Inorg. Chem. **2005**, *44*, 5753–5760

Inorganic Chemistry

Article

Structure-Directing Influence of Halide in Mercury Thiolate Clusters

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Received April 18, 2005

Under identical conditions, the reaction of 2-aminoethanethiol hydrochloride with HgX_2 (X = Cl and Br) in water yielded discrete hexanuclear $[Hg_6Cl_8(SCH_2CH_2NH_3)_8)]Cl_4\cdot 4H_2O$ (**1**) and nonanuclear $[Hg_9Br_{15}(SCH_2CH_2NH_3)_9](Cl_{0.8}Br_{0.2})_3$ (**2**) complexes with unusual coordination environments. Compound **1** crystallizes as triclinic with $a = 9.434(2)$ Å, $b = 10.999(2)$ Å, $c = 13.675(7)$ Å, $\alpha = 92.9(7)°$, $\beta = 105.2(7)°$, and $\gamma = 96.9(7)°$, whereas **2** is monoclinic with $a = 14.162(3)$ Å, $b = 8.009(16)$ Å, $c = 19.604(4)$ Å, $\alpha = \gamma = 90.0°$, and $\beta = 92.7(3)°$. In both cases, it is observed that the halide creates the secondary structure around trinuclear units (dimer in **1** and trimer in **2**) through Hg–X bonding. Two independent types of Hg atoms (four- and five-coordinate in **1**) and (three- and four-coordinate in **2**) are observed. The geometry around Hg is quite variable with bridging thiolate and both bridging and terminal halides. The angles around Hg associated with the S atoms are more obtuse than expected from mercury(II) thiolates with a coordination number of more than 2. Intermolecular hydrogen bonding involving NH_3^+, water molecules, and the halide atoms is responsible for the three-dimensional network in both compounds. Relatively short Hg···Hg interactions in **1** (3.797 and 3.776 Å) and in **2** (3.605 and 3.750 Å) are also observed. The compounds have been characterized with the help of ^1H and ^{13}C NMR, UV–Vis, infrared, Raman, and mass spectrometry, thermogravimetric analysis, and single X-ray crystallography.

Introduction

Metal thiolate chemistry is important because it provides information on the means by which metals may be bound to cysteine in living systems. Mercury thiolates have received much attention because of their involvement in the detoxification of mercury by metallothionein,[1] in a DNA binding protein,[2] and in mercury reductase and related proteins.[3] The coordination chemistry around Hg in these compounds is defined by the arrangement of the sulfur-containing groups. In contrast, simple thiols combine with HgX_2 (X = halide) to form complicated clusters or polymeric structures containing Hg–S and, in some cases, Hg–X interactions.[4] Homoleptic thiolates of mercury(II) can be mononuclear ($Hg(SR)_2$, $Hg(SR)_3$, $Hg(SR)_4$), dinuclear ($Hg_2(SR)_3$, $Hg_2(SR)_6$), trinuclear ($Hg_3(SR)_4$), tetranuclear ($Hg_4(SR)_6$), pentanuclear ($Hg_5(SR)_8$), or polynuclear ($[Hg(SR)_n]_\infty$) (and with variable charge depending on the R group).[1,4–11] In contrast, mercury(II) compounds containing both monodentate thiolate and halide are polymeric and either one-dimensional ($[Hg(SR)Cl_2]_\infty$ and $[Hg(S{-}steroid)Br]_\infty$) or two-dimensional ($[Hg(SMe)X]_\infty$ (X = Cl or Br) and $[Hg(SPr^i)Cl]_\infty$).[12–14] Molecular compounds with both thiolate and halide are rare but can be tetranuclear $\{(Ph_4P)[(\mu\text{-SEt})_5(\mu\text{-Br})(HgBr)_4]$, $(Bu^n_4N)_2[Hg_4(SR)_6X_4)$ (R = SEt, SPr^i)$\}$ and heptanuclear $[Hg_7(SC_6H_{11})_{12}X_2]$, where X = Cl, Br, or I.[8,15]

We here report novel hexa- and nonanuclear mercury thiolate clusters that differ only in the type of halide that is present. In each case, the halide appears to direct the secondary structure of the compounds. The triply bridged chloride in **1** appears to be responsible for bringing linear $[Hg(SR)_2]$ units together to form a trimeric unit. The bridging

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10.1021/ic0506005 CCC: $30.25

Table 1. Crystal Data for **1** and **2**

data	**1**	**2**
empirical formula	$C_4H_{16}C1_3Hg_{1.5}N_2OS_2$	$C_6H_{21}Br_{5.2}Cl_{0.8}Hg_3N_3S_3$
fw	579.54	1276.99
temp (K)	90.0(2)	173(1)
wavelength (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P21/n$
unit cell dimens (Å and deg)	$a = 9.4344(2)$	$a = 14.162(3)$
	$b = 10.9999(2)$	$b = 8.0090(16)$
	$c = 13.6756(2)$	$c = 19.604(4)$
	$\alpha = 92.9341(7)$	$\alpha = 90.000$
	$\beta = 105.2317(7)$	$\beta = 92.79(3)$
	$\gamma = 96.9811(7)$	$\gamma = 90.00$
V (Å^3)	1354.08(4)	2220.9(8)
Z	4	4
density calcd (mg/m^3)	2.843	3.819
abs coeff (mm^{-1})	17.879	30.412
F(000)	1060	2246
cryst size	0.14 × 0.14 × 0.08 mm	0.06 × 0.06 × 0.06 mm
reflns collected	25429	13479
independent reflns	6216 (R(int) = 0.0573)	3911 (R(int) = 0.0799)
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
GOF on F^2	1.054	0.950
final R indices [$I > 2\sigma(I)$]	R1 = 0.0285	R1 = 0.0357
	wR2 = 0.0557	wR2 = 0.0562
R indices (all data)	R1 = 0.0407	R1 = 0.0587
	wR2 = 0.0594	wR2 = 0.0619
extension coeff	0.00137(6)	0.00052(2)
largest diff peak and hole (e Å^{-3})	2.598 and −1.291	1.493 and −1.336

Table 2. Vibrational Frequencies Observed for **1** and **2** and Corresponding Hg−S and Hg−X (X = Cl, Br) Frequencies for Several Mercury(II) Thiolates[a]

compound	geometry	ν(Hg−S)	ν(Hg−X)	ref
1	distorted tetrahedral (Hg1 and Hg3) and square pyramidal (Hg3)	272 (s), 340 (as)	234 (t), 251 (br)	this work
2	distorted tetrahedral	288 (s), 339 (as)	174 (t), 196 (br)	this work
3	essentially linear	361 (as)		24, 57
$[HgCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$	distorted tetrahedral	270 (s), 308 (as)	232 (t), 233 (t)	25
$[HgBr_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$	distorted tetrahedral	263 (s), 308 (as)	155 (t)	25
$[HgCl_2(SCHN(CH_3)_2)_2]$	pseudotetrahedral	167 (s), 321 (as)	225 (t), 243 (t)	26
$[HgBr_2(SCHN(CH_3)_2)_2]$	pseudotetrahedral	177 (s), 319 (as)	153 (t), 167 (t)	26

[a] t = terminal, br = bridging, s = symmetric stretching, and as = asymmetric stretching.

bromide in **2** seems to play a more important role than bridging sulfur to form the observed cluster. These are the first structurally characterized examples of hexa- and nona-nuclear mercury thiolates containing both terminal and bridging halides.

Experimental Section

General Procedure. All reactions were carried out at room temperature in deionized (DI) water under nitrogen. The reagents 2-aminoethanethiol hydrochloride (TCI America), $HgCl_2$ (Aldrich), and $HgBr_2$ (Mellinckrodt Inc.) were used as received. ^1H and ^{13}C NMR data were obtained with JEOL GSX-400 and -270 instruments operating at 199.17 and 399.78 MHz using DMSO-d_6 as a solvent and tetramethylsilane as the reference. The IR data were recorded as KBr pellets on a Mattson Galaxy 5200 FT-IR instrument between 400 and 4000 cm^{-1}. Mass spectral data were obtained at the University of Kentucky Mass Spectrometry Facility. Raman spectra of the solid samples were obtained on a Nicolet FT-Raman 906 spectrometer ESP between 100 and 800 cm^{-1} in the Center for Applied Energy Research at the University of Kentucky. The UV−Vis studies were done on an Agilent HP 8453 instrument by using a 0.05 mM solution of **1** and **2** in DI water. The thermogravimetric analyses were done on a DSC 2950 thermal analyzer with a TGA 2950 furnace operating at 10 °C/min in an open atmosphere.

X-ray Crystallography. Crystals for **1** and **2** were obtained in good yield at 4 °C. X-ray diffraction data were collected at 90 and 173 K on a Nonius Kappa CCD diffractometer unit using Mo Kα radiation from colorless regular-shaped crystals mounted in Paratone-N oil on glass fibers. Initial cell parameters were obtained using DENZO[16] from 1° frames and were refined via a least-squares scheme using all data collection frames (SCALEPACK).[16] The structures were solved by direct methods (SHELXL97)[17] and completed by difference Fourier methods (SHELXL97).[17] Refinement was performed against F^2 by weighted full-matrix least squares, and empirical absorption correction (SADABS[17]) was applied. Hydrogen atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the *International Tables for Crystallography*, Vol. C.[18] Crystal data and selected bond distances and angles are provided in Tables 1 and 3−5, respectively.

Synthesis of $[Hg_6Cl_8(SCH_2CH_2NH_3)_8)]Cl_4 \cdot 4H_2O$ (1). To a stirring solution of 2-aminoethanethiol hydrochloride (2.28 g, 20

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Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**

Hg1−S1	2.410(14)	Hg2−S2	2.397(13)
Hg1−S3	2.394(14)	Hg2−S4	2.339(14)
Hg1−Cl1	2.732(15)	Hg2−Cl2	3.106(14)
Hg1−Cl3	2.895(13)	Hg2−Cl3	2.983(13)
Hg3−S1	2.501(14)	Hg3−S3″	2.631(15)
Hg3−S2	2.518(14)	Hg3″−S3	2.631(15)
Hg3−Cl3	2.894(13)	Hg3−Cl4	2.831(15)
Hg1···Hg2	4.927(4)	Hg1···Hg3	3.797(4)
Hg2···Hg3	3.776(4)		

Hg3−Hg1−Hg3	48.97	Hg1−Hg3−Hg2	79.87
Hg1−Hg2−Hg3	51.16	Hg1−S1−Hg3	101.24(5)
Hg2−S2−Hg3	100.34(5)	Hg1−Cl3−Hg2	159.97(5)
Hg1−Cl3−Hg3	81.94(3)	Hg2−Cl3−Hg3	79.91(3)
S1−Hg1−S3	158.06(5)	S2−Hg2−S4	171.87
S1−Hg1−Cl1	105.34(5)	S2−Hg2−Cl2	94.96
S1−Hg1−Cl3	89.26(4)	S2−Hg2−Cl3	89.15(4)
S3−Hg1−Cl1	95.03(5)	S4−Hg2−Cl2	89.06
S3−Hg1−Cl3	98.37(4)	S4−Hg2−Cl3	98.37(4)
S1−Hg3−S2	162.64(5)	S1−Hg3−S1″	100.70(4)
S2−Hg3−S3″	96.54(4)	S1−Hg3−Cl3	87.55(4)
S1−Hg3−Cl4	85.72(4)	S2−Hg3−Cl3	88.87(4)
S2−Hg3−Cl4	93.96(4)	S3″−Hg3−Cl3	95.23(4)
S3″−Hg3−Cl4	97.95(4)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for **2**

Hg1−S1	2.375(2)	Hg2−S2	2.487(2)
Hg1−S2	2.424(2)	Hg2−S3	2.482(2)
Hg1−Br2	2.935(12)	Hg2−S1B	2.811(2)
Hg1−Br2A	3.073(11)	Hg2A−S1	2.811(2)
Hg1A−Br2	3.073(11)	Hg2−Br1	2.7903(13)
Hg3−S3	2.482(2)	Hg3−Br3	2.555(11)
Hg3−Br4	2.688(11)	Hg3−Br5	2.784(13)
Hg1···Hg2	3.605(9)	Hg2···Hg3	3.750(11)

Hg1−S2−Hg2	94.43(8)	Hg1−S1−Hg2A	99.91(8)
Hg1−Br2−Hg1B	131.17(4)	Hg2−S3−Hg3	97.96(9)
S1−Hg1−S2	172.06(8)	S2−Hg2−S3	153.74(8)
S1−Hg1−Br2	105.01(5)	S2−Hg2−S1B	110.00(7)
S1−Hg1−Br2A	94.55(6)	S3−Hg2−S1B	92.94(7)
S2−Hg1−Br2	82.15(6)	S2−Hg2−Br1	98.54(6)
S2−Hg1−Br2A	85.82(6)	S3−Hg2−Br1	90.41(6)
S3−Hg3−Br3	141.34(6)	S3−Hg3−Br4	108.18(6)
S3−Hg3−Br5	99.69(7)	Br3−Hg3−Br4	99.25(4)
Br3−Hg3−Br5	98.40(4)	Br3−Hg3−Br5	105.75(4)

Table 5. Hydrogen Bond Geometry in **1** and **2**

D−H····A	D−H (Å)	H···A (Å)	D···A (Å)	DHA (deg)
		Compound **1**		
N1−H1C····Cl4	0.91	2.42	3.254	153.1
N1−H1D····Cl5	0.91	2.49	3.256	141.4
N1−H1E····Cl6	0.91	2.29	3.177	165.8
N1−H1D····O2	0.91	2.49	3.028	118.3
N2−H2C····Cl1	0.91	2.30	3.195	165.9
N2−H2E····Cl2	0.91	2.29	3.192	174.6
N2−H2D····O2	0.91	1.89	2.270	163.1
N3−H3C····Cl6	0.91	2.26	3.146	164.3
N3−H3D····Cl2	0.91	2.24	3.144	169.6
N3−H3E····Cl1	0.91	2.51	3.215	134.8
N3−H3E····S3	0.91	2.63	3.074	110.6
N4−H4C····Cl4	0.91	2.47	3.192	136.0
N4−H4D····Cl5	0.91	2.23	3.136	173.8
N4−H4E····O4	0.91	1.87	2.776	172.8
		Compound **2**		
N1−H1A····Br″#3	0.91	2.48	3.209	137.3
N1−H1B····Br1#4	0.91	2.43	3.317	166.6
N2−H2A····Br″	0.91	2.33	3.139	148.0
N2−H2B····Br″#5	0.91	2.57	3.288	135.7
N3−H3A····Br4#8	0.91	2.44	3.263	150.8
N3−H3B····Br″#3	0.91	2.27	3.131	157.5
N3−H3C····Br5#9	0.91	2.76	3.404	128.8

mmol) in DI water (40 mL) was added mercury(II) chloride (3.60 g, 10 mmol), and the resulting solution was stirred for 3 days. The solution was then allowed to stand for 2 weeks in the refrigerator at 4 °C, during which time colorless crystals formed. Crystalline yield: 3.46 g (60%); Mp: 204−206 °C. ^{1}H NMR (DMSO, 200 MHz, ppm): δ 3.00 (t, 2H, CH_2N), 3.14 (t, 2H, CH_2S), 7.91 (s, 3H, NH_3). ^{13}C NMR (DMSO, 200 MHz, ppm): δ 25.9 (CH_2S), 43.0 (CH_2N). IR (KBr, ν/cm^{-1}): 3448, 3058, 2991, 2906, 1604, 1566, 1477, 1404, 1365, 1313, 1263, 932, 881, 786, 724. Raman (solid, ν/cm^{-1}): 133, 178, 221, 234, 251, 263, 272, 285, 298, 340, 502, 691, 712. MS (EI, +ve): 356, $[Hg(SCH_2CH_2NH_3)_2 + 1]^+$; 389, $[HgCl(SCH_2CH_2NH_3)_2 - 1]^+$; 313, $[HgCl(SCH_2CH_2NH_3)]^+$; 426, $[HgCl_2(SCH_2CH_2NH_3)_2]^+$. Anal. Calcd for $[Hg_6Cl_8(SCH_2CH_2NH_3)_8)]Cl_4{\cdot}4H_2O$: C, 27.88; H, 9.35; N, 16.25. Found: C, 27.01; H, 9.13; N, 15.92.

Synthesis of $[Hg_9Br_{15}(SCH_2CH_2NH_3)_9](Cl_{0.8}{\cdot}Br_{0.2})_3$ (2). To a stirring solution of 2-aminoethanethiol hydrochloride (1.14 g, 10 mmol) in DI water (20 mL) was added mercury(II) bromide (1.80 g, 5 mmol) to obtain a white precipitate. The precipitate was removed and dried, and the filtrate was allowed to stand for 2 weeks in the refrigerator at 4 °C, during which time colorless crystals formed. Crystalline yield: 2.68 g (42%). Mp: 154−156 °C. ^{1}H NMR (DMSO, 200 MHz, ppm): δ 2.95 (t, 2H, CH_2N), 3.15 (t, 2H, CH_2S), 7.70 (s, 9H, NH_3). ^{13}C NMR (DMSO, 200 MHz, ppm): δ 27.1 (CH_2S), 42.8 (CH_2N). IR (KBr, ν/cm^{-1}): 3433, 3005, 2893, 1576, 1502, 1475, 1455, 1378, 1316, 1272, 1126, 1069, 1009, 933, 764, 717. Raman (solid, ν/cm^{-1}): 150, 174, 196, 221, 263, 268, 288, 339, 454, 604, 715, 752. MS (EI, +ve): 355, $[Hg(SCH_2CH_2NH_3)_2 + 2]^+$; 356, $[HgBr(SCH_2CH_2NH_3)]^+$; 435, $[HgBr(SCH_2CH_2NH_3)_3 - 1]^+$; 515 $[HgBr_2[SCH_2CH_2NH_3)_2]^+$. Anal. Calcd for $[Hg_9Br_{15}(SCH_2CH_2NH_3)_9](Cl_{0.8}{\cdot}Br_{0.2})_3$: C, 31.13; H, 9.14; N, 18.15. Found: C, 30.91; H, 9.35; N, 18.04.

Result and Discussion

Synthesis and Proposed Mechanism. Combination of 2-aminoethanethiol hydrochloride with $HgCl_2$ in DI water yielded $[Hg_6Cl_8(SCH_2CH_2NH_3)_8)]Cl_4{\cdot}4H_2O$ (**1**) according to the reaction shown in eq 1. The same reaction with $HgBr_2$, however, yielded $[Hg_9Br_{15}(SCH_2CH_2NH_3)_9](Cl_{0.8}{\cdot}Br_{0.2})_3$ (**2**) and not simply the bromine analogue of **1** as shown in eq 2. A similar reaction also yielded a linear two-coordinate $[Hg(SCH_2CH_2NH_3)_2]Cl_2$ (**3**; eq 3).[19]

$$6HgCl_2 + 8[SCH_2CH_2NH_3]Cl \xrightarrow{H_2O} \mathbf{1} + 8HCl \qquad (1)$$

$$9HgBr_2 + 9[SCH_2CH_2NH_3]Cl \xrightarrow{H_2O} \mathbf{2} + 9HCl_{0.6}Br_{0.4} \qquad (2)$$

$$HgCl_2 + 2[HSCH_2CH_2NH_3]Cl \xrightarrow{H_2O} \mathbf{3} + 2HCl \qquad (3)$$

However, this behavior is in contrast to other mercury thiolate complexes $[Hg(SR)X)]_n$ ($n = 2-7$) with ligands such as cysteine, where the Cl and Br derivatives are structurally similar.

The interaction of Hg with thiolate is thermodynamically favored, and stable compounds can be achieved by the formation of a number of structures of equal or similar energy with varying geometry around Hg. The ease of deformation

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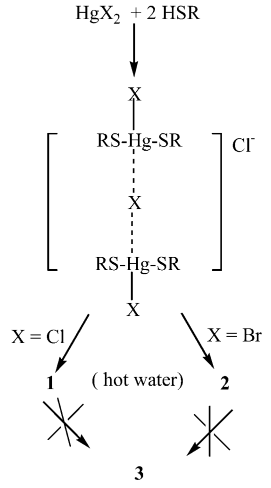
[19] Kim, C. H.; Parkin, S.; Bharara, M. S.; Atwood, D. A. *Polyhedron* **2002**, *21*, 225.

Scheme 1. Plausible Mechanistic Steps in the Formation of **1** and **2** (R = $-CH_2CH_2NH_3^+$)



of $[Hg(SR)_x]$ complexes is due to the low energy barrier separating different species. The labile nature of $[Hg(SR)_x]$ inherent in monomeric centers finds expression in complicated structures.[20,21] For instance, the reaction of cysteine with $HgCl_2$ yielded polymeric $[HgCl_2\{SCH_2CH(NH_3)COOH\}]$, which in hot water changes to a linear product $[Hg\{SCH_2CH(NH_3)COO\}\{SCH_2CH(NH_3)COOH\}]^+$ with strong Hg−S bonds.[7] The former product was considered as an intermediate en route to the latter product. The latter product was also obtained by direct addition of the reactants.

However, a similar observation could not be made for **1** and **2** because a two-coordinate derivative from either **1** or **2** could not be obtained (Scheme 1). The proposed intermediate could not be isolated from the solution but was identified by thermal analysis and mass spectrometry.

Spectroscopic Characterization

The ^1H NMR spectra in **1** and **2** show peaks at ≈3.14 ppm for SCH_2, a significant shift from the peak observed in the free ligand (2.69 ppm), which is indicative of Hg−S bonding. No observable shift in the NCH_2 group (≈3.00 ppm for **1**, **2**, and free ligand) indicates the absence of a Hg−N contact. The integration for amine protons (≈7.8 ppm) indicates the presence of an ammonium group. In ^{13}C NMR spectra, detectable shifts are observed in C attached to S [25 (**1**), 27 (**2**), and 22 ppm (free ligand)] and meager shifts in C attached to N (43 (**1**), 42.8 (**2**), and 42 ppm (free ligand)).

The IR spectra show the presence of N−H stretching frequencies at around 3440 and 3050 cm^{-1} indicative of the presence of an NH_3^+ group rather than an NH_2 species. Similar observations for the presence of NH_3^+ groups were made in $[Cd(NH_3CH(CH_2SH)COO)_2]$ (3404 and 3010 cm^{-1}).[22] Frequencies observed around 2980−3000 cm^{-1} indicate hydrogen bonding. In the Raman spectra, the proper assignment of Hg−S and Hg−X frequencies was quite difficult because of the variability of the geometry around the Hg atoms as well as the similar atomic weights of S and Cl. However, a few selected peaks clearly observed in the spectra are summarized in Table 2. The Hg−S frequencies for **1** are observed around 272 and 340 cm^{-1} for symmetric and asymmetric stretching, respectively, whereas for **2**, the corresponding bands are observed at 288 and 339 cm^{-1}. The symmetric modes are found in the ranges observed for two-coordinate (above 300 cm^{-1}) and three- and four-coordinate Hg(II) compounds (below 250 cm^{-1}). The terminal Hg−X peaks are observed around 234 and 174 cm^{-1} for **1** and **2**, respectively. The frequencies corresponding to bridging group Hg−X can be assigned to very weak peaks observed at 251 and 196 cm^{-1} for **1** and **2**, respectively. Similar values have also been proposed for the anions $[Hg_2Cl_6]^{2-}$ (233 cm^{-1}) and $[Hg_2Br_6]^{2-}$ (150 cm^{-1}).[23]

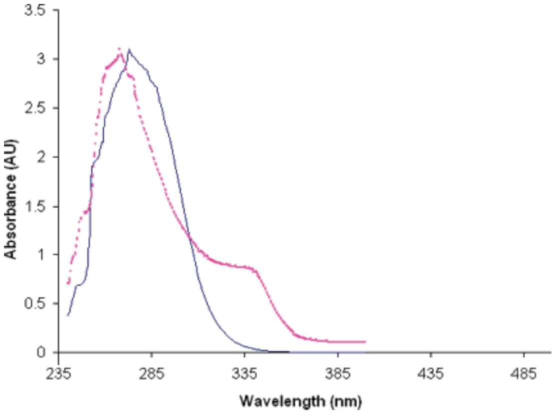


Figure 1. UV−vis spectra of a 0.05 mM solution of **1** (−) and **2** (···) in DI water.

In the UV−Vis spectrum (Figure 1), the λ_{max} for both **1** and **2** is observed around 270 nm, which is due to the S → Hg ligand-to-metal charge transfer (LMCT). In **2**, the spectra delineate a shoulder at around 340 nm. The additional shoulder in **2** may be due to the metal center where Hg is attached to three Br and only one sulfur atom as seen in the crystal structure. Similar bands observed in $[Hg(SR)_2]$ (R = Et, Pr^i),[27] mercury plastocyanin,[28] and two types of metallothionein were attributed to LMCT transition arising from a distorted tetrahedral Hg center.[29−31]

Crystallographic Studies

The cationic cluster of **1** is formed by linking two equivalent trimeric species $[Hg_3Cl_4(SCH_2CH_2NH_3)_4]^{2+}$ with

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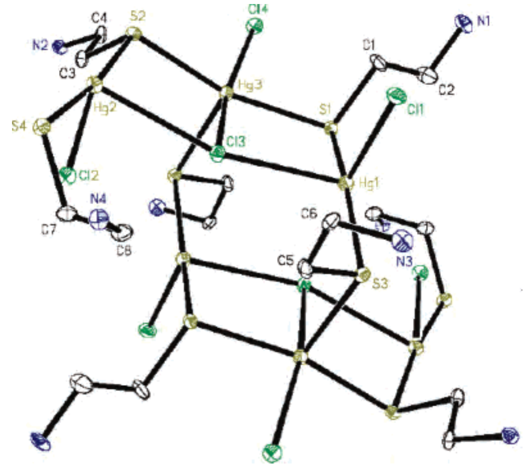

Figure 2. Molecular structure of **1** with 50% probability of the thermal ellipsoids. The counteranions and hydrogen atoms are omitted for clarity.

two bridging thiolate S atoms (Figure 2). In the molecule, two independent types of Hg [H1, Hg2 (four-coordinate), and Hg3 (five-coordinate)], Cl (bridging and terminal), and bridging S atoms (inter- and intraunit) are observed. The geometry around Hg1 and Hg2 can be best described as distorted tetrahedral and that around Hg3 as distorted square pyramidal.

The Hg−S distances are quite variable in the range 2.339−2.631 Å. The Hg1−S and Hg2−S bond distances (Table 1) are nearly equal (average 2.399 Å) except for Hg3−S4 (2.339 Å), where S4 is not a bridging atom. These distances are found in the upper range of the distances observed for two-coordinate mercury(II) thiolates with additional secondary contacts (2.316−2.395 Å)[7,32−35] but are slightly shorter than the corresponding distances observed in four-coordinate mercury(II) thiolates (2.410−2.606 Å).[13,14,36−38] The Hg3−S1 and Hg3−S2 distances (average 2.509 Å) are much longer than the Hg−S distances associated with Hg1 and Hg2. These distances are, however, smaller than the sum of the covalent radii of S and tetrahedral Hg (2.52 Å), indicating a stronger covalent bond.[10,39−41] The bridging thiolate distance between trimeric units is fairly longer (2.631 Å) than the bridging Hg−S distances observed within the units. These distances are comparable to bridging Hg−S distances observed in molecular $[Hg_2(SMe)]^{2+}$ (average 2.667 Å),[42] $[Ph_4P][Hg_3(SCH_2C_6H_4CH_2S)_4]\cdot 6MeOH$ (average 2.708 Å),[9] and polymeric $[Hg(S{-}Bu^t)_2]_n$ (average 2.625 Å) and $[Hg_2(SCH_2CH_2S)_3]_n$ (average 2.72 Å).[10]

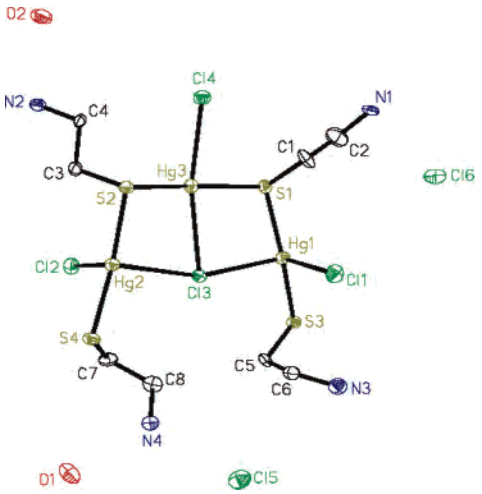

Figure 3. Trinuclear moiety of **1** showing triply bridged Cl atoms. The bridging Hg3−S″ and S3−Hg3″ bonds are not shown.

The three Hg atoms in each fragment are arranged around the triply bridged chloride at similar distances (average 2.924 Å; Figure 3). The trimeric fragment $[Hg_3Cl_4(SCH_2CH_2NH_3)_4]^{2+}$ can be compared to $[(\mu_3\text{-Cl})\{HgSC(CH_3)_2CH(NH_3)COO\}_3]^{2+}$ (**4**), where a triply bridged Cl is also observed.[43] The Hg1−Cl1 (2.73 Å) and Hg2−Cl2 (3.106 Å) distances are quite different despite similar environments. These distances are much longer than the sum of the covalent radii of Cl and tetrahedral Hg atoms (2.47 Å). The Hg−Cl distance to triply bridged chloride in **1** is much longer than the corresponding distances observed in **4** (2.37 Å). The significantly longer distance may be due to the formation of a four-membered-ring Hg_2SCl involving bridging S and Cl atoms. In **4**, the trimeric units are held together via moderately strong chloride bridges forming a three-dimensional network, in contrast to **1**, where the units are held together via bridging S atoms.

In the structure of **1**, the Hg environment is quite distorted, with primary S−Hg−S angles ranging from 171.8 to 158.0°, much more linear compared to those associated with tetrahedral Hg with a Cl_2S_2 environment such as $[HgCl_2(C_3H_4N_2S_2)_2]$ (130.8°)[39] and [Hg(L-cys)Cl_2] (112.5° and 130.2°).[7] Because of the longer secondary contacts, effective distortion around Hg is not observed. The angular distortion of S−Hg−S is directly related to secondary contacts and asymmetric primary coordination. The largest bond angles are associated with the sulfur and the more narrow angles are associated with the triply bridged chlorides (S1−Hg1−Cl3, S2−Hg2−Cl3, and S1−Hg3−Cl3, ≈88°). The reason for distortion around Hg can be attributed to the vibronic coupling mechanisms leading to a d-orbital contribution, which gives rise to a deformation or "plasticity" effect for tetrahedrally coordinated Hg(II) with sulfur donor ligands.[44]

It is interesting to observe that, despite the variation in the distances and the angles, each Hg atom is bonded to two sulfurs and two chlorides (with the exception of the long S contact to Hg3). The $Cl_{\text{triply bridged}}$−Hg−S angles in **1** (89−

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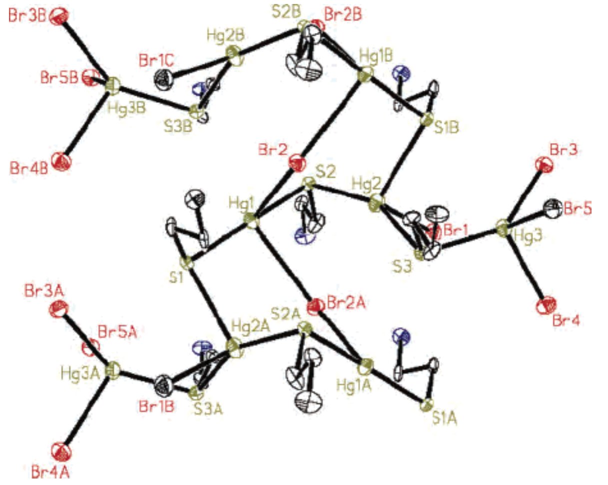

Figure 4. Molecular structure of **2** with 50% probability thermal ellipsoids. The hydrogen atoms and counteranions are omitted for clarity.

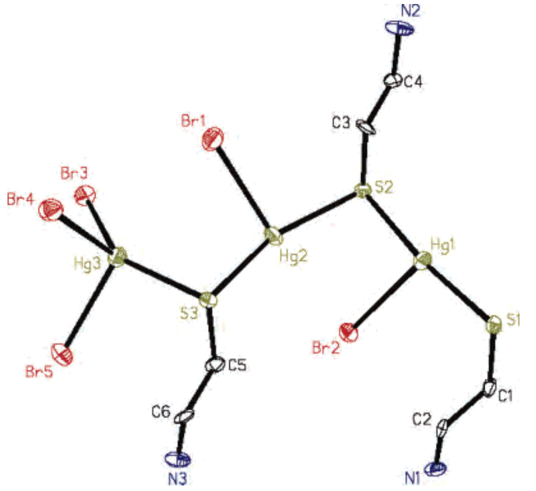

Figure 5. Asymmetric unit in the structure of **2** (without counteranions) with 50% probability thermal ellipsoids.

98°) are much more acute than their corresponding angles in **4** (167.2°) because of the involvement of bridged S atoms. The geometry defined by three Hg, two S, and one Cl atom, (Cl3) is quite planar, with Hg1−Cl3−Hg2 and S1−Hg3−S2 close to 160°. This plane is parallel to the corresponding plane present in the second unit, with the $-CH_2CH_2NH_3^+$ group pointing outside to avoid steric interactions. The terminal groups, in turn, are involved in intermolecular hydrogen bonding.

The cluster of $[Hg_9Br_{15}(SCH_2CH_2NH_3)_9](Cl_{0.8}Br_{0.2})_3$ (**2**; Figure 4) is perhaps the only known nonanuclear heteroleptic mercury thiolate. The molecule can be considered to be composed of three trinuclear $[Hg_3Br_5(SCH_2CH_2NH_3)_3]^+$ units (Figure 5) with bridging S and Br atoms. In the whole molecule, four different types of environments are observed around the Hg atoms, namely, HgSBr3, HgS2Br2, HgSBr3, and HgS2Br. Units 1 and 3 are quite similar, with unit 2 sandwiched between them.

Within a unit, three independent Hg atoms are observed. The Hg atoms are four-coordinate (except Hg1A and Hg2B, which are three-coordinate) with bridging S and either bridging or terminal Br atoms. The Hg−S distances observed (2.424−2.488 Å) within a unit are close to the range observed for similar tetrahedrally coordinated mercury thiolate complexes such as $[Hg_7(SC_6H_{11})_{12}Br_2]$ (2.36−2.42 Å) and $(Ph_4P)[(\mu\text{-SEt})_5(\mu\text{-Br})(HgBr)_4]$ (2.48−2.61 Å).[8,15] The bridging Hg−S distances (Hg2−S1B and S1−Hg2B = 2.811 Å) between the units are, however, much longer than the sum of covalent radii of S and tetrahedral Hg (2.52 Å) and the corresponding Hg−S distances within the unit.[40] This distance is indicative of a weak Hg−S bond present between the units. These distances are significantly longer than the corresponding distances observed in **1**.

Hg3 is quite unique because it is bonded to only one S atom when Hg atoms are known to have a tendency to maximize bonding with S. The Hg3−S distances are slightly longer than the distances observed in mercury(II) thiolates with a HgSBr3 moiety such as $[HgBr_2(tzdtH)]_2$ (tzdtH = 1,3-thiazolidine-2-thione) (2.435 Å).[45] This is due to the presence of sulfur at the bridging position rather than at the terminal position. The $Hg-Br_{ter}$ distances (2.559−2.790 Å) are close to the range of terminal Hg−Br distances (2.47−2.65 Å) found in the literature.[46,47] The $Hg-Br_{br}$ distances (average 3.004 Å) are close to the range observed for mercury(II) thiolates with $Hg-Br_{br}$ distances (2.73−2.90 Å).[8] Such a variation is commonly found for terminal and bridging Hg−Br distances of thiolate-bridged compounds of Hg(II).[48] The Hg−Br−Hg bridge is symmetrical (3.073(11) Å), which is in contrast to the fact that unsymmetrical Hg−Br−Hg bridges are more frequently observed.[13,49−52] The weak $Hg-S_{br}$ (between units) and normal $Hg-Br_{br}$ distances suggest that Br plays a more important role than S in holding the three different units together.

The greatest deviation from an ideal tetrahedral geometry is observed in the angles S1−Hg1−S2 = 172° and S2−Hg1−Br2 = 85°. The relatively weaker secondary contacts around Hg are responsible for the almost linear S−Hg−S angle, slightly bigger than that observed in **3** (168°). Like **1**, the broader angles observed are bonded to S atoms and the more narrow angles are associated with the bridging Br. Similar to **1**, it seems that the angles associated with Hg and S tend to form a linear structure similar to **3** but the weak secondary contacts bring the units in close proximity to form a cluster.

The Hg atoms in a unit are arranged in a zigzag pattern very much similar to that observed in $HgX_2[SCH_2CH(NH_3)$-

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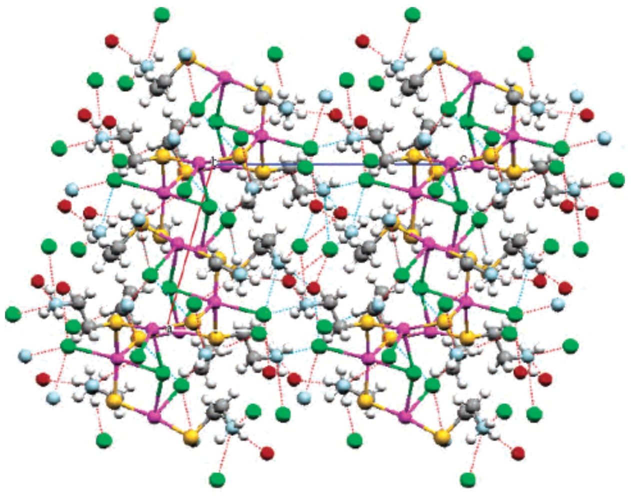
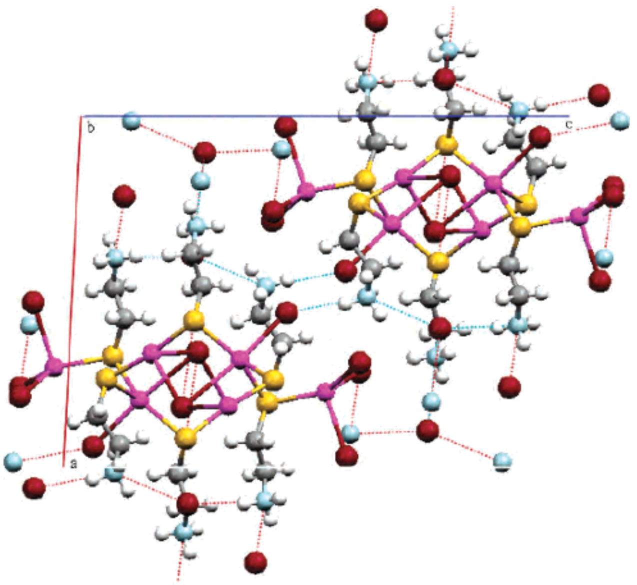


1

Figure 6. Packing diagram of **1** along the *b* axis. The H atoms are shown as white circles, and intermolecular hydrogen bonding is shown as dotted lines.



2

Figure 7. Packing diagram of **2** along the *b* axis. The H atoms are shown as white circles, and hydrogen bonding is shown as dotted lines.

COOH] (X = Cl, Br).[7] If seen along the *b* axis, it is observed that Hg atoms in unit 1 and unit 3 are on top of each other and unit 2 has been arranged in a spiral fashion with bridging thiolate and bromide atoms. Such a bonding pattern has not been observed previously. For example, in clusters such as $[Ag_9(SCH_2CH_2S)_6]^{3-}$, the Ag atoms are arranged in a tetragonal prism of eight Ag, centered by a ninth Ag atom.[53]

The Molecular Units in **1** and **2** are held together by means of extensive intermolecular hydrogen bonding (Figures 6 and 7). The terminal NH_3^+ moiety is involved with a free halide, water molecules, and S atoms (in **1**). The hydrogen-bonding geometry is summarized in Table 5. The NH···Cl (3.136−3.256 Å) and NH···Br (3.131−3.404 Å) distances are in agreement with the distances observed in similar complexes such as $[HgCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ (3.15 Å),[25] $[HgCl_2(C_3H_4N_2S)_2]$ (3.121 and 3.188 Å),[39] $[HgBr_2$(1,3-thiazolidine-2-thione)$]_2$ and $[HgBr_2$(benzo-1,3-thiazolidine-2-thione)$_2]$ (3.297 and 3.335 Å),[54] and $[HgBr_2$(1,3-imidazole-2-thione)$_2]$ (3.286 and 3.406 Å).[55,56] The NH···S distance 3.074 Å observed in **1** is shorter than the corresponding distances reported for **3** (3.26 Å),[19] $[HgI_2$(1,3-imidazole-2-thione)$_2]$ (3.419 Å),[55] and $[HgI_2$(1,3-thiazolidine-2-thione)$]_2$ (3.38 Å), indicating a stronger interaction.[45]

The distances involved in the weak Hg···Hg interaction in the asymmetric units (Hg2···Hg3 = 3.776 Å and Hg1···Hg3 = 3.797 Å in **1** and Hg1···Hg2 = 3.605 Å and Hg2−Hg3 = 3.750 Å in **2**) are longer than the Hg···Hg distances observed in metallic mercury (3 Å),[57] the $[HgMe_2)]_2$ dimer, (3.41 Å),[58] and $[(o\text{-}C_6F_4Hg)_3\cdot\mu_3$-acetone] (3.512−3.776 Å).[59] These distances are, however, in close proximity to the distances observed for mercury(II) thiolates such as [Hg(Am4DM)X]$_2$ (Am4Dm = 2-pyridineformamide *N*(4)-dimethylthiosemicarbazone and X = Cl or Br) (3.667 and 3.660 Å)[60] and $[(Bu^tS)_4Cl_4Hg_4(C_6H_7N)_2]$ (3.648−3.852 Å).[13,38]

TGA Studies

Thermograms of **1** and **2** in air indicate that total sublimation of the samples takes place around 600 °C. Weight loss in both cases occurs in two steps around 300 and 400 °C. Despite a 100 °C difference in the melting temperature, the thermograms follow a similar trend. The 60% (for **1**) and 80% (for **2**) loss in the first step indicates the breaking of the cluster to a rather simple molecule. The second step with a loss of 33% indicates evolution of the thiol ligand to form Hg_2X_n species ($n = 2$ when X = Br and $n = 5$ when X = Cl). Because of the complex nature of the compounds, it has been very difficult to accurately match the theoretical and experimental values. These thermograms show the same trend as that observed in polymeric $[HgX_2(DMTP)]_n$ (X = Cl, Br, and I; DMPT = 2,6-dimethyl-4*H*-pyran-4-thione).[61] However, there are not many reported examples in the literature dealing with thermal analysis of $[HgX_2(SR)_2]$ type compounds compared to $[Hg(SR)_n]$ type compounds. The latter have been more widely studied since they are used as unimolecular precursors for the thermolytic preparation of metal sulfide materials.

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Conclusion

Novel hexa- and nonanuclear mercury thiolate clusters have been synthesized and characterized. The halide seems to be responsible for the formation of clusters rather than a two-coordinate compound. These results are in contrast to the reaction reported for mercury(II) thiolates with simple thiol-containing ligands, where the structure is independent of the halide. The coordination around Hg in both compounds is quite fascinating because the distorted tetrahedral geometry is more inclined toward a linear geometry. This may be related to the metal sites in metallothioneins, where incorporation of more than four Hg ions leads to a progressive change from tetrahedral to essentially linear geometry.[31]

Acknowledgment. This work was supported by the University of Kentucky Tracy Farmer Center for the Environment and the State of Kentucky Research Challenge Trust Fund. NMR instruments used in this research were obtained with funds from the CRIF program of the National Science Foundation (Grant CHE 997841) and from the Research Challenge Trust Fund of the University of Kentucky.

Supporting Information Available: Syntheses, characterization information, extensive tables, an additional figure of **2**, thermograms, and crystal data. This material is available free of charge via the Internet at http://www.pubs.acs.org.

IC0506005