz, $^3J(^{31}P\text{–}^{199}Hg)$ = 71 ± 1 Hz, and $^4J(^{31}P\text{–}^{31}P)$ = 21 ± 1 Hz. In the corresponding $^{125}Te$ NMR spectrum we tentatively assign to the complex a singlet at $\delta_{Te}$ = −728 with $^1J(^{125}Te\text{–}^{199}Hg) \approx 2680$ Hz. The spectrum also shows a less intense as yet unidentified signal with $\delta_{Te}$ = −722 and $^1J(^{125}Te\text{–}^{199}Hg)$ = 2900 ± 50 Hz.

**(b) R = Ph, R′ = Et.** This cation (**4′**) can be obtained in $CH_2Cl_2$ solution either by dissolution of **4** or by preparation in situ following eq 1, $n$ = 2. Overall, the $^{31}P$, $^{125}Te$, and $^{199}Hg$ NMR spectra of such samples were very similar to those of **6′**, and it is clear that at temperatures of ca. 193 K or above the structure is $[(\mu\text{-TePh})_6(HgPEt_3)_4]^{2+}$ with time-averaged tetrahedral symmetry.[22] Representative NMR data are included in Table III.

At ca. 174 K, the $^{125}Te$ NMR spectrum of **4′**, like that of **6′**, broadens, suggesting a slowing of inversion at Te. Two significant differences exist between the spectra of **4′** and **6′**. In the $^{31}P$ NMR spectra of **4′**, the two-bond $^{199}Hg\text{–}^{199}Hg$ coupling collapses by ca. 283 K, though $^1J(^{31}P\text{–}^{199}Hg)$ persists up to ambient probe temperature. Both couplings persist to ambient probe temperature for **6′**. In the $^{125}Te$ NMR spectra of **4′**, the $^{199}Hg$ satellites are sharp, with $^1J$ = 2760 ± 50 Hz, ca. 214–ca. 252 K, and then broaden at ca. 271 K, before becoming evident again at ca. 283 K with a significantly smaller value of $^1J$, e.g. 1330 ± 100 Hz at ambient probe temperature. The $^{199}Hg$ satellites in the $^{125}Te$ NMR spectrum of **6′** have not resharpened at ambient probe temperature. As discussed above, we tentatively attribute this behavior to an unidentified intramolecular exchange process that has the effect of causing relative movement of the $Hg_4$ tetrahedron and the $Te_6$ octahedron.

**(c) R = Ph, R′ = 4-$C_6H_4Cl$.** The $^{31}P$ NMR spectrum at 174 K of a solution of this cation (**7′**) prepared in situ in $CH_2Cl_2$ according to eq 1, $n$ = 2, is shown in Figure 4. The spectrum shows a doublet and quartet, relative intensities 3 and 1, with mutual $^4J(^{31}P\text{–}^{31}P)$ coupling, both having $^{199}Hg$ satellite spectra. The most plausible explanation of this spectrum is in terms of static or time-averaged 3-fold symmetry resulting from preferred orientations of the aryl groups on Te, as discussed above for **1′**–**3′**.[19] The $^{31}P$ NMR spectrum can be analyzed on this basis as a composite of the spectra of the individual isotopomers given in Table Ib. Table III includes the NMR parameters obtained. On warming of the sample, $^4J(^{31}P\text{–}^{31}P)$ and $^3J(^{31}P\text{–}^{199}Hg)$ are lost

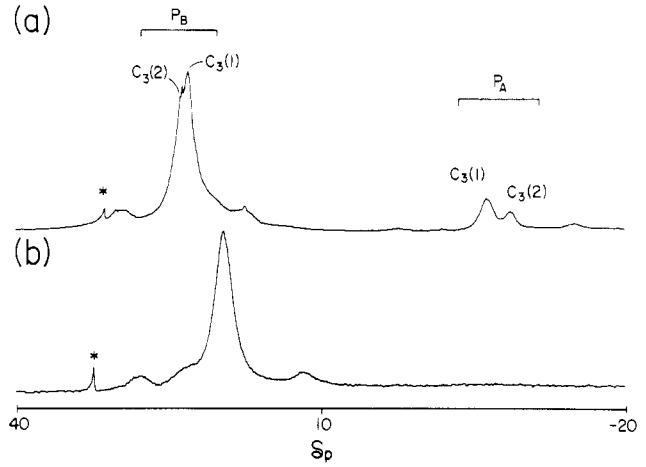


**Figure 5.** 80.98-MHz $^{31}P\{^1H\}$ NMR spectra of $[(\mu\text{-TePh})_6(HgPPh_3)_4](ClO_4)_2$ in $CH_2Cl_2$: (a) 181 K; (b) 234 K (* = impurity).

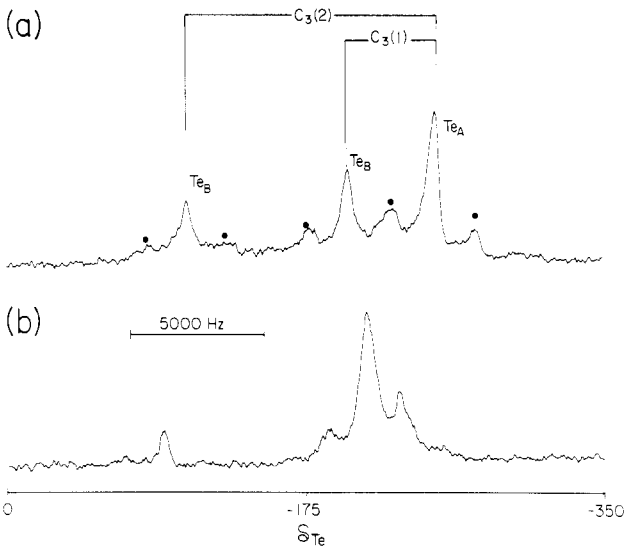


**Figure 6.** 63.14-MHz $^{125}Te\{^1H\}$ NMR spectra of $[(\mu\text{-TePh})_6(HgPPh_3)_4](ClO_4)_2$ in $CH_2Cl_2$: (a) 181 K; (b) 234 K (● = $^{199}Hg$ satellite). Note that the $^{125}Te$ NMR chemical shifts are temperature dependent.

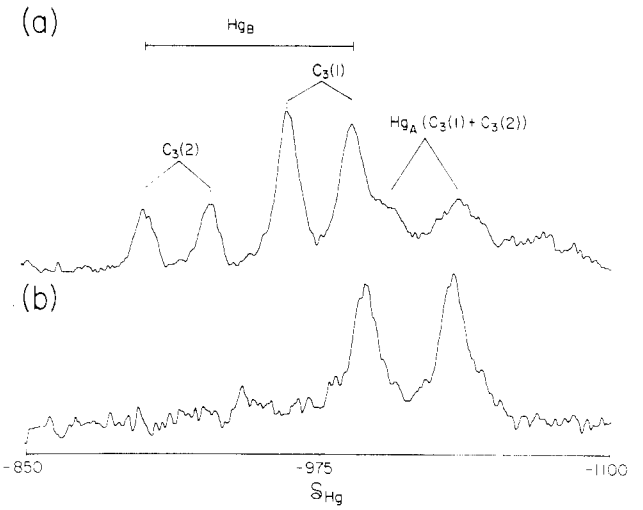


**Figure 7.** 35.75-MHz $^{199}Hg\{^1H\}$ NMR spectra of $[(\mu\text{-TePh})_6(HgPPh_3)_4](ClO_4)_2$ in $CH_2Cl_2$: (a) 181 K; (b) 234 K. Note that the $^{199}Hg$ NMR chemical shifts are temperature dependent.

by ca. 214 K. Loss of $^1J(^{31}P\text{–}^{199}Hg)$ and coalescence of the two separate regions then occurs approximately concurrently and is complete by ca. 254 K. Evidently intermolecular exchange of $P(4\text{-}C_6H_4Cl)_3$ is rapid on the time scales of $\delta_P$ and $^1J(^{31}P\text{–}^{199}Hg)$ at this temperature.

Two approximately equally intense resonances, each with $^{199}Hg$ satellites, were obtained in the $^{125}Te$ NMR spectrum of **7′** in $CH_2Cl_2$ over the range 174–234 K. These results are quite consistent with the 3-fold symmetry deduced from the $^{31}P$ NMR spectra at reduced temperature. By comparison with the spectrum of the $PPh_3$ analogue (see below), we tentatively assign the resonance at −271 ppm to $Te_A$, which is bound to the unique mercury. The signal from $Te_B$, which is in the basal plane (see Figure 2), is then that at −109 ppm. At ambient probe temperature, 294 K, the $^{125}Te$ NMR spectrum has collapsed into a single broad line ($\delta_{Te} = -152$, $\Delta\nu_{1/2} \approx 700$ Hz) with a pair of $^{199}Hg$ satellites ($^1J \approx 3275$ Hz). Under these conditions the $(\mu\text{-Te})_6Hg_4$ core is long-lived on the $^1J(^{199}Hg\text{–}^{125}Te)$ time scale, but inversion at Te is rapid and random on the $\delta_{Te}$ time scale, giving time-averaged tetrahedral symmetry.

The $^{199}Hg$ NMR spectrum of **7′** in $CH_2Cl_2$ at 174 K shows signals in two regions. These are doublets, from $^1J(^{31}P\text{–}^{199}Hg)$, with relative intensities ca. 3 and 1 from low to high frequency. From the relative intensities and a correlation of $^1J(^{31}P\text{–}^{199}Hg)$ with the values obtained in the $^{31}P$ NMR spectrum, the less and more intense doublets can be assigned to $Hg_A$ and $Hg_B$, the unique and basal Hg atoms, respectively, of a cation with 3-fold symmetry (see Figure 2). At 294 K, the $^{199}Hg$ NMR spectrum consists of a single broad line ($\delta_{Hg} = -1073$, $\Delta\nu_{1/2} \approx 300$ Hz) with $^{125}Te$ satellites. This result confirms that at ambient probe temperature both intermolecular phosphine exchange and inversion at Te are rapid, while the $(\mu\text{-Te})_6Hg_4$ core is long-lived.

**(d) R = Ph, R′ = Ph.** The isolated compound **1** is poorly soluble in $CH_2Cl_2$, but it dissolves in the presence of an equimolar amount of $PPh_3$. NMR studies, summarized in Table III, confirm that the solution contains $[(\mu\text{-TePh})_6(HgPPh_3)_4]^{2+}$ (**8′**).

Figures 5a, 6a, 7a show the $^{31}P$, $^{125}Te$, and $^{199}Hg$ NMR spectra of a solution of **8′** in $CH_2Cl_2$ at 181 K. The signals in the $^{31}P$ NMR spectrum fall into two regions, the relative intensities of the more and less shielded regions being approximately 1 and 3. Most significantly, there are clearly two sets of signals in each of the regions, with relative intensities approximately 1:2. The spectrum can be accounted for in terms of an equilibrium mixture of the two possible $C_3$ isomers in a ratio of ca. 1:2. All the $^{31}P$ resonances have $^{199}Hg$ satellites, but the absence of the expected fine structure due to $^4J(^{31}P\text{–}^{31}P)$ and $^3J(^{31}P\text{–}^{199}Hg)$ (compare Figure 5a with Figure 4) indicates residual exchange; i.e., this is a slow exchange but not a limiting spectrum. Again, we arbitrarily label the more abundant isomer $C_3(1)$ and the less abundant $C_3(2)$.

At 181 K, the $^{125}Te$ NMR spectrum (Figure 6a) consists of three lines, each with $^{199}Hg$ satellites. Both $C_3(1)$ and $C_3(2)$ should give rise to two lines, and there is evidently some overlap. Following the arguments already used for **3′**, we believe that the most intense line in Figure 6a, at −253 ppm, comprises overlapping resonances from $Te_A$ in $C_3(1)$ and $C_3(2)$. On the basis of intensities (and behavior at higher temperatures), we assign the signal at −201 ppm to $Te_B$ in $C_3(1)$ and that at −106 ppm to $Te_B$ in $C_3(2)$. The $^{199}Hg$ NMR spectrum (Figure 7a) can be assigned in a consistent manner by using relative intensities and the values of $^1J(^{31}P\text{–}^{199}Hg)$ from the $^{31}P$ spectrum. The intense doublet at −976 ppm, with $^1J \approx 1000$ Hz, is due to the basal mercury atoms, $Hg_B$, in $C_3(1)$. Similarly, the less intense doublet at −916 ppm, with $^1J \approx 900$ Hz, is due to $Hg_B$ in $C_3(2)$. As discussed above for **3′**, we expect the signals from the unique mercury atoms, $Hg_A$, to be in the same region for $C_3(1)$ and $C_3(2)$, and we assign the broad $^{199}Hg$ resonance at −1005 ppm, with $^1J \approx 1200$ Hz, to superimposed $Hg_A$ signals from both isomers.

As the temperature of the sample is increased, several changes occur in the NMR spectra. The intensity ratio $C_3(2)$:$C_3(1)$ decreases until at ca. 244 K the spectra show no evidence for $C_3(2)$. (The $^{125}Te$ NMR spectrum is a particularly sensitive indicator of this.) Concurrently, the $^{31}P$ and $^{125}Te$ NMR spectra assigned to $C_3(1)$, *but not those assigned to* $C_3(2)$, collapse to give single lines with $^{199}Hg$ satellites, while the two doublets in the $^{199}Hg$ NMR spectrum of $C_3(1)$ collapse to one doublet. These changes are evident from a comparison of Figures 5a, 6a, and 7a with

Figures 5b, 6b, and 7b, which show spectra measured at 233 K. Evidently time averaging of the spectra of $C_3(1)$ is occurring as a result of an intramolecular exchange process that causes rapid reorientation of the $C_3$ axis in this isomer. An analogous process does not become important for the $C_3(2)$ isomer up to the temperature where this isomer becomes undetectable. Above ca. 244 K, the $^{31}P$, $^{125}Te$, and $^{199}Hg$ NMR spectra observed for **8′** are evidently those of the $C_3(1)$ isomer only. The $^1J(^{31}P–^{199}Hg)$ coupling in the $^{31}P$ NMR spectrum is lost above ca. 265 K, indicating the onset of rapid intermolecular exchange of $PPh_3$. However, at 294 K the $^{125}Te$ and $^{199}Hg$ NMR spectra each consist of a single resonance with one pair of satellites, from $^{199}Hg$ and $^{125}Te$, respectively. The satellite:center band intensity ratios are ≈0.18 and ≈0.09 in the $^{125}Te$ and $^{199}Hg$ NMR spectra, in fair agreement with the values of 0.196 and 0.113 expected from statistics[17] for a $(\mu\text{-Te})_6Hg_4$ core of time-averaged tetrahedral symmetry.

Inspection of models shows that reorientation of the $C_3$ axis of either $C_3$ isomer of $(\mu\text{-TeR})_6Hg_4$ (see above) requires a minimum of three inversions at Te. Reorientation in three inversions also causes racemization, which is required to account for the occurrence of only one set of satellites in both $^{125}Te$ and $^{199}Hg$ NMR spectra of the $C_3(1)$ isomer of **8′** at 294 K. (However, racemization is faster than reorientation of the $C_3$ axis, since some racemization is not accompanied by reorientation.) For either $C_3$ isomer, axis reorientation/racemization can occur through one or both of the $C_1$ isomers, but does not require that the other $C_3$ isomer be traversed. Therefore, rapid equivalencing of sites in one $C_3$ isomer does not require the same in the other $C_3$ isomer or rapid interconversion of the two different $C_3$ isomers. This is consistent with our experimental observations.

**(e) R = Ph, R′ = 4-$C_6H_4$Me.** The behavior of this complex (**9′**) in $CH_2Cl_2$ is generally similar to that of **8′**, with two important differences. The rates of intramolecular rearrangement and intermolecular phosphine exchange are faster and slower, respectively, than for **8′**.

A slow-exchange $^{31}P$ NMR spectrum of **9′** could not be obtained at or above 181 K. At 181 K, the spectrum is consistent with one $C_3$ isomer undergoing slow intramolecular rearrangement, as evidenced by relatively sharp signals at $\delta_P = -2.7$ and 22.4 assignable to $P_A$ and $P_B$, respectively. A second (probably $C_3$) isomer is evidently undergoing intramolecular rearrangement at an intermediate rate, giving a relatively broad line at ca. 20 ppm, as expected for the resonance of $P_B$ as it approaches coalescence with that of $P_A$. At 181 K, the $^{125}Te$ NMR spectrum shows three broad resonances, consistent with the presence of two $C_3$ isomers in roughly comparable amounts. The whole $^{31}P$ NMR spectrum is collapsed to a single resonance with $^{199}Hg$ satellites by 214 K. At this temperature the $^{125}Te$ NMR spectrum is a single broad line, but this becomes a sharp singlet with $^{199}Hg$ satellites from 234–294 K. The ratio $^{199}Hg$ satellite:center band ≈ 0.18, consistent with a persistent TePh-bridged species.

**(f) R = Me, R′ = Ph.** Solutions of this complex (**5′**) in $CH_2Cl_2$ can be prepared by direct dissolution of **5**. Alternatively, **5′** may be prepared in situ in the supernatant solution made from a mixture of the components according to eq 1, $n = 2$. (In the latter case incremental addition of the impure $Hg(TeMe)_2$ must be made until the $^{31}P$ NMR spectrum of the supernatant liquid shows no sign of $Hg(PPh_3)_4^{2+}$.) Complicated but reproducible NMR spectroscopic behavior is observed for **5′**.

The $^{31}P$ NMR spectrum of **5′** in $CH_2Cl_2$ at 190 K occurs in the region $\delta_P \approx -1.2$ to 5.3, as shown in Figure 8. From the number of resonances it is immediately clear that a mixture of isomers must be present. The occurrence of a quartet at −1.2 ppm seems to indicate the presence of a $C_3$ isomer, but there are too many lines in the overall spectrum for the mixture to consist of only the two possible $C_3$ isomers. Evidently at least one of the $C_1$ isomers is being formed, but because of signal overlap definitive assignments were not possible. The $^{31}P$ NMR spectrum collapses when the solution is warmed and becomes a single broad line without $^{199}Hg$ satellites at ca. 214 K, showing that intermolecular exchange of $PPh_3$ is rapid at this temperature.

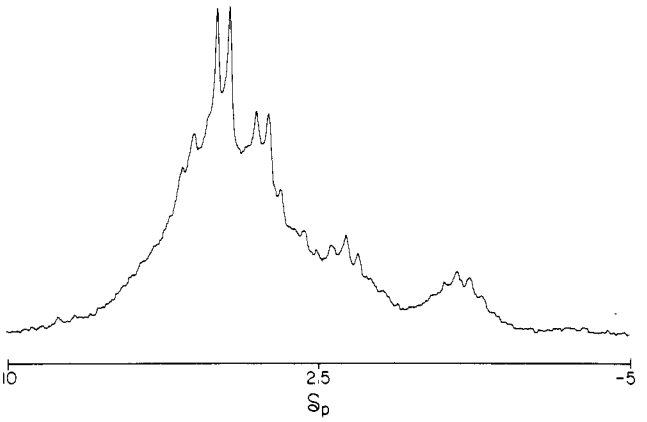


**Figure 8.** 80.98-MHz $^{31}P\{^1H\}$ NMR spectrum of $[(\mu\text{-TeMe})_6(HgPPh_3)_4](ClO_4)_2$ in $CH_2Cl_2$ at 190 K.

The $^{125}Te$ NMR spectrum of **5′** in $CH_2Cl_2$ at 190 K consists of many lines with $^{199}Hg$ satellites, with $\delta_{Te}$ (and $^1J(^{31}P–^{199}Hg)$) as follows: ≈−547 (≈2300 Hz), −614 (2790 ± 50 Hz), −620 (2830 ± 50 Hz), −661 (2730 ± 50 Hz), −692 (2930 ± 50 Hz), −698 (2790 ± 50 Hz), −736 (2730 ± 50 Hz). A copy of this spectrum has been deposited as supplementary material. The number of resonances again makes it clear that at least one of the $C_1$ isomers is being formed. (A total of at most four resonances is expected for a mixture of the two $C_3$ isomers (see above).) It seems likely that the two approximately equally intense lines at −614 and −698 ppm can be assigned to a $C_3$ isomer, as they appear to broaden at equal rates when differential broadening and collapse occur as the sample is warmed. Also, the resonances with $\delta_{Te} = -620$, −661, −692, and −736 ppm appear to have equal intensities, and we tentatively attribute these to a $C_1$ isomer. The broader more intense signal at −547 ppm could include the remaining two resonances expected for this isomer. At 294 K, the spectrum has collapsed to a single relatively sharp line ($\Delta\nu_{1/2} \approx 125$ Hz), with a pair of $^{199}Hg$ satellites. The intensity ratio $^{199}Hg$ satellite:center band is approximately 0.19. This confirms the integrity of the $(\mu\text{-TeMe})_6Hg_4$ core and shows that the isomers present do indeed interconvert intramolecularly.

Mercury-199 NMR spectra of $CH_2Cl_2$ solutions of **5′** are not very informative. In the 190 K spectrum the signals fall in the three regions −1070 to −1110, ≈−1150, and −1175 to −1200, but there is evidently extensive signal overlap. At room temperature this spectrum collapses to a single line ($\Delta\nu_{1/2} \approx 100$ Hz) with one pair of $^{125}Te$ satellites, as expected for a $(\mu\text{-Te})_6Hg_4$ core of time-averaged tetrahedral symmetry. Pertinent NMR parameters are included in Table III.

**(iv) $[(\mu\text{-TePh})_{6-m}(\mu\text{-EPh})_m(HgP\{4\text{-}C_6H_4Me\}_3)_4]^{2+}$ (E = S, Se).** To provide supporting evidence for and further information about the Te-bridged adamantanoid $Hg_4$ clusters, we have investigated a series of complexes with mixed-chalcogen cores. The $P(4\text{-}C_6H_4Me)_3$ complexes are ideal for this purpose, since there is a temperature range for **9′** in which intramolecular exchange is rapid but intermolecular exchange of phosphine is slow. In this range the $^{31}P$, $^{125}Te$, and $^{199}Hg$ NMR spectra are all simple yet show the expected satellites.

The complexes $[(\mu\text{-EPh})_6(HgP\{C_6H_4Me\}_3)_4]^{2+}$ (E = S (**10′**), Se (**11′**)) have not been described before, though the $PPh_3$ analogues have.[1] The new complexes are readily and cleanly preparable in situ in $CH_2Cl_2$ from a 1:2:3 mixture of $Hg(P\{4\text{-}C_6H_4Me\}_3)_2(ClO_4)_2$, $P(4\text{-}C_6H_4Me)_3$, and $Hg(EPh)_2$. At 234 K with a concentration of 0.05 mol/L of $CH_2Cl_2$, **10′** is characterized by the parameters $\delta_P = 38.2 \pm 0.1$, $\delta_{Hg} = -465 \pm 1$, $^1J(^{31}P–^{199}Hg) = 4363 \pm 3$ Hz, $^2J(^{199}Hg–^{199}Hg) = 460 \pm 10$ Hz, $^3J(^{31}P–^{199}Hg) = 31 \pm 1$ Hz, and $^4J(^{31}P–^{31}P) = 11 \pm 1$ Hz. Under the same conditions, $\delta_P = 32.1 \pm 0.1$, $\delta_{Se} = 9.8 \pm 0.2$, $\delta_{Hg} = -697 \pm 1$, $^1J(^{31}P–^{199}Hg) = 3212 \pm 3$ Hz, $^2J(^{199}Hg–^{199}Hg) = 480 \pm 10$ Hz, $^2J(^{31}P–^{77}Se) = 28 \pm 2$ Hz, $^3J(^{31}P–^{199}Hg) = 46 \pm 1$ Hz, and $^4J(^{31}P–^{31}P) = 15 \pm 1$ Hz for **11′**. The values of $^1J$ are ca. 200 Hz larger for the new species than for the $PPh_3$ analogues, but otherwise the NMR spectral parameters of the $PPh_3$ and P(4-

$C_6H_4Me)_3$ clusters are very similar.

Mixtures of **9′** and **10′** in $CH_2Cl_2$ at 234 K show a total of four groups of $^{31}P$ resonances with $\delta_P$ and $^1J(^{31}P-^{199}Hg)$ being approximately 36 and 4250 Hz, 32 and 3130 Hz, 25 and 1970 Hz, and 18 and 1400 Hz. From the NMR spectra of the parent species and the order of appearance, and following the logic used earlier for similar S:Se mixtures,[1] the groups of signals can be attributed to $^{31}P$ in the local environments $PHg(\mu\text{-}S)_3$, $PHg(\mu\text{-}S)_2(\mu\text{-}Te)$, $PHg(\mu\text{-}S)(\mu\text{-}Te)_2$, and $PHg(\mu\text{-}Te)_3$ in order of increasing shielding. Similarly, the $^{199}Hg$ NMR spectra of the mixtures contain groups of signals (all doublets from $^1J(^{31}P-^{199}Hg)$) in four regions centered at approximately −450, −639, −822, and −1004 ppm that can be assigned to $PHg(\mu\text{-}S)_3$ through to $PHg(\mu\text{-}Te)_3$. Clearly, redistribution is occurring to give equilibrium mixtures of $[(\mu\text{-}TePh)_{6-m}(\mu\text{-}SPh)_m(HgP\{C_6H_4Me\}_3)_4]^{2+}$, and the intensities in the $^{31}P$ NMR spectra, especially, show that the redistribution is close to statistical.[17]

The $^{125}Te$ NMR spectra of the **9′**:**10′** mixtures show resonances in a total of five regions: $\delta_{Te} \approx -178$ (a singlet, $^1J(^{125}Te-^{199}Hg) = 2630 \pm 50$ Hz), −184, −197, −208 ($^1J \approx 2900$ Hz), and −218 (a singlet, $^1J(^{125}Te-^{199}Hg) = 2740 \pm 50$ Hz). The last chemical shift is close to that of the $Te_6$ parent. If the chalcogen chemical shift is most sensitive to the nature of the geminal bridging atoms, as has been found in other cases,[24] then the five regions of $^{125}Te$ signals can be attributed to $^{125}Te$ with four through zero cis sulfur atoms in order of increasing shielding. Again, the existence of the mixed-chalcogen cores is evident.

The NMR spectroscopic behavior of **9′**:**11′** mixtures in $CH_2Cl_2$ at 234 K is very similar to that of the S:Te (and earlier S:Se[1]) mixtures and once more gives evidence for approximately statistical scrambling of chalcogens to produce clusters with mixed-bridging chalcogen atoms. The $PHg(\mu\text{-}Se)_3$, $PHg(\mu\text{-}Se)_2$, $PHg(\mu\text{-}Se)(\mu\text{-}Te)_2$, and $PHg(\mu\text{-}Te)_3$ moieties have $^{31}P$ resonances with $\delta_P$ ($^1J(^{31}P-^{199}Hg)$) approximately 33 (3100), 29 (2470), 23 (1740), and 18 (1540 Hz). Mercury-199 resonances for the same groupings fall at approximately −698, −791, −890, and −1002 ppm, respectively. Resonances occur in five regions in both the $^{77}Se$ and $^{125}Te$ NMR spectra. In the $^{77}Se$ NMR spectra $\delta_{Se}$ (with $^1J(^{77}Se-^{199}Hg)$ where observed) is −14.5, −6.2 (≈990 Hz), −1.9, 3.3 (≈1000 Hz), and 10.2 (≈930 Hz) for $^{77}Se$ with four through zero geminal Te atoms. In the $^{125}Te$ NMR spectra $\delta_{Te}$ (with $^1J(^{125}Te-^{199}Hg)$ where observed) is −186 (≈2910 Hz), −197 (≈2920 Hz), −206, −209 (≈2860 Hz), and −218 (≈2800 Hz) for $^{125}Te$ with four through zero geminal Se atoms.

**(v) Correlation of Data.** The differing temperature dependences of the NMR spectra of the various complexes $[(\mu\text{-}TePh)_6(HgPR'_3)_4]^{2+}$ show that the rate of intramolecular rearrangement, and therefore the rate of inversion at Te, varies with R′ in the order alkyl > 4-$C_6H_4Me$ > Ph > 4-$C_6H_4Cl$. This is the order of basicities of the phosphines, at least in the solution phase.[25] Presumably, it is also the inverse of the order of effective electronegativities of the $HgPR'_3$ moieties in the clusters. Therefore, our results are consistent with earlier work on pyramidal inversion,[26] in which it was found that the barrier to an inversion becomes lower as the electronegativity of the atoms attached to the inversion center become lower. In the series $[(\mu\text{-}EPh)_6(HgPPh_3)_4]^{2+}$ (E = S, Se, Te), only the tellurium complex undergoes inversion at a rate that is slow enough for NMR detection at some temperatures. Again, this is in agreement with a large body of evidence[26] showing that relative rates of inversion are Te < Se < S. It may be that by using a less electron-rich phosphine inversion can be brought into an NMR accessible range for the selenolate clusters also.

Comparison of NMR data for **4′** with those obtained previously[1] for $[(\mu\text{-}EPh)_6(HgPEt_3)_4]^{2+}$ (E = S, Se) shows that in the series $[(\mu\text{-}EPh)_6(HgPEt_3)_4]^{2+}$ (E = S, Se, Te) $\delta_P$, $\delta_{Hg}$ and $^1J(^{31}P-^{199}Hg)$ vary in the order S > Se > Te, while $^2J(^{199}Hg-^{199}Hg)$, $^3J(^{31}P-^{199}Hg)$, and $^4J(^{31}P-^{31}P)$ vary in the reverse order, Te > Se > S. The variation of $\delta_P$ and $\delta_{Hg}$ with chalcogen, i.e. association of most shielding with the heaviest donor atom, is analogous to the well-known "normal halogen dependence".[27] The positive[28] coupling $^1J(^{31}P-^{199}Hg)$ is thought[29] to be dominated by the Fermi contact term. We have suggested previously[1] that the reverse dependences of $^1J$ and the longer range couplings on chalcogen imply a dominant Fermi contact mechanism for the latter also. The current data further support this suggestion.

The values of $^1J(^{125}Te-^{199}Hg)$ we obtain for the tellurolate-bridged clusters cover the approximate range 1300–4300 Hz. (They are temperature dependent.) These values can be compared with 5080 Hz found[30] for tetrahedrally coordinated Hg in powdered HgTe[31] and 6500 and 6470 Hz reported[32] for linear[33] $HgTe_2^{2-}$ and presumably linear $HgTeSe^{2-}$, respectively.

One-bond $^{31}P-^{199}Hg$ couplings in $[(\mu\text{-}EPh)_6(HgPR'_3)_4]^{2+}$ (E = S, Se; R′ = alkyl, Ph, 4-$C_6H_4Me$, 4-$C_6H_4Cl$)[1,34] with time-averaged tetrahedral symmetry vary in the order alkyl > 4-$C_6H_4Me$ > Ph > 4-$C_6H_4Cl$ for a constant bridging chalcogen. For E = Te, the order is alkyl > 4-$C_6H_4Me$ > Ph;[35] it was not possible to obtain a value for $[(\mu\text{-}TePh)_6(HgP\{4\text{-}C_6H_4Cl\}_3)_4]^{2+}$ with time-averaged tetrahedral symmetry. The sequence found for the clusters is the reverse of the order observed[9,12] in mononuclear complexes of the type $Hg(PR'_3)_n^{2+}$. However, it is considered[9] that changes in the acceptor, $Hg(PR'_3)_{n-1}^{2+}$, caused by change of R′ dominate the couplings in the mononuclear species. In contrast, change of R′ should have only a minor effect on the distant acceptor site in the acceptor $[(\mu\text{-}EPh)_6(HgPR'_3)_3(Hg)]^{2+}$. Therefore, the couplings in the $Hg_4$ clusters are dominated by change in the donor, $PR'_3$, and in this case the observed variation is expected.[9]

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**Supplementary Material Available:** Figures showing the $^{31}P$ NMR spectrum of $[(\mu\text{-}TePh)_6(HgPBu_3)_4]^{2+}$ in $CH_2Cl_2$ at 214 K and the $^{125}Te$ NMR spectrum of $[(\mu\text{-}TeMe)_6(HgPPh_3)_4]^{2+}$ in $CH_2Cl_2$ at 190 K (2 pages). Ordering information is given on any current masthead page.

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(34) In $[\mu\text{-}SPh)_6(HgP\{4\text{-}C_6H_4Cl\}_3)_4]^{2+}$ in $CH_2Cl_2$ at 234 K, $\delta_P = 36.1$, $\delta_{Hg} = -886$, $^1J(^{31}P-^{199}Hg) = 3900 \pm 2$ Hz, $^2J(^{199}Hg-^{199}Hg) = 430 \pm 10$ Hz, $^3J(^{31}P-^{199}Hg) = 39 \pm 1$ Hz, and $^4J(^{31}P-^{31}P) = 13 \pm 1$ Hz. For the Se analogue under the same conditions, $\delta_P = 29.5$, $\delta_{Hg} = -716$, $\delta_{Se} = 1.2$, $^1J(^{31}P-^{199}Hg) = 2740 \pm 2$ Hz, $^1J(^{77}Se-^{199}Hg) = 935 \pm 10$ Hz, $^2J(^{31}P-^{77}Se) = 25 \pm 5$ Hz, $^2J(^{199}Hg-^{199}Hg) = 480 \pm 10$ Hz, $^3J(^{31}P-^{199}Hg) = 53 \pm 2$ Hz, and $^4J(^{31}P-^{31}P) = 17 \pm 1$ Hz.
(35) In $CH_2Cl_2$ at 234 K and with the concentrations given in Table III, $^1J = 2200 \pm 2$, $2230 \pm 2$, $1300 \pm 15$, and $1570 \pm 10$ Hz for R′ = Et, *n*-Bu, Ph, and 4-$C_6H_4Me$, respectively.