

different in presenting a relatively nonpolar and, in some cases, hydrocarbon interface to potential guests.

Discussion

There is some geometrical analogy between the structure of crystalline AgSAr compounds and the monolayers of thiols that can be formed on clean gold surfaces.^{13-15,21-23} In both cases, there is a two-dimensional lattice of coinage-metal atoms, with a layer of sulfur atoms and with substituents on the sulfur atoms arrayed orthogonally or at a steep angle to the layer. The substituents shield the metal. There are also significant chemical

differences between the two systems. One is the Ag-SR bond contrasted with the Au-HSR adsorption. A second is that the Au-HSR monolayer presents an accessible interface with other media, allowing the investigations of physical, optical, and electrochemical properties of the interface. The AgSR compounds are bulk crystals, but **5** adopts a platy habit, which presumably presents the AgSR layer at the surface. A third difference is that the packing density of substituents is determined by the Ag₂S lattice structure and not the cross section of the substituent as it is in the Au monolayers. Fourth, arenethiolate layers are known only for the Ag compounds.

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Contribution from the School of Chemistry,
University of New South Wales, P.O. Box 1, Kensington, NSW 2033, Australia

Mercury Polysulfide Complexes, $[\text{Hg}(\text{S}_x)(\text{S}_y)]^{2-}$: Syntheses, ^{199}Hg NMR Studies in Solution, and Crystal Structure of $(\text{Ph}_4\text{P})_4[\text{Hg}(\text{S}_4)_2]\text{Br}_2$

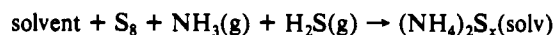
Trevor D. Bailey, R. M. Herath Banda, Donald C. Craig, Ian G. Dance,* Ida N. L. Ma, and Marcia L. Scudder

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Mercury polysulfide complexes $[\text{Hg}(\text{S}_x)(\text{S}_y)]^{2-}$ have been prepared in DMF solution by the reaction $\text{HgS} + \text{Na}_2\text{S} + \text{S}_8$. The nominal compositions $[\text{Hg}(\text{S}_m)_n]$ of these solutions can be varied widely, with the average polysulfide chain length m ranging from 3 to 8 and the nominal ligand to metal ratio n ranging from 2 to 4. ^{199}Hg NMR spectroscopy reveals the existence of at least three distinct $[\text{Hg}(\text{S}_x)(\text{S}_y)]^{2-}$ complexes that are in equilibrium and undergo chemical exchange which is slow on the NMR time scale at room temperature. The three principal species are $[\text{Hg}(\text{S}_4)_2]^{2-}$, $[\text{Hg}(\text{S}_4)(\text{S}_2)]^{2-}$, and $[\text{Hg}(\text{S}_2)_2]^{2-}$, and there is evidence for $[\text{Hg}(\text{S}_3)(\text{S}_6)]^{2-}$. Addition of Ph_4Br to the $[\text{Hg}(\text{S}_4)_2]^{2-}$ solution causes crystallization of the new complex $(\text{Ph}_4\text{P})_4[\text{Hg}(\text{S}_4)_2]\text{Br}_2$ (**1**), which contains well-separated tetrahedral $[\text{Hg}(\text{S}_4)_2]^{2-}$, Ph_4P^+ , and Br^- ions, with no secondary bonding. Crystal data for **1**: space group $I\bar{4}$, $a = 19.563(4)$ Å, $c = 11.531(2)$ Å, $V = 4413(1)$ Å³, $Z = 2$ ($[\text{Hg}(\text{S}_4)_2](\text{PPh}_4)_4\text{Br}_2$), 1661 independent observed reflections ($\text{Mo K}\alpha$, $1/\sigma(I) > 3$), $R = 0.024$.

Introduction

Homoleptic metallapolysulfane complexes $[\text{M}(\text{S}_x)_n]^{2-}$ containing polysulfide chains as chelating ligands have been known for a very long time.^{1,2} The chemistry of these compounds has been revived recently³⁻⁶ by the deployment of nonaqueous media, which increase the thermodynamic activities of polysulfide ions in solution and therefore expand the range of complexes that can exist in solution equilibria. The principal method for the formation of nonaqueous $(\text{S}_x)^{2-}$ has been the direct analogue of the aqueous method,⁷ namely



applied by Müller et al.⁸⁻¹¹ The use of gaseous reagents in this preparation has led to variability of composition of the $(\text{NH}_4)_2\text{S}_x$

solutions and can introduce difficulties in attaining reproducible metallapolysulfane stoichiometry.

We have used alternative methods for the controlled generation of active nonaqueous solutions of $(\text{S}_x)^{2-}$, for reaction with suitable transition- or post-transition-metal precursors. These methods include the use of salts such as $(\text{Bu}_4\text{N})_2\text{S}_6^{12}$ and $(\text{Ph}_4\text{P})_2\text{S}_6^{13}$ which are soluble in aprotic solvents of interest, and the in situ formation of Na_2S_x in DMF by the reactions of Na or Na_2S with S_8 . We also use sulfides of the post transition metals in reactions with the polysulfide solutions, in order to avoid the introduction of anions that could compete with the polysulfide ligands.

Although an astonishing variety of molecular structures has been revealed in the crystal structures of metal polysulfides, it is recognized that such structures need not be representative of the complexes existing in solution, and the crystal structures do not provide information about the species, reactions, and equilibria that occur in solution, information which could be used to support rational syntheses and applications. Therefore, we have used ^{199}Hg NMR spectroscopy to probe solutions of mercury polysulfides.

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Table I. Solutions of Nominal Composition $[\text{Hg}(\text{S}_m)_n]$ Prepared by $\text{HgS} + \text{Na}_2\text{S} + \text{S}_8$ in DMF

<i>m</i>	<i>n</i>	vol of DMF, ^a mL	color
8	4	10	intense red
7	2.5	5	intense red
5	4	5	brown red
5	3	6	red
5	2.5	5	brown red
4	2.5	5	intense green
4	2	5	intense green
3	4	5	green, white residue
3	2	5	green, yellow residue
1.5	1.5	5	green, yellow residue
8	2	5	red, buff residue

^a Volume required to dissolve 1 mmol of Hg.

In view of the wide chemical shift range for metals such as Hg,^{14,15} it would be expected that the frequency separations between different Hg sites would be large enough to ensure slow exchange NMR conditions at ambient temperatures, thereby allowing full observation of all species in solution. We use the nonintegral symbols *m* and *n* to differentiate the average solution composition $[\text{Hg}(\text{S}_m)_n]^{2-2n}$ from the compositions $[\text{Hg}(\text{S}_x)(\text{S}_y)]^{2-}$ of specific complexes. In this paper we present the NMR data and the preparation and crystal structure of $(\text{Ph}_4\text{P})_4[\text{Hg}(\text{S}_4)_2]\text{Br}_2$ (1). The compounds $(\text{Ph}_4\text{P})_2[\text{Hg}(\text{S}_4)_2]$ (2)^{16,17} and $(\text{Et}_4\text{N})_2[\text{Hg}(\text{S}_6)_2]$ (3)¹⁸ have been prepared and characterized crystallographically by Müller et al.

In parallel studies, we have applied these strategies to cadmium polysulfides¹⁹ and tin polysulfides,²⁰ using ¹¹³Cd and ¹¹⁹Sn NMR respectively. This is part of a systematic investigation of metal polychalcogenide species and equilibria, particularly for post transition metals.

Experimental Section

Materials. $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was partially dehydrated by heating it in a stream of N_2 at 90 °C for 6 h and finally at 120 °C to obtain a white solid. DMF was purified by drying with MgSO_4 , followed by vacuum distillation, and was stored over molecular sieves. HgS, precipitated from dilute aqueous nitric acid solution, was thoroughly washed and dried. $(\text{Bu}_4\text{N})_2\text{S}_6$ was prepared as described previously.¹⁹

All preparations were performed under nitrogen as inert gas. Solvents were deoxygenated before use.

$(\text{Ph}_4\text{P})_4[\text{Hg}(\text{S}_4)_2]\text{Br}_2$ (1). $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (0.26 g, 1 mmol) was partially dehydrated, and HgS (0.20 g, 1 mmol) and sulfur (0.19 g, 6 mmol S) were added, followed by DMF (5 mL). On ultrasonication, the solids quickly dissolved to yield a dark green solution. After removal of a small amount of white solid, a solution of Ph_4PBr (0.84 g, 2 mmol) in acetonitrile (6.5 mL) was added. Red crystals of the product began to grow within 4 h and were separated after 2 days, cleaned with filter paper, and vacuum-dried: yield 0.36 g; mp ca. 250 °C. This compound is hygroscopic and decomposes quickly to HgS in a moist atmosphere.

Preparation of Solutions. There is evidence that NO_3^- oxidizes polysulfides in aprotic DMF and CH_3CN solutions,^{19,21} and therefore $\text{Hg}(\text{NO}_3)_2$ has been avoided as the source of mercury. Solutions of nominal composition $[\text{Hg}(\text{S}_m)_n]$ were prepared from mixtures of HgS (*a* mol), Na_2S (*b* mol) and S_8 (*c*/8 mol) in appropriate proportions ($m = (a + b + c)/(a + b)$; $n = (a + b)/a$) in DMF, with heating as necessary to

Table II. Selected Crystallographic Details for $(\text{PPh}_4)_4[\text{Hg}(\text{S}_4)_2]\text{Br}_2$ (1)

	$[\text{Hg}(\text{S}_4)_2](\text{PPh}_4)_4\text{Br}_2$, 1972.5
formula, fw	tetragonal, $I\bar{4}$
space group	19.563 (4)
<i>a</i> , Å	11.531 (2)
<i>c</i> , Å	4413 (1)
<i>V</i> , Å ³	21
temp, °C	1.48
ρ_{obs} (by flotation in $\text{CCl}_4/\text{cyclohexane}$), g cm ⁻³	2
<i>Z</i>	1.48
ρ_{calc} , g cm ⁻³	0.71069 (Mo)
λ (radiation), Å	29.37
μ , cm ⁻¹	0.70, 0.60
max, min trans coeff	0.024
$R = \sum F_o / \sum F_o $	0.029
$R_w = [\sum w F_o ^2 / \sum w F_o ^2]^{1/2}$	1.04
$s = [\sum w F_o ^2 / (m - n)]^{1/2}$	

Table III. Parameters for Non-Hydrogen Atoms for $(\text{PPh}_4)_4[\text{Hg}(\text{S}_4)_2]\text{Br}_2$ (1)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Hg	1.0000	0.0000	0.5000
S1	0.9047 (1)	0.0229 (1)	0.3556 (2)
S2	0.9514 (1)	-0.0200 (1)	0.2135 (2)
Br	0.5000	0.0000	0.9689 (1)
P	0.2786 (1)	0.1609 (1)	0.4895 (1)
C11	0.1957 (2)	0.1984 (3)	0.4705 (4)
C21	0.1864 (3)	0.2680 (3)	0.4841 (7)
C31	0.1226 (3)	0.2960 (3)	0.4691 (7)
C41	0.0690 (3)	0.2563 (4)	0.4371 (7)
C51	0.0767 (3)	0.1867 (4)	0.4211 (6)
C61	0.1406 (3)	0.1574 (3)	0.4385 (5)
C12	0.2971 (3)	0.1063 (3)	0.3688 (5)
C22	0.2635 (4)	0.1141 (3)	0.2639 (6)
C32	0.2817 (5)	0.0746 (4)	0.1684 (6)
C42	0.3337 (4)	0.279 (3)	0.1789 (6)
C52	0.3681 (4)	0.0192 (4)	0.2832 (7)
C62	0.3493 (3)	0.0583 (3)	0.3785 (5)
C13	0.2833 (3)	0.1160 (3)	0.6249 (5)
C23	0.3464 (3)	0.0940 (3)	0.6656 (5)
C33	0.3504 (4)	0.0564 (3)	0.7688 (6)
C43	0.2911 (5)	0.0437 (4)	0.8301 (6)
C53	0.2278 (4)	0.0660 (3)	0.7909 (5)
C63	0.2239 (3)	0.1022 (3)	0.6891 (5)
C14	0.3403 (2)	0.2284 (2)	0.4931 (6)
C24	0.3549 (3)	0.2612 (3)	0.5971 (5)
C34	0.3981 (4)	0.3186 (4)	0.5972 (6)
C44	0.4245 (3)	0.3418 (3)	0.4971 (8)
C54	0.4093 (4)	0.3086 (4)	0.3939 (6)
C64	0.3679 (3)	0.2528 (3)	0.3903 (6)

complete the dissolution. In some cases, residues of negligible mass were removed before the NMR spectra were recorded. Compositions, colors, and concentrations of the solutions are recorded in Table I.

Reaction of $(\text{Bu}_4\text{N})_2\text{S}_6$ (0.5 mmol) with HgS (1 mmol) in DMF (5 mL) yielded after heating a solution with the intense green color characteristic of the S_3^- radical ion.^{22,23}

A mixture of HgS (1 mmol) and Na_2S (1 mmol) suspended in DMF (8 mL) reacted under ultrasonication at room temperature to yield a yellow powder in a pale green solution. When the mixture was heated, the color of the solution changed reversibly to intense green at 110 °C and blue at 135 °C. There was no evidence that HgS (1 mmol) reacted with S_8 (7 mmol S) in DMF solution under ultrasonication.

Crystal Structure Determination. Crystallographic examinations of single crystals of $[\text{Hg}(\text{S}_4)_2](\text{PPh}_4)_4\text{Br}_2$ (1) were made with a Nonius CAD4 diffractometer. Reflections with high 2θ values and moderate intensity were accurately centered to yield the unit cell dimensions. Intensity data were measured as follows: (i) aperture width (1.00 + 1.00 tan θ)°; (ii) maximum scan time 60 s; (iii) intensity standard measured after 2000 s; (iv) orientation control checked every 200 reflections. Absorption corrections were calculated by numerical integration over a 6 × 6 × 6 grid oriented approximately parallel to the crystal morphology.

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Details of the crystal lattice, the diffraction data, and the least-squares refinement are included in Table II.

The compound crystallized in the tetragonal crystal system. Systematic absences ($h + k + l$ odd) restricted the choice of space group to $I4$, $I\bar{4}$, or $I4/m$. From consideration of the cell contents and the likely molecular symmetry, $I\bar{4}$ was selected as the most probable space group, and this was subsequently confirmed by the successful structure solution and refinement. All non-hydrogen atoms were located by Fourier methods and included in the refinement with anisotropic temperature factors and anomalous scattering corrections for neutral atoms.²⁴ The enantiomorph selection was unambiguous. All phenyl hydrogen atoms were located on a difference map and included at idealized positions (C-H 0.95 Å). The final R factor was 0.024, and no extinction was apparent. On the final difference map, the strongest peak was $0.3 \text{ e} \text{ \AA}^{-3}$ at 0.1 Å from Hg. Coordinates for non-hydrogen atoms are listed in Table III. Full tabulations of atomic parameters and all distances and angles are included in the supplementary material.²⁵ Root-mean-square vibrational amplitudes average 0.26 Å, with only S2 showing any evidence of anisotropy with components 0.20, 0.31, and 0.50 Å.

¹⁹⁹Hg NMR Spectroscopy. The ¹⁹⁹Hg spectra were measured at 53.6 MHz with a Bruker CXP 300 spectrometer, fitted with a 10-mm multinuclear probe locked to acetone-*d*₆ in an insert. Solutions were deoxygenated by sparging with nitrogen. Temperatures in the sample tube were controlled to ± 1 °C and were calibrated by replacement with a sample tube containing a platinum thermometer. Spectra typically required 2000–5000 pulses (pulse width 30 μ s; ca. 40° pulse angle). Spin-lattice relaxation times for Hg in the Hg/(S_x)²⁻/DMF solutions were not measured as such but were estimated by assessing the effect of the length of the repetition delay on the resonance intensities under the relevant spectrometer conditions. At 300 K, the principal resonances were about 60% relaxed after 0.5 s and almost fully relaxed after 2 s. In general, the spectra were recorded with delays insufficient for full relaxation, and therefore the relative intensities reported are approximate, although all spectra where relative intensities are compared were run under the same conditions. Line widths at half-height range from 25 to 50 Hz. Hg(C₆H₅)₂ in 1.0 M CHCl₃ solution was used as a secondary chemical shift reference, set as -751 ppm (at 300 K), relative to the primary standard of neat Hg(CH₃)₂ = 0 ppm.^{14,26} Because the chemical shifts are strongly temperature dependent, the lines are identified by their chemical shift values at 300 K. The changes in chemical shift (ppm) with temperature for the three principal lines are as follows: “-180”, -156 (240 K), -180 (300 K), -198 (350 K); “-326”, -299 (240 K), -326 (300 K); “-456”, -425 (240 K), -456 (300 K). Resonance “-180” relaxed more slowly than resonance “-326”.

Results

The results in Table I show that our method for the preparation of mercury polysulfide complexes, namely HgS + Na₂S + S₈ in DMF solution, is versatile in terms of stoichiometry and extends from nominal composition [Hg²⁺ + 4(S₈)²⁻] to nominal composition {Hg²⁺ + 1.5(S_{1.5})²⁻}, at concentrations of ca. 0.2 M. Non-sulfide anions are not present, and the solutions contain no competing anionic ligands that could solubilize the Hg²⁺ by coordination. Limitations to the formation of soluble polysulfide complexes occur when n is small (≤ 2) and m is large (≥ 8) or small (≤ 3).

The composition of the solution from which (Ph₄P)₄[Hg(S₄)₂]Br₂ (**1**) crystallized was [Hg(S₄)₂]²⁻ + 2Ph₄P⁺ + 2Br⁻ + 2Na⁺, and therefore only half of the mercury polysulfide crystallized. Although the nominal polysulfide and metal stoichiometry of the solution from which (Ph₄P)₂[Hg(S₄)₂] (**2**) was crystallized^{16,18} is not known, Br⁻ was present. It is likely that the main reason for the difference between the crystallizations of **1** and **2** is the solvent, methanol in the case of **2** and DMF/acetonitrile for **1**.

It is evidently possible to extend this method to form a product in which the polysulfide is completely reduced as sulfide, namely Na₂[HgS₂], but this product is not as soluble in DMF as it is in water.²⁷ Nevertheless, we have crystallized Na₈Hg₁₂S₁₆·8H₂O from one such mixture.²⁸

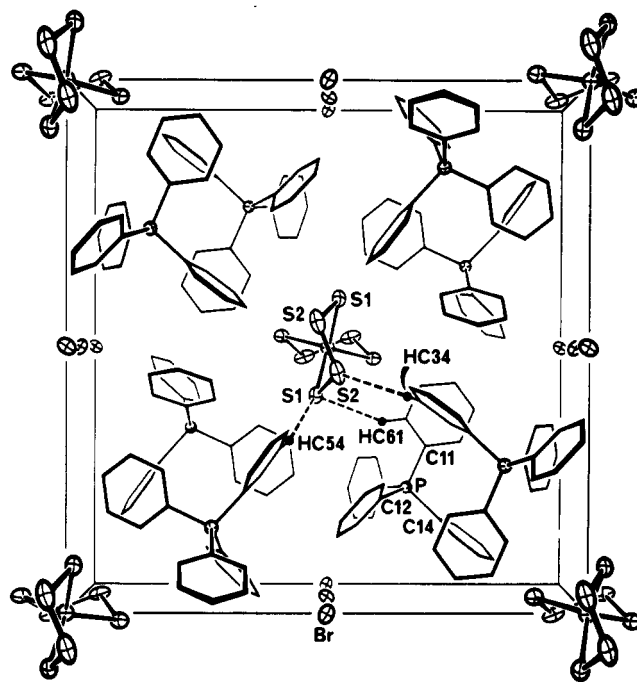


Figure 1. Body-centered tetragonal unit cell of (Ph₄P)₄[Hg(S₄)₂]Br₂ (**1**), drawn with perspective along the c axis. For clarity, not all of the cell contents are shown: four [Hg(S₄)₂]²⁻ ions and four (PPh₄)⁺ ions at the back of the cell in this view have been omitted. The single atoms are the Br⁻ ions. Hg, S, Br, and P ellipsoids are drawn at 15% probability. Phenyl hydrogen atoms have been omitted except for the three involved in short S...H nonbonded contacts. S...H nonbonded contacts (Å) related by symmetry to those drawn are also omitted: S1...HC61, 2.903; S1...HC54, 2.755; S2...HC34, 2.895.

Table IV. Dimensions of [Hg(S₄)₂]²⁻ in **1** in Comparison with Mean Values for [Hg(S₄)₂]²⁻ in **2** and [Hg(S₆)₂]²⁻ in **3**^a

	1	2	3
Hg-S1	2.540 (2)	2.55 [1] ^b	2.54 [5]
S1-S2	2.057 (3)	2.049 [6]	2.004 [9]
S2-S2 ⁱ	2.056 (6)	2.043 [3]	2.04 [3] ^c
S1-Hg-S1 ⁱ	98.1 (1)	96.3 [2]	115 [2]
S1-Hg-S1 ⁱⁱ	115.4 (6)	117 [7]	106 [5]
Hg-S1-S2	97.1 (1)	99.2 [0]	108 [4]
S1-S2-S2 ⁱ	104.8 (1)	105.8 [2]	109 [1] ^c
Chelate Ring Torsional Angles (deg)			
Hg-S1-S2-S2 ⁱ	-47.9 (1)	46 [3]	74 [18]
S1-S2-S2 ⁱ -S1 ⁱ	68.9 (2)	-65 [2]	-96 [7]
S2-S1-Hg-S1 ⁱ	17.2 (1)	-16 [4]	<i>d</i>

^aKey: (i) 2 - x , - y , z (i.e., same chelate ring); (ii) 1 + y , 1 - x , 1 - z . ^bValues in square brackets are standard deviations of the sample populations. ^cAveraged over all nonterminal S-S bonds. ^dComparison not valid due to very different ring conformation.

Crystal and Molecular Structure. The unit cell of **1** is composed of two [Hg(S₄)₂]²⁻ complexes with $\bar{4}$ crystallographic symmetry, eight (PPh₄)⁺ ions in general positions, and four Br⁻ ions on 2-fold axes. All ions are chemically unconnected; the closest Hg-Br distance is 9.8 Å, and no secondary bonding exists between these two components. Figure 1 shows the lattice packing. Each [Hg(S₄)₂]²⁻ is surrounded by twelve (PPh₄)⁺, which can be divided into two types: four “equatorial” and eight “axial” relative to the c axis. The four “equatorial” phosphorus atoms are at ± 0.121 Å from the (001) plane through Hg, while four “axial” phosphorus atoms are at ± 5.644 Å and the other set of four “axial” phosphorus atoms are at ± 5.887 Å. The shortest Br⁻Br⁻ separations are $c/2$, i.e. 5.7 Å. The crystal lattice is dominated by the cations: the van der Waals volume of each of the four the Ph₄P⁺ cations is greater than that of the [Hg(S₄)₂]²⁻ ion.

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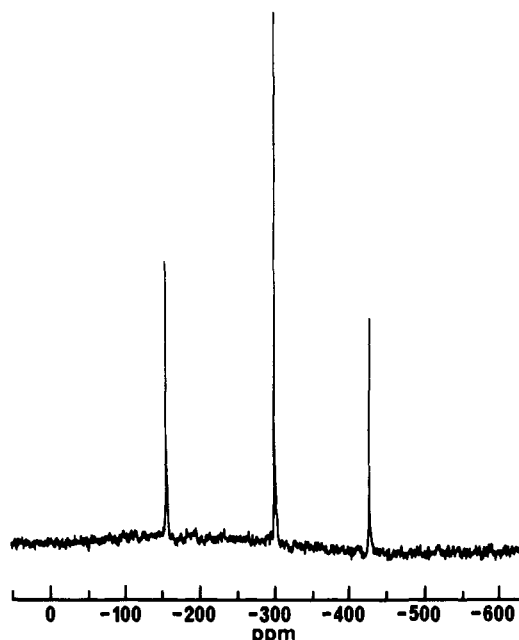


Figure 2. ^{199}Hg NMR spectrum of a solution (ca. 0.2 M Hg) of nominal composition $\text{Hg}^{2+} + 2.5(\text{S}_3)^{2-}$ in DMF, at 240 K. A total of 2000 pulses were used, and a line broadening of 20 Hz was applied. The resonances at -156, -299, and -425 ppm are those denoted in the text as “-180”, “-326”, and “-456”, respectively.

The comparison of geometrical parameters in the mercury polysulfide ions of 1-3 is presented in Table IV. The $[\text{Hg}(\text{S}_4)_2]^{2-}$ ions in 1 and 2 are very similar geometrically. There are however significant differences with $[\text{Hg}(\text{S}_6)_2]^{2-}$ in 3. The terminal S-S bond lengths in 3 are 0.04 Å shorter than those in 1 and 2, while in the larger chelate ring the intrachelate S-Hg-S angles are larger and the interchelate angles are smaller, as expected. Further, in the HgS_6 ring the torsional angles in the ring approach the unstrained ideal angle of ca. 90° .^{29,30}

The HgS_4 ring has the half-chair conformation in both 1 and 2, and the torsional angles are close to the averages for 11 other occurrences of the MS_4 ring. In 1, both enantiomorphs of the half-chair conformation occur around each Hg, with the result that the bischelate $\text{Hg}(\text{S}_4)_2$ complex has the *ob* conformation, whereas only one ring enantiomorph occurs in 2 where $\text{Hg}(\text{S}_4)_2$ is *lel*.

^{199}Hg NMR Results. A solution of 1 in DMF gives a single sharp resonance at -180 ppm (300 K). Other solutions prepared by the reaction $\text{Na}_2\text{S} + \text{S}_8 + \text{HgS}$ in DMF possess additional lines, the intensities of which are dependent on solution composition. In the following description, the various resonances are labeled by their chemical shift (ppm) at 300 K. The three principal lines, “-180”, “-326”, and “-456”, show substantial and different temperature dependences of chemical shift (see Experimental Section). A representative spectrum, at 240 K, is shown in Figure 2.

Line widths at half-height are 23, 57, and 46 Hz for “-180”, “-326”, and “-456”, respectively, at 300 K. At lower temperatures, the resonances are narrower, while at 350 K they show some broadening. Thus the rates of interchange of the species responsible for the principal resonances are less than 10^4 s^{-1} at ambient temperature and ca. 0.2 M concentration.

Exploration of the range of mercury polysulfide complexes formed in solution was undertaken with solutions prepared by the reaction $\text{Na}_2\text{S} + \text{S}_8 + \text{HgS}$ in DMF (Table I), devoid of heteroanions. The symbols *m* and *n* are used to define the nominal total composition of the solution, $[\text{Hg}(\text{S}_m)_n]$. Attempts to maximize the concentrations of the mercury polysulfide complexes resulted in some unidentified insoluble residue in some preparations: removal of this prior to recording the spectra introduced

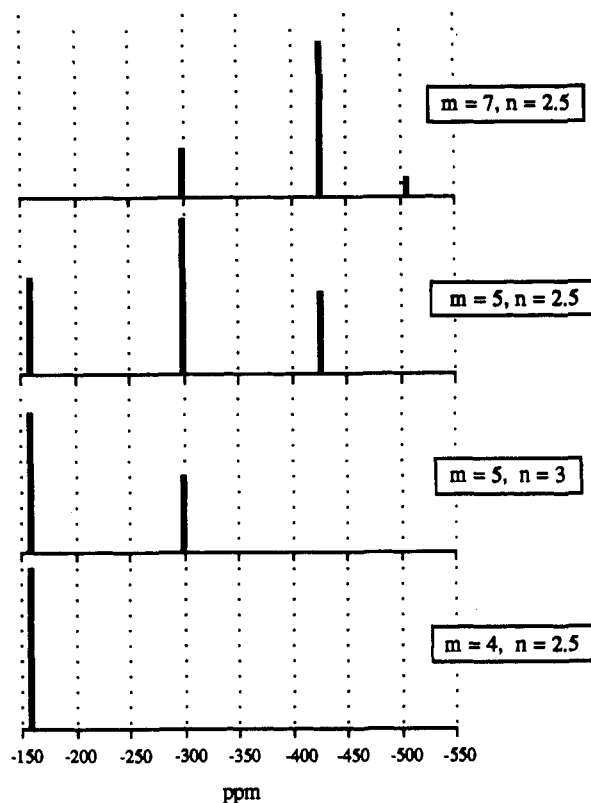
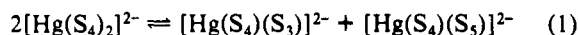


Figure 3. Diagram of $\delta(^{199}\text{Hg})$ and relative intensities of ^{199}Hg resonances for DMF solutions with nominal compositions $[\text{Hg}(\text{S}_m)_n]$, recorded at 240 K. The lines at -156, -299, and -425 ppm are those denoted in the text ($\delta(^{199}\text{Hg})$ at 300 K) as “-180”, “-326”, and “-456”, respectively.

a minor uncertainty into the nominal composition of these solutions.

The intensities but not the positions of the resonances depend on the solution composition. The variation with composition for $4 \leq m \leq 7$, $n = 2.5$ or 3, at 240 K, is plotted diagrammatically in Figure 3. Attempts to prepare solutions with smaller values of *m* and *n* resulted in substantial amounts of insoluble residue, which introduced uncertainty into the composition of the solution: ^{199}Hg NMR spectroscopy revealed either “-180” with low intensity or no signal. Solutions from mixtures with $n = 4$ and $m = 3$ or 5 showed weak “-180” resonances, while the solution with $n = 4$ and $m = 8$ possessed the lines “-326” and “-456”, which were broadened even at 300 K.

Clearly there exist in these solutions equilibria involving at least three species. Lines at more negative $\delta(\text{Hg})$ gain intensity mainly as *m* increases but also as *n* decreases. Since the solution of 1 and the independently prepared solutions with $m = 4$ and $n = 2$ both show only “-180”, the Br^- in 1 is not coordinated to Hg in DMF solution, and the “-180” resonance is assigned to the species $[\text{Hg}(\text{S}_4)_2]^{2-}$. Disproportionation of the polysulfide chain, as in eq 1, would require additional resonances in the spectrum



of 1, which are not detected. The lines “-326” and “-456” are assigned to complexes $[\text{Hg}(\text{S}_x)(\text{S}_y)]^{2-}$ in which *x* and/or *y* > 4. This assignment is supported by the more negative chemical shifts associated with larger chelate rings in the $[\text{Cd}(\text{S}(\text{CH}_2)_p\text{S})_2]^{2-}$ series^{19,31} and is fully consistent with our analysis of the ^{113}Cd NMR of $[\text{Cd}(\text{S}_x)(\text{S}_y)]^{2-}$ species.¹⁹ We have no reason to expect other than monotonic increase in metallapolysulfane chelate ring size, and therefore the proposed assignments are $[\text{Hg}(\text{S}_4)(\text{S}_3)]^{2-}$ for “-326” and $[\text{Hg}(\text{S}_5)_2]^{2-}$ for “-456”. Values of $\Delta\delta(^{199}\text{Hg})$ due to insertion of one S atom into the first and then into the second

(29) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1949**, *35*, 495.
 (30) Hordvik, A. *Acta Chem. Scand.* **1966**, *20*, 1885.

(31) Carson, G. K.; Dean, P. A. W.; Stillman, M. J. *Inorg. Chim. Acta* **1981**, *56*, 39.

chelate ring are comparable, -145 and -130 ppm, respectively.

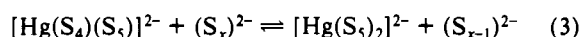
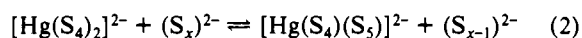
This interpretation does not include $[\text{Hg}(\text{S}_6)_2]^{2-}$, known in the crystalline state, but we note that metal polysulfide species in crystals do not necessarily represent species in solution, because the crystal lattices are often cation dominated. Further, there is no necessary direct correspondence between the nominal compositional variables m and n of the solutions of Figure 3 and the compositional variables x and y of the $[\text{Hg}(\text{S}_x)(\text{S}_y)]^{2-}$ species extant, particularly where there is excess polysulfide present. The data of Figure 3 indicate that when n is closer to 2, x and y are closer to m . The resonance at -503 ppm in the solution with $m = 7$, $n = 2.5$ could be due to $[\text{Hg}(\text{S}_5)(\text{S}_6)]^{2-}$. If so, $\Delta\delta(^{199}\text{Hg})$ for progression from $[\text{Hg}(\text{S}_5)_2]^{2-}$ to $[\text{Hg}(\text{S}_5)(\text{S}_6)]^{2-}$ would be less than that for insertion of a S atom into the smaller metallapolsulfane rings, but there is precedent for this in the comparable $[\text{Cd}\{\text{S}(\text{S})_p\text{S}_q\}_2]^{2-}$ and $[\text{Cd}\{\text{S}(\text{CH}_2)_q\text{S}_2\}_2]^{2-}$ species.¹⁹

The intensely green solution produced by heating 0.5 mmol $(\text{Bu}_4\text{N})_2\text{S}_6$ and 1 mmol HgS in DMF yielded a spectrum at 240 K containing mainly "-180", about 15% "-326", and a very weak line at -321 ppm (at 240 K), not seen in other solutions.

Discussion

The preparation of mercury polysulfide complexes from HgS is straightforward in DMF and yields a range of solutions of different polysulfide compositions, uncomplicated by the presence of competing anions. ^{199}Hg NMR has revealed at least three different mercury polysulfide species in equilibrium that are interchanging on a time scale which is probably seconds or less at ambient temperature but which is nevertheless in the NMR slow-exchange regime. This result for chelating polysulfide ligands on mercury contrasts notably with the NMR fast exchange of monodentate thiolate ligands on mercury.^{32,33} The usual difficulties in using Hg NMR to monitor solution equilibria do not occur in the polysulfide system.

Despite the fact that only the complexes $[\text{Hg}(\text{S}_4)_2]^{2-}$ and $[\text{Hg}(\text{S}_6)_2]^{2-}$ have been characterized in crystals, we believe that, at least in our solutions, $[\text{Hg}(\text{S}_4)_2]^{2-}$, $[\text{Hg}(\text{S}_4)(\text{S}_5)]^{2-}$, and $[\text{Hg}(\text{S}_5)_2]^{2-}$ with tetrahedral Hg coordination are the most probable species. A substantial proportion of long-chain polysulfide in solution is required to generate the larger mercurapolsulfane rings, as in eqs 2 and 3.



(32) Carson, G. K.; Dean, P. A. W. *Inorg. Chim. Acta* **1982**, *66*, 157. The reported value is $\delta(^{199}\text{Hg}) = 2193$ ppm relative to 0.1 M aqueous $\text{Hg}(\text{ClO}_4)_2$, which we have converted to the $\text{Hg}(\text{CH}_3)_2$ reference by subtraction of 2255 ppm.¹⁴

(33) Dance, I. G.; Garbutt, R. G.; Bailey, T. D. *Inorg. Chem.*, in press.

The crystallization of $[\text{Hg}(\text{S}_4)_2]^{2-}$ in two different lattices with Ph_4P^+ , one containing unbound Br^- , and the absence of NMR evidence for coordination by excess Br^- in aprotic solvents indicate that the complex is unperturbed and apparently unperturbable. The occurrence in crystals of $[\text{Hg}(\text{S}_6)_2]^{2-}$ but not yet $[\text{Hg}(\text{S}_5)_2]^{2-}$ (or complexes with disordered chain lengths such as those occurring with cadmium and tin polysulfides^{19,20}) does not change our belief that $[\text{Hg}(\text{S}_5)_2]^{2-}$ has geometrically favorable ring dimensions and exists in solution. It has been observed⁴ that MS_x rings with x even occur more frequently in crystals when M has a closed-shell electronic configuration, and x odd occurs more frequently when M has an open-shell electron configuration. In view of our results with mercury and other post transition metals, we regard this supposed correlation as an artifact of crystallization. Attempts to crystallize the $[\text{Hg}(\text{S}_5)_2]^{2-}$ ion are in progress.

There are evident differences between the comparable cadmium and mercury polysulfide complexes $[\text{M}(\text{S}_x)_2]^{2-}$ in solution: when $\text{M} = \text{Cd}$, $x = 5, 6$, and 7, but for $\text{M} = \text{Hg}$, $x = 4, 5$, and possibly 6. The crystalline complex $[\text{Cd}(\text{S}_6)_2]^{2-}$ disproportionates its ring size to $[\text{Cd}(\text{S}_5)(\text{S}_6)]^{2-}$ and $[\text{Cd}(\text{S}_6)(\text{S}_7)]^{2-}$ on dissolution in DMF,¹⁹ while $[\text{Hg}(\text{S}_4)_2]^{2-}$, which is at the end of the series of different ring sizes, does not.

The ^{199}Hg chemical shifts of the $[\text{Hg}(\text{S}_x)_2]^{2-}$ complexes are entirely consistent with literature data, the best comparison being with the ethanedithiolate complex $[\text{Hg}(\text{SCH}_2\text{CH}_2\text{S})_2]^{2-}$ for which $\delta(^{199}\text{Hg}) = -62$ ppm³² is close (on the full mercury chemical shift range of 4000 ppm^{14,15}) to our value of -180 ppm for $[\text{Hg}(\text{S}_4)_2]^{2-}$. Similar comparisons between the metal chemical shifts of $[\text{M}(\text{S}_x)_2]^{2-}$ and $[\text{M}\{\text{S}(\text{CH}_2)_{x-2}\text{S}_2\}_2]^{2-}$ complexes of the same chelate ring size have been made for Cd,¹⁹ where $\delta(^{113}\text{Cd})$ for the polysulfide complex is 50 ppm more positive than that of the α,ω -alkanedithiolate complex. We are not aware of $\delta(^{199}\text{Hg})$ data for other α,ω -alkanedithiolate complexes comparable in chelate ring size with the postulated $[\text{Hg}(\text{S}_4)(\text{S}_5)]^{2-}$ and $[\text{Hg}(\text{S}_5)_2]^{2-}$ complexes. Neither are we aware of $\delta(^{199}\text{Hg})$ data for HgS or $[\text{HgS}_2]^{2-}$, but note that our $[\text{Hg}(\text{S}_x)_2]^{2-}$ values are consistent with extrapolation from $[\text{HgTe}_2]^{2-} = -2169$ and $[\text{HgSe}_2]^{2-} = -796$ ppm.³⁴

Acknowledgment. This research is supported by the Australian Research Council. R.M.H.B. thanks the Australian Development Assistance Bureau for financial support.

Supplementary Material Available: Table S1, listing full crystallographic details, Tables S2 and S3, listing positional and thermal parameters for all atoms, and Tables S4 and S5, listing interatomic distances and angles (4 pages); Table S6, containing observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

(34) Burns, R. C.; Devereux, L. A.; Granger, P.; Schrobilgen, G. J. *Inorg. Chem.* **1985**, *24*, 2615.