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Mercury-199 NMR Studies of Thiacrown and Related Macrocyclic Complexes: The Crystal Structures of $[Hg(18S6)](PF_6)_2$ and $[Hg(9N3)_2](ClO_4)_2$

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We wish to report the first measurements of ^{199}Hg NMR chemical shift data for a series of homoleptic Hg(II) complexes with thiacrown ligands and related aza and mixed thia/aza macrocycles. In mercury(II) complexes containing trithiacrown through hexathiacrown ligands, we observed ^{199}Hg NMR chemical shifts in the range of –298 to –1400 ppm. Upfield chemical shifts in these NMR spectra are seen whenever (a) the number of thioether sulfur donors in the complex is decreased, (b) a thioether sulfur donor is replaced by a secondary nitrogen donor, and (c) the size of the macrocycle ring increases without a change in the nature or number of the donor atoms. Changes in noncoordinating anions, such as hexafluorophosphate and perchlorate, have little effect on the ^{199}Hg chemical shift. For several complexes, we observed $^{3}J(^{199}\text{Hg}–^{1}\text{H})$ coupling in the range of 50–100 Hz, the first example of proton–mercury coupling through a C–S thioether bond. Also, we obtained unusual upfield ^{13}C NMR chemical shifts for methylene resonances in several of the thiacrown complexes which correspond to distortions within the five- and six-membered chelate rings bound to the mercury ion. We report the X-ray crystal structure of the complex $[Hg(18S6)](PF_6)_2$ (18S6 = 1,4,7,10,13,16-hexathiacyclooctadecane). The molecule crystallizes in the rare trigonal space group $P\bar{3}m1$ with hexakis(thioether) coordination around the Hg(II) center confirming previous X-ray photoemission spectroscopic data on the compound. The lack of an observable ^{199}Hg NMR signal for the complex is the result of the identical length (2.689(2) Å) of all six Hg–S bonds. We additionally report the X-ray structure of the complex $[Hg(9N3)_2](ClO_4)_2$ (9N3 = 1,4,7-triazacyclononane) which shows hexakis(amine) coordination of the 9N3 to form a distorted trigonal prismatic structure. Solution dissociation of the one of the 9N3 ligands from the mercury ion is confirmed by multinuclear NMR experiments. For six-coordinate macrocyclic Hg(II) complexes, N6 donor sets have a preference for trigonal prisms while S6 donor sets favor octahedral structures.

Introduction

The coordination chemistry of mercury(II) has received increased attention lately, in part, because of the concerns regarding its environmental and toxicological impacts. Although ^{113}Cd NMR studies have been performed on many of Cd(II) complexes, particularly with thiol and thiolate ligands,[1−4] reports of ^{199}Hg NMR measurements are much more limited.[5,6] Both nuclei have spins of 1/2, and ^{199}Hg NMR offers several advantages including a larger chemical shift range, stronger heteronuclear coupling, and faster relaxation times which enable more rapid data collection. Given these favorable attributes, there is considerable current interest in employing this nucleus as a metallobioprobe and expanding the available ^{199}Hg NMR data for its coordination compounds.[7] Even more limited are reports of ^{199}Hg NMR

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measurements on thioether complexes, especially for thiacrown complexes. This aspect of Hg coordination chemistry is somewhat surprising giving the general thiophilic nature of heavy metals such as mercury, the biological relevance of Hg−sulfur binding, and the potential for thioether-based ligands to be developed as heavy metal environmental remediators.[8] Indeed, a publication by Baumann and coworkers cites the use of a polystyrene-bound pentathiacrown ligand which completely removes mercury(II) from aqueous solution.[9]

Chart 1. Structures of Thioether Ligands Discussed in This Paper

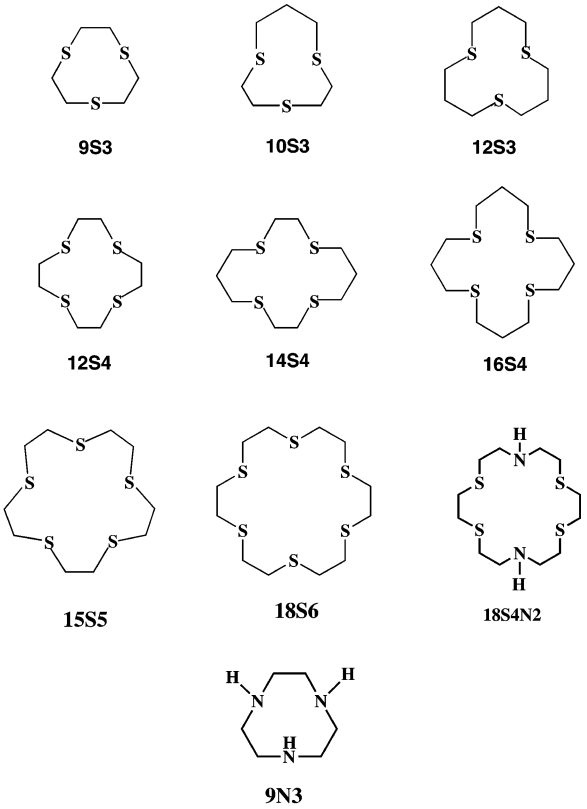
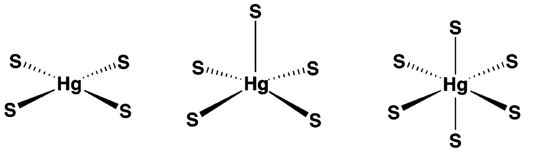


Chart 2. General Coordination Modes of Thiacrown Ligands with Hg(II)



S4 Coordination square planar
S5 Coordination square pyramidal
S6 Coordination octahedral

The goal of this report is to expand NMR studies using ^{199}Hg NMR to include homoleptic thiacrown complexes and related macrocyclic ligands. We believe that thiacrown complexes of Hg(II) are particularly well suited for the development of key empirical structure−spectroscopic correlations in ^{199}Hg NMR spectroscopy. Thiacrowns are less labile sulfur donor ligands than their acyclic analogues and, accordingly, may alleviate rapid exchange problems which are sometimes problematic for this nucleus. During the past fifteen years, several crystal structures of mercury(II) complexes involving thiacrown ligands have been obtained, and they constitute examples of well-defined mononuclear and binuclear complexes for empirical structure−spectroscopic relationships.[10−19] The thiacrowns and other related ligands discussed in this paper are illustrated in Chart 1. The polythioether macrocycles have the ability to force different coordination modes on the Hg(II) center, in contrast to the tetrahedral and linear geometries usually observed in the coordination chemistry of this ion.[20] These unusual mercury(II) geometries are presented in Chart 2 and include square planar (S$_4$), square pyramidal (S$_5$), and octahedral (S$_6$) structures. Our group is interested in examining how structural modifications within the thioethers affect their ability to bind toxic heavy metals and other transition metal ions, and we have now prepared a series of new Hg(II) metal complexes with several macrocyclic polythioethers.[14−16] Furthermore, we are now engaged in the development of a set of structural−spectroscopic correlations employing ^{199}Hg and other heavy metal NMR spectral data for the characterization of thiacrown complexes, as they remain relatively unexplored in that capacity. Our hope is that such structure−spectroscopic correlations will prove useful in the further development of remediation and detection agents for mercury, cadmium, and lead environmental contamination, and we believe that accumulation of chemical shift data can be useful in the continued development of ^{199}Hg NMR spectroscopy as a probe for biological molecules. For example, a recent report of a mercury complex with a macrocyclic ligand shows the ligand to be an excellent and selective fluorescent chemosensor for Hg(II),[21] but its solution structure remains uncertain. We believe that ^{199}Hg NMR offers the promise for the determination of solution state structures on molecules such as these. In prior ^{199}Hg NMR studies, changes in the nature of the donor atoms, the coordination number, and complex geometry all influenced the chemical shift of the Hg nucleus,[5] and we will accordingly examine how these different structural factors in macrocyclic complexes affect their NMR spectra. The evaluation of solution

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structures by NMR complements solid-state measurements and can provide a direct probe of how the ligand is complexed to the metal in solution. To our knowledge, our work represents the first detailed study of thiacrown complexes using ^{199}Hg NMR spectroscopy.

Experimental Section

Materials and Measurements. Commercially available thiacrown, azacrown, and mixed aza thiacrown ligands and mercury reagent salts and solvents were used as received without additional purification. The ligand 12S3 (1,5,9-trithiacyclododecane) was prepared by the reported procedure.[22] The previously reported Hg(II) complexes $[Hg(9S3)_2](ClO_4)_2$ **(7a)** (9S3 = 1,4,7-trithiacyclononane**)**,[11] $[Hg(9S3)_2](PF_2)_2$ **(7b)**,[10] $[Hg(10S3)_2](ClO_4)_2$ **(8a)** (10S3 = 1,4,7-trithiacyclodecane**)**,[14] $[Hg(10S3)_2](PF_6)_2$ **(8b)**,[15] [Hg(15S5)**]**-**(**$PF_6)_2$ **(9)** (15S5 = 1,4,7,10,13-pentathiacyclopentadecane),[19] and $[Hg(18S_4N_2)](PF_6)_2$ **(10)**[23] ($18S_4N_2$ = 1,4,10,13-tetrathia-7,16-diazacyclooctadecane) were prepared as previously reported. ***Caution!!!*** *Although the perchlorate salts prepared in this report do not appear to be shock-sensitive, they should be handled with caution and only in very small quantities. Mercury is a toxic heavy metal and its compounds should be treated accordingly.*

Infrared spectra were obtained on a Nicolet Impact 4100 FT-IR spectrometer using dry preweighed KBr packets (500 mg) and an ATR accessory. Elemental analyses were performed by Atlantic Microlab Inc. of Atlanta, Georgia. ^{1}H, ^{13}C{^{1}H}, and ^{199}Hg{^{1}H} NMR spectra were obtained on a Varian Gemini 300 MHz spectrometer operating at 300.1, 75.46, and 53.73 MHz, respectively, using CD_3NO_2 for the deuterium lock. The CD_3NO_2 was used as the reference for the ^{1}H and ^{13}C{^{1}H} NMR spectra. The ^{199}Hg{^{1}H} NMR spectra were collected at 25 °C using a delay time of 1.0 s and referenced to a 0.10 M solution of $Hg(ClO_4)_2$ in D_2O at −2250 ppm.[5,6] The referencing for all of the ^{199}Hg{^{1}H} NMR spectra was verified using concentrated $Hg(NO_3)_2$ in D_2O which gave a chemical shift of −2400 ppm, matching its literature value.

Synthesis of Hg(II) Complexes. The new complexes were prepared either as perchlorate salts using the method of Rosen and Busch[24] or as hexafluorophosphate salts using the method of Schröder.[10]

Preparation of $[Hg(18S6)](PF_6)_2$ (1a). An X-ray photoemission spectrum of this compound has been reported, but no synthetic, crystallographic, or spectroscopic data were included.[25] A mixture of $HgSO_4$ (39.0 mg, 0.131 mmol) and 18S6 (53.0 mg, 0.147 mmol) (18S6 = 1,4,7,10,13,16-hexathiacyclooctadecane) in 12 mL of water/methanol (1:1 v/v) was refluxed for 1.45 h. The solution was initially yellow but became colorless during reflux. When the solution was cooled to room temperature, NH_4PF_6 (88.0 mg, 0.540 mmol) was added, and a white precipitate formed immediately. After the solution was cooled at 0 °C for 1 h, the colorless solid was filtered, washed with ether (3 × 10 mL), and air dried to yield 93.0 mg (84.0%) of $[Hg(18S6)](PF_6)_2$ as a white crystalline solid. Colorless crystals suitable for X-ray studies were grown from the solution by solvent diffusion of diethyl ether into a $MeNO_2$ solution. FT-IR (KBr, cm^{-1}): ν 2987, 2935, 1422, 1292, 1267, 1189, 1150, 1116, 1047, 1025, 935, 853 (s, PF_6^-), 667, 560(s, PF_6^-), 473. ^{1}H NMR (CD_3NO_2, 25 °C): δ 3.32 (s, with two ^{199}Hg satellites, $^3J(^{199}Hg-^1H) = 51.3$ Hz). ^{13}C{^{1}H} NMR (CD_3NO_2, 25 °C): δ 31.1 (s). No ^{199}Hg NMR signal could be detected for a 20 mM solution of the complex after 3 days of data collection.

Preparation of $[Hg(18S6)](ClO_4)_2$ (1b). A solution of 18S6 (41.2 mg, 0.114 mmol) in 8 mL of $MeNO_2$ was added to a solution of $Hg(ClO_4)_2 \cdot 3H_2O$ (52.0 mg, 0.115 mmol) in 2 mL of $MeNO_2$ and 4 drops of acetic anhydride. A colorless precipitate formed immediately. The precipitate was filtered, washed with ether (3 × 5 mL), and vacuum dried to yield 66.3 mg (76.5%) of $[Hg(18S6)](ClO_4)_2$ as a colorless microcrystalline solid. Anal. Calcd for $C_{12}H_{24}Cl_2O_8HgS_6$: C, 18.96; H, 3.18, S, 25.30. Found: C, 19.05; H, 3.32, S, 25.25**.** FT-IR (KBr, cm^{-1}): ν 2968, 2918, 1546, 1411, 1258, 1204, 1135, 1092−1067 (s, b, ClO_4^-), 924, 899, 859, 710, 619. ^{1}H NMR (d^6-DMSO, 25 °C): δ 3.32 (s, with two ^{199}Hg satellites, $^3J(^{199}Hg-^1H) = 49$ Hz). ^{13}C{^{1}H} NMR (d^6-DMSO, 25 °C): δ 29.2(s). No ^{199}Hg NMR signal could be detected for a 5 mM solution of the complex in d^6-DMSO after 3 days of data collection.

Preparation of $[Hg(9N3)_2](ClO_4)_2$ (2). The hexafluorophosphate salt of this complex cation has been previously synthesized, but no structural or spectroscopic data were reported.[26] A solution of 1,4,7-triazacyclononane, 9N3, (63.6 mg, 0.492 mmol) in 7 mL of CH_3OH was added to a solution of $Hg(ClO_4)_2 \cdot 3H_2O$ (102 mg, 0.225 mmol) in 10 mL of CH_3OH, and the mixture was stirred overnight. A white microcrystalline precipitate of $[Hg(9N3)_2](ClO_4)_2$ formed which was filtered, washed with anhydrous diethyl ether (3 × 10 mL), and vacuum dried. Addition of 75 mL of diethyl ether to the filtrate yielded a second crop of crystals. Both precipitates had identical FT-IR spectra so they were combined to yield 111 mg (69.4%) of $[Hg(9N3)_2](ClO_4)_2$ as a white solid. FT-IR (KBr, cm^{-1}): ν 3332 (NH), 3254 (NH), 2926, 2845, 1560, 1461, 1357, 1280, 1236, 1103 (s, ClO_4^-), 995, 887, 840, 801, 624, 555. Slow diffusion of diethyl ether into a concentrated $MeNO_2$ solution formed colorless prisms which were suitable for X-ray diffraction and NMR studies. ^{1}H NMR (CD_3NO_2, 25 °C): δ 4 non-first order broad poorly resolved multiplets centered at 3.24 (6H, methylene), 3.08 (6H, methylene), 2.91 (6H, methylene), 2.77 (6H, methylene), and a broad singlet at 2.99 (6H, N−H). ^{13}C{^{1}H} NMR (CD_3NO_2, 25 °C): δ 45.2 (s), 45.0 (s), 43.9 (s). ^{199}Hg{^{1}H}-NMR (CD_3NO_2, 25 °C): δ −948 (s, $\nu_{1/2} = 141$ Hz), −1313 ppm (s, $\nu_{1/2} = 167$ Hz) in a 1.0/1.1 ratio, respectively.

Complexation Studies of Hg/12S4 Complexes (3). A solution of 1,4,7,10-tetrathiacyclododecane (12S4) (81.0 mg, 0.337 mmol) in 12 mL of hot anhydrous $MeNO_2$ was added to a solution of $Hg(ClO_4)_2 \cdot 3H_2O$ (45.0 mg, 0.0992 mmol) in 2 mL of anhydrous $MeNO_2$ and 4 drops of acetic anhydride. When the mixture was cooled to room temperature, a white solid precipitated which was confirmed by NMR measurements to be unreacted 12S4 ligand. The excess ligand was removed by filtration, and the solution was concentrated to half volume using a rotary evaporator. A volume of anhydrous diethyl ether (75 mL) was then added to the solution, and a white precipitate formed immediately. The precipitate was removed by filtration, washed with anhydrous diethyl ether (3 × 10 mL), and vacuum dried to yield 48.0 mg of a white solid. FT-IR (KBr, cm^{-1}): ν 2987, 293, 1547, 1430, 1366, 1305, 1275, 1189, 1094 (s, ClO_4^-), 896, 857, 680, 620. ^{1}H NMR (CD_3NO_2, 25 °C): δ 3.41 (s). ^{13}C{^{1}H} NMR (CD_3NO_2, 25 °C): δ 30.8(s). Anal. Calcd for $C_{16}H_{32}Cl_2O_8HgS_8$: C, 21.83, H, 3.66, S, 29.13. Found: C, 19.05; H, 3.32; S, 25.25. Calcd for the $[Hg(12S4)](ClO_4)_2/[Hg(12S4)_2](ClO_4)_2$ mixture (1:1): C, 19.0; H, 3.2; S, 25.3. A satisfactory

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analysis consistent with the exclusive formation of either a mono- or bis-12S4 complex was not obtained. However, our analyses are consistent with the presence of both complexes in a near 50/50 mixture.[27]

The hexafluorophosphate salt was also prepared. $HgSO_4$ (60.4 mg, 0.204 mmol) was refluxed for 16 h with 12S4 (108 mg, 0.449 mmol) in 150 mL of H_2O/MeOH (1:1 v/v). Because of the limited solubility of the 12S4 ligand, an additional 20 mL of CH_3CN was added to the reaction mixture, and the solution was filtered to remove excess 12S4. A mass of NH_4PF_6 (0.130 g, 0.798 mmol) was added to the solution which was concentrated on a rotary evaporator and cooled to 0° for 12 h. A white precipitate formed which was removed by filtration, washed with anhydrous diethyl ether (3 × 10 mL), and vacuum dried to give 28.4 mg (19.0% yield) of $[Hg(12S4)](PF_6)_2$ as a white microcrystalline solid. Anal. Calcd for $C_{16}H_{32}P_2F_{12}HgS_8$: C, 13.15, H, 2.21, S, 17.64. Found: C, 16.34; H, 3.06; S, 21.39. Calcd for the $[Hg(12S4)](PF_6)_2$/$[Hg(12S4)_2](PF_6)_2$ mixture (1:1): C, 16.5; H, 2.8; S, 21.8. Despite repeated recrystallizations, again we could not obtain a satisfactory analysis for either a mono- or a bis-12S4 complex as the hexafluorophosphate salt. FT-IR (KBr, cm^{-1}): ν 2945, 2917, 2890, 2814, 2594, 2426, 2359, 1421, 1290, 1211, 1138, 1034, 834 (s, PF_6^-), 559 (s, PF_6^-), 452. ^1H NMR (CD_3NO_2, 25 °C): δ 3.44 (s). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ 30.9(s). $^{199}Hg\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ −718 (s, $\nu_{1/2} = 159$ Hz).

Preparation of $[Hg(12S3)_2](ClO_4)_2$ (4). A solution of 1,5,9-trithiacyclododecane (12S3) (61.4 mg, 0.276 mmol) in 8 mL of anhydrous $MeNO_2$ was added to a solution of $Hg(ClO_4)_2$·$3H_2O$ (42.0 mg, 0.0926 mmol) in 2 mL of anhydrous $MeNO_2$ and 5 drops of acetic anhydride. The solution was concentrated to half volume using a rotary evaporator. A volume of anhydrous diethyl ether (75 mL) was then added to the solution, and a white precipitate formed immediately. The precipitate was removed by filtration, washed with anhydrous diethyl ether (3 × 10 mL), and vacuum dried to give 52.3 mg (66.9% yield) of $[Hg(12S3)_2](ClO_4)_2$ as a white solid. Anal. Calcd for $C_{16}H_{32}Cl_2O_8HgS_6$: C, 25.61; H, 3.68; S, 22.78; Cl, 8.40. Found: C, 25.53; H, 3.73; S, 22.39; Cl, 8.38. FT-IR (KBr, cm^{-1}): ν 2977, 2931, 1547, 1425, 1365, 1275, 1189, 1100−1050 (s, ClO_4^-), 894, 855, 679, 623. ^1H NMR (CD_3NO_2, 25 °C): δ 3.47 (12H, b s, α-methylene), 2.44 (6H, b s, β-methylene). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ 36.5 (6C, s, α-methylene), 27.4 (3C, s, β-methylene). $^{199}Hg\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ −795 (s, $\nu_{1/2} = 136$ Hz).

Preparation of $[Hg(16S4)](ClO_4)_2$ (5). The crystal structure of this compound has been previously reported, but no NMR data were given (16S4 = 1,5,9,13-tetrathiacyclohexadecane).[16] The complex was prepared by the published method. ^1H NMR (CD_3NO_2, 25 °C): δ 3.40 (16H, t, $^3J(^1H-^1H) = 6.00$ Hz, α-methylene with two ^{199}Hg satellites, $^3J(^{199}Hg-^1H) = 93.6$ Hz), 2.46 (8H, q, $^3J(^1H-^1H) = 6.15$ Hz, β-methylene). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ 36.3 (8C, s, α-methylene with two ^{199}Hg satellites, $^2J(^{199}Hg-^{13}C) = 24$ Hz), 24.7 (4C, s, β-methylene). $^{199}Hg\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ −1120 (s, $\nu_{1/2} = 322$ Hz).

Preparation of $[Hg(14S4)](ClO_4)_2$·H_2O (6). The structure of this complex has been previously reported, but we report here its synthesis by a higher yield route as well as its spectroscopic data.[17] A solution of 1,4,8,11-tetrathiacyclotetradecane (14S4) (38.3 mg, 0.143 mmol) in 8 mL of anhydrous $MeNO_2$ was added to a solution of $Hg(ClO_4)_2$·$3H_2O$ (41.2 mg, 0.0908 mmol) in 2 mL of anhydrous $MeNO_2$ and 4 drops of acetic anhydride. The solution was concentrated using a rotary evaporator. A volume of anhydrous diethyl ether (70 mL) was then added to the solution, and a white precipitate formed immediately. The precipitate was removed by filtration, washed with anhydrous diethyl ether (3 × 10 mL), and vacuum dried to give 53.0 mg (85.1% yield) of $[Hg(14S4)](ClO_4)_2$·H_2O as a white solid. Anal. Calcd for $C_{10}H_{22}Cl_2O_9HgS_4$: C, 17.51; H, 3.23; Cl, 10.34. Found: C, 17.46; H, 3.52; Cl, 10.36. FT-IR (KBr, cm^{-1}): ν 3614 (O−H), 2979 (C−H), 2931, 2426, 2245, 2017, 1629, 1430, 1292, 1258, 1090 (s, ClO_4^-), 900, 861, 831, 621 (C−S). ^1H NMR (CD_3NO_2, 25 °C): δ 3.49 (8H, s, $-CH_2CH_2-$), 3.35 (8H, t, $^3J(^1H-^1H) = 5.50$ Hz, $-CH_2CH_2CH_2$-), 2.38 (4H, q, $^3J(^1H-^1H) = 5.50$ Hz, $-CH_2CH_2CH_2-$). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ 36.7 (4C, s, $-CH_2CH_2-$), 34.5 (4C, s, $-CH_2CH_2CH_2-$), 28.7 (2C, s, $-CH_2CH_2CH_2-$). $^{199}Hg\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ −827 ($\nu_{1/2} = 436$ Hz).

NMR Characterization of $[Hg(9S3)_2](ClO_4)$ (7a), $[Hg(9S3)_2](PF_6)$ (7b), $[Hg(10S3)_2](ClO_4)$ (8a), $[Hg(10S3)_2](PF_6)$ (8b), $[Hg(15S5)](PF_6)_2$ (9), and $[Hg(18S_4N_2)](PF_6)_2$ (10). Saturated samples in CD_3NO_2 of the compounds were prepared for the NMR studies which were carried out at 25 °C. $^{199}Hg\{^1H\}$ NMR chemical shifts and corresponding line widths are below along with $^{13}C\{^1H\}$ NMR and ^1H NMR data not previously published.

7a. ^1H NMR (CD_3NO_2, 25 °C): δ 3.27 (m, ABCD pattern with ^{199}Hg satellites, $^3J(^{199}Hg-^1H) = 71$ Hz). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ 28.5 (s). $^{199}Hg\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ −275 (s, $\nu_{1/2} = 47$ Hz). Variable-temperature $^{13}C\{^1H\}$ NMR studies (CD_3NO_2): 45 °C, 28.5 ($\nu_{1/2} = 4$ Hz); 22 °C, 28.5 ($\nu_{1/2} = 3$ Hz); 0 °C, 28.5 ($\nu_{1/2} = 3$ Hz); −29 °C, 28.5 ($\nu_{1/2} = 4$ Hz) (see Supporting Information Figure 4a and b for spectra).

7b. ^1H NMR (CD_3NO_2, 25 °C): δ 3.26 (m, ABCD pattern). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ 28.4 (s). $^{199}Hg\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ −273 (s, $\nu_{1/2} = 28$ Hz).

8a. ^1H NMR (CD_3NO_2, 25 °C): δ 3.52 (8H, b m), 3.48 (8H, b m), 3.26 (8H, vb s), 2.35 (4H, vb s). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ 34.9 (4C, b s), 33.3 (4C, b s), 30.3 (4C, b s), 29.1 (2C, vb s). Variable-temperature $^{13}C\{^1H\}$ NMR studies in CD_3CN show the disappearance of these four resonances at −20 °C, suggesting a fluxional process (see Supporting Information Figure 7). $^{199}Hg\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ −598 (s, $\nu_{1/2} = 326$ Hz).

8b. ^1H NMR (CD_3NO_2, 25 °C): δ 3.52 (8H, b m), 3.48 (8H, b m), 3.25(8H, vb s), 2.34(4H, vb s). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ 34.9 (4C, b s), 33.2 (4C, b s), 30.2 (4C, b s), 29.1 (2C, b s). $^{199}Hg\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ −596 (s, $\nu_{1/2} = 161$ Hz).

9. ^1H NMR (CD_3NO_2, 25 °C): δ 3.8−3.0 (vb s). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ 33.1 (vb s, $\nu_{1/2} = 51$ Hz). $^{199}Hg\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ −484 (s, $\nu_{1/2} = 335$ Hz). Variable-temperature $^{13}C\{^1H\}$ NMR studies (CD_3NO_2): 45 °C, 33.1 ($\nu_{1/2} = 14$ Hz); 25 °C, 33.1 ($\nu_{1/2} = 17$ Hz); 0 °C, 33.1 ($\nu_{1/2} = 23$ Hz); −19 °C, 33.1 ($\nu_{1/2} = 30$ Hz); −29 °C, 32−34 (peak too broad to measure linewidth) (see Supporting Information Figure 9).

10. $^{199}Hg\{^1H\}$ NMR (CD_3NO_2, 25 °C): δ −737 (s, $\nu_{1/2} = 124$ Hz), −816 (s, $\nu_{1/2} = 211$ Hz). The ^1H and $^{13}C\{^1H\}$ NMR spectra of the complex have been previously reported.[23]

X-ray Data Collection, Structure, and Solution. Crystals of **1a** and **2**, suitable for X-ray diffraction, were grown by slow (multiday) solvent diffusion of diethyl ether into a concentrated $MeNO_2$ solution at ambient temperatures. A summary of key crystallographic details for both structures is presented in Table 1. Selected bond distances and angles in both structures are presented in Table 2. For the two structures, intensity data were collected on a Siemens SMART 1K CCD diffractometer,[28] and the structures were solved using direct methods.[29]

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(27) We would note that for the cadmium(II) analogue, we have obtained a crystal structure of the bis-12S4 complex in the solid state which rapidly loses one 12S4 ligand in solution. Helm, M. L.; Hill, L. L.; VanDerveer, D. G.; Grant, G. J. Manuscript in preparation, 2005.

Table 1. Crystallographic Data Summary for $[Hg(18S6)](PF_6)_2$ (**1a**) and $[Hg(9N3)_2](ClO_4)_2{\cdot}MeNO_2$ (**2**)

	1a	**2**
empirical formula	$C_{12}H_{24}F_{12}HgP_2S_6$	$C_{13}H_{27}Cl_2HgN_7O_{10}$
fw (amu)	851.20	712.91
cryst size (mm)	0.48 × 0.04 × 0.02	0.53 × 0.36 × 0.24
appearance	colorless, needles	colorless, needles
cryst syst	trigonal	monoclinic
space group	$P\bar{3}m1$	$P2_1/n$
a (Å)	11.4427(16)	9.5125(19)
b (Å)	11.4427(16)	9.840(2)
c (Å)	5.4851(11)	26.205(5)
α (deg)	90	90
β (deg)	90	94.79(3)
γ (deg)	120	90
V (Å^3)	621.97(18)	2444.3(8)
Z	1	4
ρ_{calcd} (g cm^{-3})	2.273	1.937
μ (mm^{-1})	6.911	6.576
T (K)	298(2)	173(2)
reflns collected	5418	17854
reflns unique	433	3930
R_{merge}	0.0397	0.0386
$R_1{}^a$	0.0398	00318
$R_2{}^b$	0.1102	0.0754

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ for observed data $I > 2\sigma(I)$. [b] $R_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ for all data.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Hg(18S6)](PF_6)_2$ (**1a**) and $[Hg(9N3)_2](ClO_4)_2{\cdot}MeNO2$ (**2**)[a]

	$[Hg(18S6)](PF_6)_2$ (**1a**)		
Hg(1)−S(1)	2.689(2)	Hg(1)−S(1)#2	2.689(2)
S−C	1.791(9)	C−C	1.480(17)
S(1)#1−Hg(1)−S(1)#2	180.0	S(1)#1-Hg(1)−S(1)#3	97.79(6)
S(1)#2-Hg(1)−S(1)#3	82.21(6)	C(2)#6-S(1)−C(2)	111.2(8)
C(2)#6-S(1)−Hg(1)	101.8(3)	C(2)#7-C(2)−S(1)	121.3(5)
	$[Hg(9N3)_2](ClO_4)_2{\cdot}MeNO2$ (**2**)		
Hg1−N16	2.412(5)	Hg1−N10	2.412(5)
Hg1−N4	2.448(6)	Hg1−N13	2.442(5)
Hg1−N7	2.353(4)	Hg1−N1	2.443(5)
N16−Hg1−N10	74.2(2)	N10−Hg1−N13	73.0(9)
N16−Hg1−N13	72.85(16)	N4−Hg1−N7	73.97(19)
N7−Hg1−N1	73.46(18)	N4−Hg1−N1	73.5(2)
N16−Hg1−N4	89.57(18)	N4−Hg1−N13	142.2(2)
N10−Hg1−N4	134.6(2)	N16−Hg1−N7	142.5(2)
N10−Hg1−N7	140.2(2)	N13−Hg1−N7	99.79(16)
N16−Hg1−N1	134.4(2)	N10−Hg1−N1	87.98(18)
N13−Hg1−N1	141.68(18)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-y, x - y, z$; #2 $y, -x + y, -z + 1$; #3 $-x + y, -x, z$; #4 $-x, -y, -z + 1$; #5 $x - y, x, -z + 1$; #6 $-x + y, y, z$; #7 $-x, -x + y, -z + 1$; #8 $-x + y + 1, -x + 1, z$; and #9 $-y+1, x - y, z$.

For **1a**, the *h*, *k*, and *l* ranges used during its structure solution and refinement were −12/13, −13/13, and −6/6. Of the 5418 measured reflections, 433 were unique. The merging R values on intensities were 0.0472. The structure was refined by a full-matrix least-squares method on F^2 using 433 unique reflections and 35 parameters. The residuals were as follows: for reflections with $I > 2\sigma(I)$, $R = 0.0397$, $R_w = 0.1101$, and GOF = 1.094 and for all reflections, $R = 0.0398$ and $R_w = 0.1102$. In the last D map, the deepest hole was −0.855 e/Å^3, and the highest peak was 1.085 e/Å^3.

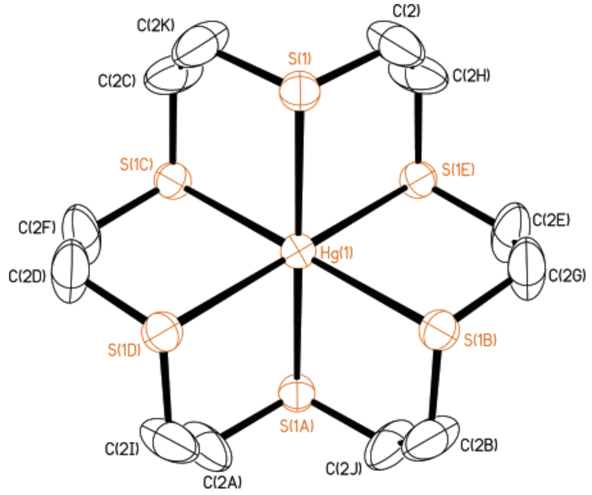

Figure 1. Thermal ellipsoid perspective (50% probability) of the cation in $[Hg(18S6)](PF_6)_2$. (**1a**).

For **2**, the *h,k,* and *l* ranges used during its structure solution and refinement were −11/10, −11/11, and −31/31. Of the 4340 measured reflections, 3930 were unique. The merging R values on intensities were 0.0295. The structure was refined by a full-matrix least-squares method on F^2 using 3930 unique reflections and 358 parameters. The residuals were as follows: for reflections with $I > 2\sigma(I)$, $R = 0.0318$, $R_w = 0.0754$, and GOF = 1.096 and for all reflections, $R = 0.0386$ and $R_w = 0.0730$. In the last D map, the deepest hole was −1.064 e/Å^3, and the highest peak was 1.775 e/Å^3.

Results and Discussion

Syntheses. Mercury(II) complexes were generally prepared under anhydrous conditions from mercury perchlorate or using the procedure of Rosen and Busch in order to minimize hydrolysis problems.[24] For two of the complexes, the perchlorate salt proved to be too insoluble for NMR study, and an alternative hexafluorophosphate salt was prepared from mercury(II) sulfate to increase solubility.[19] Hexafluorophosphate salts were also prepared for several complexes to compare the effects of the nature of the anion upon chemical shift. The FT-IR spectra of the complexes confirmed that both the macrocycle and the noncoordinating anion (either $ClO4^-$ or $PF6^-$) were present. Complexation of Hg(II) by the thiacrown ligand was typically confirmed by downfield shifts in both the ^1H and $^{13}C\{^1H\}$ NMR spectra of the complexes compared to the free ligands, except where noted below. Compounds **1a** and **2** were further characterized by single-crystal X-ray crystallography.

Structures. X-ray Structure of $[Hg(18S6)](PF_6)_2$. The structure crystallizes in a trigonal unit cell with the rare space group $P\bar{3}m1$, and a thermal ellipsoid perspective is shown in Figure 1.[30] Each unit cell is surprisingly compact and consists of a singular molecular unit with one $[Hg(18S6)]^{2+}$ cation and two $PF6^-$ anions with only C and H occupying general positions within the cell. No solvents are incorporated into the lattice. For homoleptic hexadentate 18S6 complexes,

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(28) The programs used for data collection, solution, and refinement of this structure were as follows: *SMART*, version 5.054; *SAINT*$^+$, version 6.01; *SHELXTL*, version 5.1; Bruker AXS: Madison, WI, 1998−1999.

(29) (a) Sheldrick, G.M. *SADABS*; Bruker AXS: Madison, WI. (b) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(30) To our knowledge, only 11 compounds in the current Cambridge Crystallographic Database have structures which exhibit this particular space group. *Cambridge Structural Database*, version 5.26; Cambridge Crystallographic Data Centre: Cambridge, U.K., 2004.

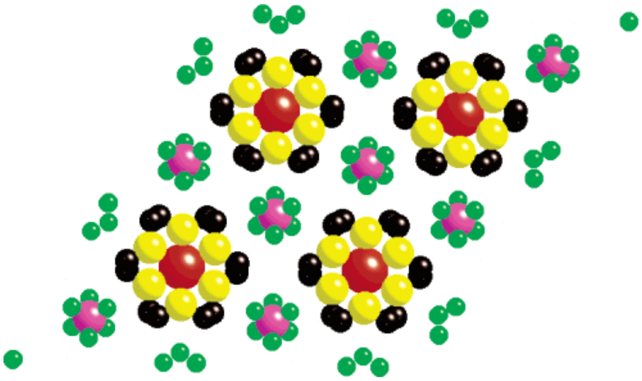
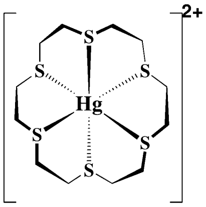
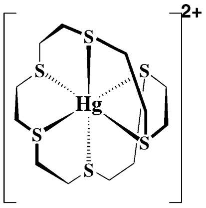


Figure 2. Space filling model of packing diagram for [Hg(18S6)]$(PF_6)_2$ (**1a**); 3329 atoms are shown. View is parallel to *c* axis of the crystal.

two diastereoisomers are possible as shown below, a meso isomer and a d−l racemic (rac) isomer. On the basis of the known preference of C−S bonds to adopt gauche conformations, the meso isomer is the preferred stereoisomer, and indeed, it is the structure that we obtained.[31] The cation has a molecular point group of *D3d* for this particular stereoisomer. The exclusive presence of this diastereoisomer is confirmed by a single resonance in the ^{13}C NMR spectrum of the complex.



Meso



Rac

All six Hg−S bonds are equal in length, and the observed bond distance is 2.689(2) Å. The distance is similar to Hg−S bond lengths seen in other hexakis(thioether) Hg(II) complexes, $[Hg(9S3)_2]^{2+}$ (Hg−S = 2.68−2.69 Å) and $[Hg(10S3)_2]^{2+}$ (Hg−S = 2.69−2.71 Å).[11−15] One distinction, however, is the effect of the rigid 18S6 encapsulating the mercury ion. Whereas the mercury−sulfur distances are necessarily identical in the 18S6 structure, the six other hexakis(thioether) structures show definite distortions in their S6 coordination spheres via either an elongation, which is the more common, or compression of the Hg−S bonds.[11−15] The S−Hg−S chelate angle in the structure is 82.21(6)°, much smaller than an ideal octahedral value but one commonly observed in five-membered chelate rings in the 9S3 and 10S3 mercury(II) complexes.[11−15] There is little difference in the C−C or C−S bond lengths in the coordinated 18S6 ligand compared to the structure of the free 18S6.[31]

A packing diagram of the structure is shown in Figure 2 with the view oriented along the *c* axis of the crystal. The C_3 axes for both the complex cation and the hexafluorophosphate anion lie parallel to the *c* axis of the crystal. As can be seen, the packing is quite efficient, resulting in a single molecular unit per unit cell. There have been three previous reports of the structures of complexes of 18S6 and Hg(II),[32−34] and all of them have exclusively been heteroleptic complexes with bridging halides, resulting in dimeric and polymeric structures. Our report represents the first structural example of a mononuclear 18S6 complex with mercury and demonstrates that a homoleptic hexakis(thioether) environment around the ion can indeed be obtained with 18S6, provided a noncoordinating anion like hexafluorophosphate is present. The Hg−S bond distances in our homoleptic complex are shorter than those of the heteroleptic complexes which exhibit Hg−S distances ranging from 2.7165(5) to 2.8765(5) Å.[32−34] Importantly, our structural results also confirm the hexakis(thioether) environment in the compound as was previously assigned on the basis of X-ray photoemission spectroscopic measurements by Nelson and co-workers.[25]

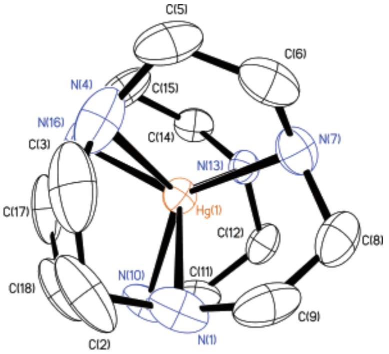


Figure 3. Thermal ellipsoid perspective (50% probability) of the cation in $[Hg(9N3)_2](ClO_4)_2$·MeNO2. (**2a**).

X-ray Structure of $[Hg(9N3)_2](ClO_4)_2$. The structure crystallizes in a monoclinic unit cell with the space group *$P2_1/n$*, and its thermal ellipsoid perspective is shown in Figure 3. Each unit cell contains four molecular units with one $[Hg(9N3)_2]^{2+}$ cation and two perchlorates all occupying general positions within the cell. One $MeNO_2$ molecule per complex is incorporated into the lattice. Two 9N3 ligands are coordinated in bis fashion (N6 environment) to the Hg(II) center in a distorted trigonal prismatic structure. The trigonal planes defined by the three nitrogen donors in each 9N3 ligand (N1−N4−N7 and N10−N13−N16) are nearly eclipsed. There are six different Hg−N bond lengths which range from 2.353(4) to 2.448(6) Å with an average Hg−N bond length of 2.418(5) Å. These structural results are similar to those of $[Hg(18N6)]^{2+}$ which is also a trigonal prismatic N6 complex and also shows six different Hg−N bond distances that average 2.44(2) Å.[35] The distances are slightly longer than those found in six-coordinate N6 complexes with nonmacrocyclic ligands such as pyridine and phen which range from 2.400(5) to 2.445(5) Å.[20] Also, they are longer than the Hg−N bonds found for small mixed donor four-coordinate macrocycles (e.g., 12N3S) where the Hg(II)

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(33) Herceg, M.; Matkovic-Calogovic, D. *Z. Kristallogr.* **1995**, *210*, 36.

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cannot be complexed within the macrocyclic ring (Hg−N average = 2.37 Å).[36,37] However, the Hg−N distances in the azacrown complexes are shorter than those found in larger mixed donor macrocycles. For example, the complex $[Hg(18S_4N_2)](PF_6)_2$ contains Hg−N distances that are 2.473(14) Å,[23] while the Hg−N distances in $[Hg(18N_2O_4)I_2]$ ($18N_2O_4$ = 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) are 2.724(10) Å.[38]

In the current structure, the N−Hg−N chelate angles are highly compressed from normal octahedral values, ranging from 72.1(15) to 76.7(13)°, and average 73.7(13)°. The C−N and C−C distances range from 1.453(11) to 1.486(10) Å and 1.501(13) to 1.520(9) Å, respectively. They average 1.469(8) and 1.510(9) Å, respectively, with both the C−N and C−C bonds being slightly shorter on average than those in the Cd(II) analogue.[40] The N−N distances between pairs of nitrogen donors in each trigonal face range from 3.372(5) to 3.669(5) Å with the N14−N16 distance being much greater compared to the other two distances. The angle of rotation of one triangular face relative to the other is 3°, slightly larger than 0° for an ideal trigonal prism. Both 9N3 ligands adopt the symmetrical [333] conformation.[41] The oxygen atoms in the perchlorate orient toward the rectangular faces of the trigonal prism, and the anions lie between the complex cations, similar to other Hg(II) trigonal prismatic structures.[39] The Hg(II) complex of 9N3 is in contrast with $[Cd(9N3)_2](ClO_4)_2$ which shows a distorted octahedral structure.[40] The metal ligand distances follow the expected trend of the ionic radii with the Hg−N distances longer than the Cd−N distances (average 2.361(1) Å). Furthermore, the 9N3 complex is in contrast with the four structures of $[Hg(9S3)_2]^{2+}$, each with a different anion, but all with a distorted octahedral environment around Hg(II) center.[10−13] Thus, the two different donors sets (N6 vs S6), in six-coordinate mercury(II) coordination chemistry for both cyclononane and cyclooctadecane macrocycles, result in two different geometries, trigonal prism and octahedron, respectively. Indeed, trigonal prismatic Hg(II) structures are limited to nitrogen donor ligands whereas hexakis(thioether) coordination shows exclusively octahedral geometries.[39,42]

NMR Spectroscopy. ^{199}Hg NMR Studies. The paucity of available ^{199}Hg NMR chemical shift data on small structurally characterized molecules containing thioether and amine donor ligands has been an impediment in the development of the technique as a metallobioprobe for protein active sites.[43,44] The ^{199}Hg NMR chemical shift data for the thirteen mercury(II) complexes containing thiacrown and azacrown ligands in this report are presented in Table 3, and a graphical overview is given in Figure 4. A representative ^{199}Hg NMR spectrum for the complex $[Hg(10S3)_2](ClO_4)_2$ is shown in Figure 5. We have obtained ^{199}Hg NMR data on these complexes exclusively in CD_3NO_2 at 25 °C to minimize solvent, solvolysis, and temperature effects. Furthermore, we have used only the perchlorate salt of these complexes to minimize anion effects except in those few instances where the perchlorate salt proved too insoluble and a hexafluorophosphate salt was used instead. However, as can be clearly seen for the 9S3 and 10S3 complexes, changing between these two anions produces only a minor 1 or 2 ppm change in the ^{199}Hg NMR chemical shift of the complex cation. Note that all four 9S3 and 10S3 Hg(II) complexes have been crystallographically characterized.[10,14,16] Furthermore, there are few differences in the line-widths of the mercury NMR signals for identical complex cations. Thus, changes in noncoordinating anions have little effect upon ^{199}Hg NMR chemical shifts.

Table 3. ^{199}Hg NMR Chemical Shifts for Homoleptic Hg(II) Complexes

ligand	complex	ligand environment	chemical shift (ppm)
9S3	$[Hg(9S3)_2](ClO_4)_2$	S6	−275
9S3	$[Hg(9S3)_2](PF_6)_2$	S6	−273
10S3	$[Hg(10S3)_2](ClO_4)_2$	S6	−598
10S3	$[Hg(10S3)_2](PF_6)_2$	S6	−596
12S3	$[Hg(12S3)_x](ClO_4)_2$	S6	−795
12S4	$[Hg(12S4)](PF_6)_2$	S4	−718
14S4	$[Hg(14S4)](ClO_4)_2$	S4	−827
16S4	$[Hg(16S4)](ClO_4)_2$	S4	−1120
15S5	$[Hg(15S5)](ClO_4)_2$	S5	−484
18S6	$[Hg(18S6)](PF_6)_2$	S6	not observed
18S6	$[Hg(18S6)](ClO_4)_2$	S6	not observed
$18S_4N_2$	$[Hg(18S_4N_2)](PF_6)_2$	S_4N_2	−737, −816
9N3	$[Hg(9N3)_2](ClO_4)_2$	N6	−948, −1313

Curiously, we have not been able to observe a ^{199}Hg NMR signal for the 18S6 complex. This observation is true for both the PF6$^-$ salt of $[Hg(18S6)]^{2+}$ in CD_3NO_2 as well as its ClO4$^-$ salt in d^6-DMSO. The lack of the observed NMR signal cannot be a sensitivity problem for the complex since we readily detect the characteristic ^{13}C NMR singlet of the complex within 100 transients. Nor can this be a problem with ligand exchange since the proton spectra clearly show $^3J(^{199}Hg-^1H)$ coupling, eliminating ligand exchange. We propose that the lack of a ^{199}Hg NMR signal is the result of

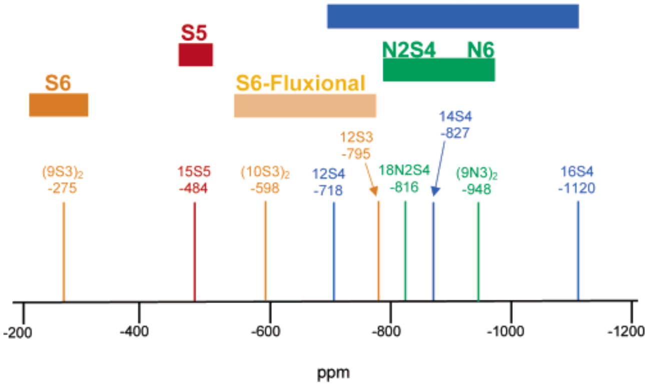

Figure 4. ^{199}Hg NMR chemical shifts for compounds in this report.

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(36) Marcus, S. T.; Bernhardt, P. V.; Grondahl, L.; Gahan, L. R. *Polyhedron* **1999**, *18*, 3451.

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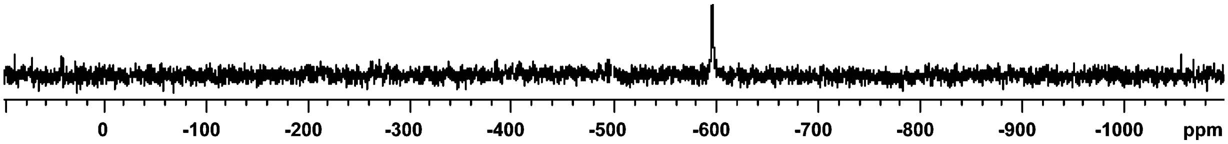

Figure 5. ^{199}Hg NMR spectrum of $[Hg(10S3)_2](ClO_4)_2$ in CD_3NO_2.

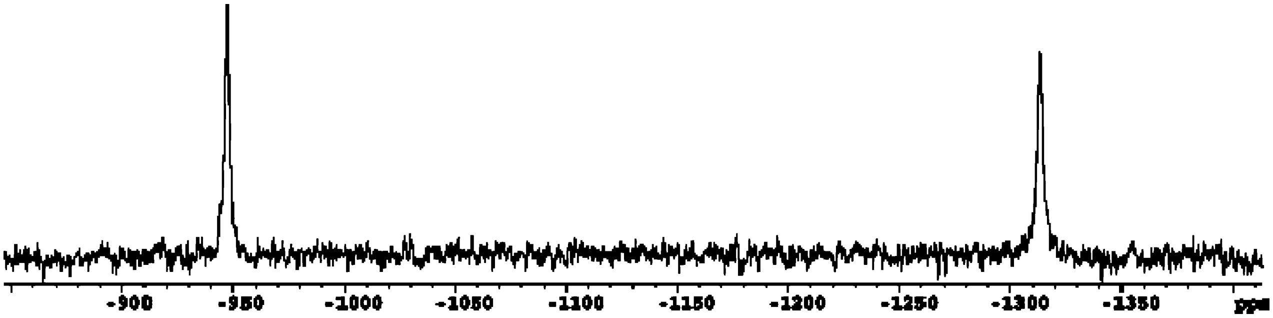

Figure 6. ^{199}Hg NMR spectrum of $[Hg(9N3)_2](ClO_4)_2$ in CD_3NO_2.

the unusual environment around the Hg nucleus. Given that all six Hg−S bond lengths are identical, there is an increase in the rate of relaxation of the nucleus, resulting in a broadened NMR signal. Experiments are currently underway with the Cd(II) analogue to see if a similar ^{113}Cd NMR behavior is obtained. The mercury(II) complex with the related hexadentate macrocycle, $[Hg(18S_4N_2)](PF_6)_2$, shows two distinct ^{199}Hg NMR resonances at −737 and −816 ppm (see Supporting Information Figure 1). The two peaks correspond to two different diastereoisomeric forms of the Hg complex which result from the relative orientations of the two NH protons.[23] Although the reported X-ray crystal structure only yielded a single diastereoisomer, the presence of both diastereoisomers in solution had been detected from ^{13}C NMR work. Our ^{199}Hg NMR data confirm both are indeed there, and the ratio of the two diastereoisomers in the spectrum is approximately 1:2 (−737 ppm peak/−816 ppm peak).

We observed ^{199}Hg NMR chemical shifts in the range of −273 ppm to −1120 ppm for the homoleptic thiacrown complexes. Several empirical trends can be seen in Table 3. First, there is a definite correlation between the chemical shift and the number of thioether sulfur donors. As the number of coordinated sulfurs increases, the ^{199}Hg NMR resonance shifts downfield. That is, as the coordination number increases, the Hg nucleus is increasingly shifted downfield, possibly because of an electron-withdrawing effect by the thiacrown ligand. These data are similar to the observations of the ^{199}Hg NMR chemical shifts in Hg(II) complexes with thiolate ligands.[45] Second, whenever an amine nitrogen donor replaces a thioether sulfur donor, there is an noticeable upfield shift. This is seen in a steady transition for the hexakis(thioether) environment (S6) through the S_4N_2 environment to the hexakis(amine) (N6) environment. Increased shielding of mercury nuclei has been previously reported whenever a nitrogen or oxygen donor replaces a sulfur donor.[5,6,44] Third, whenever the ring size of the thioether macrocycle increases with the number of sulfur donors remaining the same, there is a definite upfield chemical shift. The third trend is best seen in the 16S4 to 12S4 series of tetrathiacrown complexes. Also, the trend and magnitude of the chemical shifts we observed are similar to those reported in methylmercury complexes with the trithiacrowns 9S3 and 12S3.[13] Smaller chelate rings show downfield ^{199}Hg NMR chemical shifts in the thioether complexes. Four-coordinate thioether complexes show upfield ^{199}Hg NMR chemical shifts relative to four-coordinate thiolate mercury complexes.[45] Interestingly, the ^{199}Hg NMR line widths in tetrathioether complexes are significantly larger than in the tetrathiolate complexes which have typical line widths in the 4−75 Hz range (compared to the 150−430 Hz range for the thiacrown complexes).[46]

We observed two ^{199}Hg NMR resonances for $[Hg(9N3)_2]$-$(ClO_4)_2$ in CD_3NO_2, and its spectrum is shown in Figure 6. We propose that both a mono-9N3 and a bis-9N3 complex are present in solution, giving rise to the two signals. The downfield peak is assigned to the $[Hg(9N3)_2]^{2+}$ complex while the upfield peak is assigned to a mono-9N3 Hg(II) species, probably with water occupying a fourth coordination site on the mercury. Better σ-donor ligands which contain oxygen or nitrogen coordination sites result in increased shielding, and the upfield peak also has a larger line width which is consistent with a less symmetrical coordination sphere around the mercury.[5] The replacement of one 9N3 ligand with water, present in CD_3NO_2, is thus supported by the observed upfield chemical shifts. The ratio of the mono/bis species obtained via integration of the two ^{199}Hg NMR peaks is nearly 1:1. Additionally, ^{13}C NMR measurements on the complex show three peaks, again consistent with the presence of $[Hg(9N3)_2]^{2+}$, a second mono-9N3 Hg(II) complex, and the uncomplexed 9N3 ligand in solution. The complexity of the proton NMR spectrum prevents clear identification of the three species. We would note that the Cd(II) analogue, $[Cd(9N3)_2]^{2+}$, shows only a single resonance in both its ^{13}C and ^{113}Cd NMR spectra, suggesting that only one complex is presenting in solution.[27] Also, the predominate species in complexation studies of 9N3 with Cd(II) in

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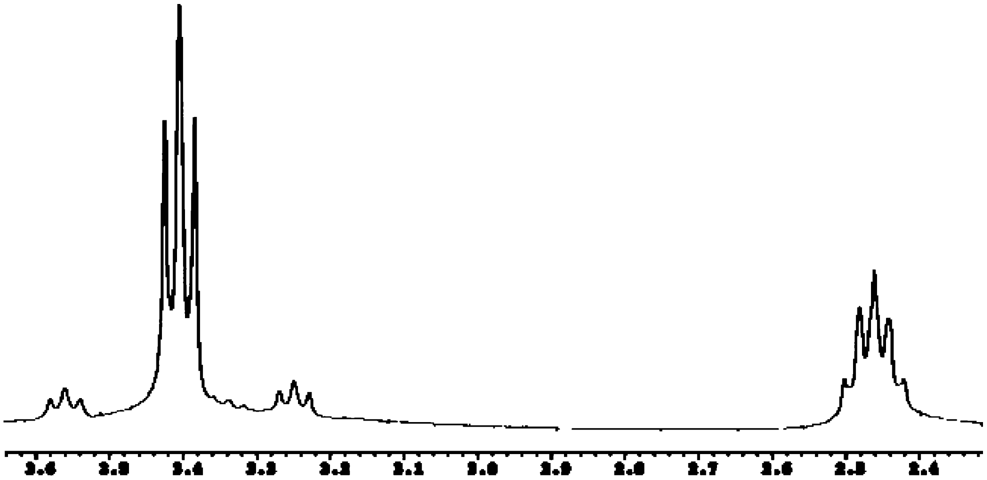

Figure 7. ^{1}H NMR spectrum of $[Hg(16S4)](ClO_4)_2$ in CD_3NO_2.

aqueous solution is a mono species ($[Cd(9N3)(H_2O)]^{2+}$) and not the bis complex.[47] The contrast of the solution behavior of the Cd(II) and Hg(II) complexes of 9N3 may result from the different structures (octahedral vs trigonal prism) or a heightened sensitivity toward solvolysis for Hg(II).

Proton NMR Studies. Proton NMR studies were generally used to verify thiacrown complexation to Hg(II) via downfield chemical shift changes relative to the free ligand and coupling in the spectra. However, the most distinctive feature in the proton NMR spectra of the complexes is the presence of ^3J coupling between the α-methylene protons of the coordinated thiacrown and the ^{199}Hg nucleus. We observe this coupling for three complexes, $[Hg(16S4)]^{2+}$, $[Hg(9S3)_2]^{2+}$, and $[Hg(18S6)]^{2+}$, and the representative ^{1}H NMR spectrum for the 16S4 complex is shown in Figure 7 (^{1}H NMR spectrum for the 9S3 complex is shown in Figure 10 in the Supporting Information). The presence of the two ^{199}Hg satellites can be clearly seen, and they are centered on the α-methylene proton signal. The $^3J(^{199}Hg-^1H)$ coupling is superimposed on the homonuclear coupling between the two sets of methylene protons. There are two aspects of the coupling that are noteworthy. First, the value is large (94 Hz), indeed among the largest reported for this type of coupling.[48] Values for $^3J(^{199}Hg-^1H)$ coupling constants in nitrogen donor systems typically fall in the 20−80 Hz range. Also, to our knowledge, this is the first case of observed $^3J(^{199}Hg-^1H)$ coupling occurring via a carbon−sulfur thioether bond.[5] Additionally, we observe a $^2J(^{199}Hg-^{13}C)$ coupling between the α-methylene carbon in the 16S4 and the mercury nucleus (see Supporting Information Figure 2). Curiously, this is one of the smallest couplings of this type observed.[45] The values of the $^3J(^{199}Hg-^1H)$ couplings in the three complexes range from 94 Hz in the 16S4 complex to 52 Hz in the 18S6 complex, a difference of almost a factor of 2. Interestingly, the Hg−S−C−H dihedral angles in the two structures also differ significantly (156(2)° vs 93.4(2)°). Changes in the coupling could possibly come from a Karplus-type relationship, but the large variations in Hg−S bond distances (16S4, Hg−S = 2.597(2) Å; 18S6, Hg−S = 2.689(2) Å) could also be a critical factor. Nevertheless, the presence of the mercury−proton coupling is an important indicator of slow ligand exchange in the three Hg(II) complexes.

^{13}C NMR Studies. Downfield ^{13}C NMR chemical shifts in the ligand are usually seen upon its coordination to Hg(II), and we have used these chemical shifts to confirm ligand complexation. However, several complexes contain unusual upfield ^{13}C NMR chemical shifts, most notably for the α-methylene carbons in $[Hg(9S3)_2](ClO_4)_2$. Here the single resonance of the coordinated 9S3 is shifted by 6.5 ppm upfield relative to the free ligand. Other researchers have noted this shift and explained it by "the electrophilic effect of the mercury ion" or "relativistic effects".[35] However, we believe that the upfield chemical shift arises from the distortions in the tetrahedral environment around the α-methylene carbon in the coordinated 9S3 ligand. The C−C−S angle in the structure averages 117(7)°, highly distorted from an ideal tetrahedral value.[11] Indeed, a plot of ^{13}C NMR chemical shift (ppm) vs the S−C−C angle (degrees) for the six structurally characterized Group 8 and Group 12 $[M(9S3)_2]^{2+}$ octahedral complexes shows a linear correlation of 0.951 (see Supporting Information Figure 3). This trend is most distinctly observed for the Group 12 complexes which have ^{13}C NMR chemical shifts of 30.49 ppm for Zn(II), 29.60 ppm for Cd(II), and 28.50 ppm for Hg(II) with a high linear correlation ($R^2 = 0.99$) between these data and the S−C−C angle in their structures. The distortion within the 9S3 chelate rings results from the smaller S−M−S angles in the heavier congeners. For example, the S−Hg−S chelate angle in $[Hg(9S3)_2]^{2+}$ is 82.7(1)°. Furthermore, we see similar upfield changes in the β-methylene resonances for both the 16S4 and 14S4 Hg(II) complexes, upfield shifts by 4.9 and 1.3 ppm compared to the free ligands, respectively. In contrast, the α-methylene resonances in both complexes are shifted downfield relative to free ligand with a 4.6 ppm downfield shift for the 16S4 complex. There is a significant degree of ring strain in the six-membered chelate rings in the two complexes. Again, the C−C−C angles in these

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structures are associated with a high degree of ring strain and distortion from idealized tetrahedral environments. For example, the C−C−C angle is 117(2)° in the structure of $[Hg(16S4)]^{2+}$.[16]

We have performed variable-temperature ^{13}C NMR experiments on several of the Hg(II) complexes to study the dynamics of ligand exchange on the mercury center. The $[Hg(9S3)_2]^{2+}$ complex shows no line broadening in its single resonance over a 75 °C temperature range (see Supporting Information Figure 4a and b). The lack of a temperature effect on the line width suggests there is no ligand exchange process occurring, in agreement with the presence of mercury−proton coupling in the complex (see above). We would note that there is a reaction between 9S3 and $[Hg(9S3)_2]^{2+}$ in the presence of excess 9S3 ligand. In the presence of 9S3 ligand, the resonances for both the ligand and $[Hg(9S3)_2]^{2+}$ completely vanish and cannot be seen even down to −29 °C (see Supporting Information Figure 4c).[49] In contrast, at 25 °C the 15S5 Hg(II) complex does show a ligand exchange process which has been previously noted because the presence of a single broad resonance is not consistent with its square pyramidal solid-state structure.[19] The resonance of $[Hg(15S5)]^{2+}$ shows significant line width effects with temperature, but we cannot observe slow exchange of the 15S5 ligand down to −29 °C, the freezing point of the solvent (see Supporting Information Figure 5a and b). Furthermore, variable-temperature experiments involving the complex and excess 15S5 ligand show that an intermolecular ligand exchange process is involved as we cannot observe distinct resonances for both the complex and the ligand (see Supporting Information Figure 5c and d). A similar exchange of the 12S3 ligand is also clearly seen in the broad peaks in ^{13}C NMR spectrum of its Hg(II) complex (see Supporting Information Figure 6). The $[Hg(10S3)_2]^{2+}$ complex also shows an exchange process as the four ^{13}C NMR resonances broaden with lowering temperature and then disappear around −20 °C (see Supporting Information Figure 7). The same complex with an excess of the 10S3 ligand shows just a simple four line ^{13}C NMR (see Supporting Information Figure 8). These data also support an intermolecular exchange between the 10S3 ligand and Hg(II), like we observe for the 15S5 complex, because we cannot observe separate ^{13}C NMR resonances for the ligand and complex. Thus, out of this series, only $[Hg(9S3)_2]^{2+}$ appears not to undergo a ligand exchange process.

Conclusions

For homoleptic thiacrown ligands, ^{199}Hg NMR chemical shifts occur in the range of −298 to −1400 ppm. The chemical shifts are sensitive to the number of sulfur donors, replacement of sulfur donors with nitrogen donors, and the ring size of the macrocycles. However, changes in noncoordinating anions do not appear to affect the chemical shift. For three complexes, we observe $^3J(^{199}Hg-^1H)$ coupling in the ranges of 50−100 Hz, the first example of proton−mercury coupling through a C−S thioether bond, indicative of slow ligand exchange. Upfield ^{13}C NMR chemical shifts in the complexes relative to free ligand appear to result from distortions around the carbon from the ideal tetrahedral values. The complex $[Hg(18S6)](PF_6)_2$ crystallizes in an unusual space group ($P\bar{3}m1$) with six equivalent Hg−S bond lengths. The equivalency of the coordination environment effects the relaxation of the ^{199}Hg nucleus, resulting in the lack of an observable NMR signal. The $[Hg(9N3)_2](ClO_4)_2$ complex forms a distorted trigonal prismatic structure, and solution dissociation of the one of the 9N3 ligands from the mercury ion in solution is detected in NMR experiments. For six-coordinate Hg(II) complexes, macrocyclic amines prefer trigonal prismatic structures, while thiacrowns exclusively show octahedral geometries.

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Supporting Information Available: Additional NMR spectra and crystallographic data for the two structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(49) Similarly, the 10S3 ligand also undergoes a reaction with $[Hg(10S3)_2]^{2+}$ as demonstrated in its ^{13}C NMR titration data (see Supporting Information Figure 8). We observed averaged NMR signals for the coordinated and free 10S3 ligand.