Mercury Thiolato Complexes: Syntheses, Crystal Structures, and Decomposition Pathways

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Received June 16, 1995. Revised Manuscript Received October 18, 1995[⊗]

Complexes of the general formula ClHgSR (R = benzyl, neopentyl, isopropyl) and the mercury bis(thiolate) compound $[Hg(SBz)_2]_\infty$ each have been prepared and characterized by single crystal X-ray diffraction. ClHgSBz·TMEDA crystallizes in the triclinic space group $P\bar{1}$ with cell constants $a = 8.136(2)$ Å, $b = 9.958(7)$ Å, $c = 11.834(3)$ Å, $\alpha = 108.71(2)°$, $\beta = 92.93(2)°$, $\gamma = 109.05(2)°$, and $Z = 2$. Refinement of 2534 observed reflections yields $R = 0.050$ and $R_w = 0.056$. $[ClHgS\text{-iso-}Pr]_\infty$ crystallizes in the monoclinic space group $C2$ with cell constants $a = 21.430(7)$ Å, $b = 4.678(2)$ Å, $c = 6.724(2)$ Å, $\beta = 90.43(2)°$, and $Z = 2$. Refinement of 528 observed reflections yields $R = 0.039$ and $R_w = 0.033$. $[ClHg(S\text{-neo-Pent})\cdot 0.5Py]_\infty$ crystallizes in the monoclinic space group $C2$ with cell constants $a = 16.732(2)$ Å, $b = 11.200(1)$ Å, $c = 11.929(2)$ Å, $\beta = 104.21(1)°$, and $Z = 4$. Refinement of 2561 observed reflections yields $R = 0.035$ and $wR_2 = 0.081$. $[Hg(SBz)_2]_\infty$ crystallizes in the monoclinic space group $C2/c$ with cell constants $a = 22.599(4)$ Å, $b = 4.334(1)$ Å, $c = 29.566(5)$ Å, $\beta = 106.76(1)°$, and $Z = 8$. Refinement of 1264 observed reflections yields $R = 0.036$ and $wR_2 = 0.116$. The solid-state thermal decompositions of the chloromercury thiolate compounds have been studied and the XRPD patterns of the resultant solid-state materials were obtained. The formation of Hg_2Cl_2 is observed upon thermolysis of $[ClHg(S\text{-neo-Pent})\cdot 0.5\ Py]_\infty$ or $[ClHgS\text{-iso-}Pr]_\infty$ at 200 °C, whereas ClHgSBz·TMEDA produces HgS under identical conditions. Upon mixing equimolar quantities of $HgCl_2$ and Ph_3CSH in EtOH, moderately crystalline HgS is produced at ambient temperature. The volatile products liberated during the thermal decomposition have been isolated and characterized by GC/MS techniques. For the cases involving the production of HgS from ClHgSR (R = Bz, Ph_3C), the reaction coproduct was identified as RCl. In the instances where Hg_2Cl_2 was synthesized from ClHgSR (R = iso-Pr, neo-Pent), R−$(S)_n$−R (n = 2, 3, 4) have been identified. The decomposition pathways of the various chloromercurythiolate compounds are discussed, and mechanisms consistent with the observed reaction products are presented.

Introduction

The soft RS^- ligand displays a high affinity for many metals, particularly toward mercury. The structural chemistry of mercury bis(thiolate) compounds and species of the general formula ClHgSR has been studied.[2] These compounds show a remarkable structural variety, mainly due to the flexible coordination properties of mercury. They have a tendency to form oligomers or polymers by intermolecular Hg−S or Hg−Cl interactions, or both. Their solubility in polar organic solvents and their thermal instability combine to make these compounds potential candidates as unimolecular precursors for the thermolytic preparation of metal sulfide materials. This property has ramifications for the more thermally labile metal selenolates and tellurolates, which potentially could serve as precursors in the preparation of compositions such as HgTe or $Hg_{1-x}Cd_xTe$, materials displaying interesting electrical and optical properties.[3]

Recently, we have explored the possibility of designing simple unimolecular precursors which can be converted into solid-state materials and reported previously that the decomposition of the metal bis(thiolate) compounds of lead, zinc and cadmium proceeds under mild conditions to yield binary metal sulfides.[4] These investigations complemented those from other groups[5] which indicated that, under certain conditions, the decomposition of unimolecular precursors leads to the formation

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⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1995.
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0897-4756/96/2808-0360$12.00/0

Table 1. Crystallographic Data

	ClHgSBz·TMEDA	$[ClHgS\text{-}iso\text{-}Pr]_\infty$	$[ClHg(S\text{-}neo\text{-}Pent)\cdot 0.5Py]_\infty$	$[Hg(SBz)_2]_\infty$
mol formula	$C_{13}H_{23}N_2ClSHg$	$C_6H_{14}Cl_2S_2Hg_2$	$C_{15}H_{27}NCl_2S_2Hg_2$	$C_{14}H_{14}S_2Hg$
mol wt/g mol^{-1}	475.27	622.42	757.60	446.97
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2$	$C2$	$C2/c$
a/Å	8.136(2)	8.136(2)	21.430(7)	16.732(2)
b/Å	9.958(7)	9.958(7)	4.678(2)	11.200(1)
c/Å	11.834(3)	11.834(3)	6.724(2)	11.929(2)
α/deg	108.71(2)			
β/deg	92.93(2)	92.93(2)	90.43(2)	104.21(1)
γ/deg	109.05(2)			
V/Å^3	845.3	674.0	2167.1	2775.6
Z	2	2	4	8
D_c/g cm^{-3}	1.847	3.07	2.322	2.139
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα
temp/°C	25	25	−70	−40
abs coeff/cm^{-1}	93.28	234.1	145.9	113.7
diffractometer	CAD-4	Siemens P3	Siemens P4	Siemens P4
no. of reflns measd	2991	1219	5663	3711
no. of unique reflns	2991	601	2643	2399
no. of significant reflns	2543	528	2561	1264
final R (R_w)	5.0 (5.6)	3.9 (3.3)	3.5 (8.1)[a]	3.6 (11.6)[a]
goodness of fit	1.31	1.54	1.083	0.971

[a] wR_2 reported.

of unusual phases. This was observed in the case of cadmium bis(benzylthiolate), which decomposed under mild conditions yielding the cubic (high temperature) phase of cadmium sulfide, while other cadmium bis(thiolate) compounds examined produced the expected hexagonal phase under comparable conditions.[6]

The knowledge of transformations occurring when a molecular precursor is converted into a solid-state material often is sparse. Some studies suggest that structural elements of the molecular precursors may be preserved during the decomposition and are found in the solid-state materials.[7] If this observation is confirmed as widely applicable, it ultimately could lead to the rational design of molecular precursors suitable for the preparation of a wide variety of desired phases. To probe the notion that there is a connection between the structure of a molecular precursor and the solid-state material obtained by the thermolytic decomposition of that precursor, mercury thiolate compounds have been prepared and structurally characterized, and their decompositions have been examined. Herein, the syntheses, crystal structures and solid-state decompositions of several chloromercury thiolate compounds are reported.

Additionally, the product of the reaction of mercury dichloride and triphenylmethylthiol (tritylmercaptan) was included in these studies. The resulting compound, presumably $ClHgSCPh_3$, was reported over eight decades ago to be unstable under ambient conditions, but no details were provided relative to its decomposition.[8] Finally, a new mercury bis(thiolate) compound has been prepared and its crystal structure is reported herein.

Experimental Section

General Comments. The chemicals $HgCl_2$ (Aldrich), HgO (Aldrich), and sodium (Fisher-Scientific) were used without further purification. Benzylthiol (Aldrich) and isopropylthiol were distilled before use. Neopentylthiol[9] and triphenylmethylthiol[10] were prepared according to literature methods and identified as authentic by comparison of their boiling point and melting point, respectively, with that reported previously. Additionally, the compounds were characterized by GC/MS. Ethanol (Florida Distillers) was distilled before use, and tetramethylethylenediamine was refluxed over clean K, distilled, and stored under a nitrogen atmosphere. Pyridine was refluxed over KOH and distilled.

Gas chromatograph/mass spectral data were collected with a Hewlett Packard GC 5890 Series II, MS5971A spectrometer. X-ray powder diffraction data were obtained on a Siemens Kristalloflex diffractometer. NMR spectra were recorded on a Gemini-300 spectrometer and processed on a Sun 4/110 data station. Melting points were obtained using a Mel-Temp II apparatus. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Syntheses. $[Hg(SBz)_2]_\infty$[11] and $[ClHgS\text{-}iso\text{-}Pr]_\infty$[12] were prepared according to literature methods. The preparation of ClHg(S-neo-Pent) and ClHgSBz each was carried out following a procedure which was comparable to the method described in reference 11 (eq 1). The TMEDA adduct of ClHgSBz was obtained by slow cooling of a saturated solution of ClHgSBz in tetramethylethylenediamine from 60 to 25 °C overnight. The pyridine adduct of ClHg(S-neo-Pent) was prepared by the slow evaporation of solvent from a solution of ClHg(S-neo-Pent) in pyridine.

$$HgCl_2 + R{-}SH \xrightarrow[25\ °C]{EtOH} ClHgSR + HCl \qquad (1)$$

ClHgSBz: yield 79%; mp 180 °C (dec); ^{1}H NMR ($CDCl_3$) 7.3 (m, 5H), 3.9 (s, 2H). Elemental Anal. (Calcd): C, 25.97% (23.41%); H, 2.42% (1.97%). (This compound appears to be somewhat light sensitive and decomposed partially before its composition could be determined.)

ClHg(S-neo-Pent): Yield 85%; mp 190 °C (dec). Elemental Anal. (Calcd): C, 17.41% (17.71%); H, 3.33% (3.27%); S, 9.30% (9.45%).

The reaction of $HgCl_2$ with triphenylmethylthiol was carried out as described previously (eq 2):[8]

$$HgCl_2 + Ph_3CSH \xrightarrow[25\ °C,\ -HCl]{EtOH} \text{“}ClHgSCPh_3\text{”} \xrightarrow{4\ h} HgS + ClCPh_3 \qquad (2)$$

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Table 2. Selected Interatomic Distances (Å)

ClHgSBz·TMEDA		[ClHgS-iso-Pr]$_n$		[ClHg(S-neo-Pent)·$^1/_2$Py]$_n$		[Hg(SBz)$_2$]$_n$	
S−Hg	2.34	Hg(1)−S(1)	2.362(6)	Hg(1)−S(1)	2.420(3)	Hg−S(1)	2.34(3)
Cl−Hg	2.38	Hg(1)−Cl(1)	3.29(1)	Hg(2)−Cl(1)	2.687(4)	S(1)−C(11)	1.77(2)
N(1)−Hg	2.47	Hg(2)−S(1)	2.560(8)	Hg(1)−Cl(1)	3.109(4)	S(2)−C(2)	1.79(1)
N(2)−Hg	2.54	Hg(2)−Cl(1)	2.503(9)	Hg(2)−Sl(1)	2.480(3)	Hg−S(2)	2.341(3)
		Hg(1)−Cl(1b)	3.07(1)	Hg(3)−S(2)	2.432(4)	S(1)−C(12)	1.88(3)
		S(1)−C(1)	1.83(3)	S(1)−C(1)	1.86(1)		
		Hg(1)−Hg(2)	3.578(2)	Hg(1)−N(2)	2.35(1)		
				Hg(2)−C1(2)	2.472(5)		
				Hg(3)−Cl(1)	3.100(4)		
				Hg(2)−S(2)	2.471(4)		
				Hg(3)−N(2)	2.33(1)		
				S(2)−C(2)	1.85(1)		
				Hg(1)−Hg(2)	3.555(1)		
				Hg(2)−Hg(3)	3.577(2)		

Table 3. Selected Interatomic Angles (deg)

ClHgSBz·TMEDA		[ClHgS-iso-Pr]$_n$		[ClHg(S-neo-Pent)·$^1/_2$Py]$_n$		[Hg(SBz)$_2$]$_n$	
S−Hg−Cl	152.1	Cl(1)−Hg(1)−Cl(1d)	176.5(3)	S(1)−Hg(1)−N(1)	108.03(9)	S(1)−Hg−S(2)	174.7(1)
Cl−Hg−N(1)	105.3	Cl(1)−Hg(1)−Cl(1c)	81.8(3)	N(1)−Hg(1)−S(1A)	108.03(9)	Hg−S(1)−C(12)	103.8(9)
Cl−Hg−N(2)	97.5	S(1)−Hg(1)−Cl(1b)	80.5(3)	Cl(1)−Hg(2)−S(1)	96.7(1)	Hg−S(1)−C(11)	105.6(7)
S−Hg−N(2)	103.5	S(1)−Hg(1)−Cl(1c)	99.1(3)	S(1)−Hg(2)−S(2)	129.3(1)		
N(1)−Hg−N(2)	74.6	Cl(1)−Hg(2)−S(1)	100.0(3)	S(2)−Hg(3)−S(2b)	135.0(2)		
		Cl(1)−Hg(2)−S(1b)	110.6(2)	Cl(1)−Hg(1)−Cl(1a)	170.1(1)		
		S(1)−Hg(2)−S(1b)	116.9(4)	Cl(1)−Hg(1)−S(1)	87.7(1)		
		Hg(1)−Cl(1)−Hg(2)	75.0(3)	Cl(1)−Hg(1)−N(1)	85.1(2)		
		Hg(1)− S(1)−Hg(2)	93.2(3)	Cl(1)−Hg(3)−S(2a)	93.0(1)		
		Hg(1)− S(1)−Cl(1)	105.5(9)	Hg(1)−Cl(1)−Hg(3)	147.9(7)		
		Cl(1)−Hg(1)−Cl(1b)	94.6(3)	Hg(1)−Cl(1)−Hg(2)	75.3(7)		
		Cl(1b)−Hg(1)−Cl(1d)	88.9(3)	Hg(1)−S(1)−Hg(2)	93.01(7)		
		S(1)−Hg(1)−S(1a)	174.6(5)	Hg(1)−Cl(1)−Hg(3)	147.9(7)		
		S(1)−Hg(1)−Cl(1a)	85.0(3)	Hg(1)−Cl(1)−Hg(2)	75.3(7)		
		Cl(1)−Hg(2)−Cl(1a)	119.6(4)	Hg(1)−S(1)−Hg(2)	93.01(7)		
		S(1)−Hg(2)−Cl(1a)	110.6(2)	Hg(2)−S(1)−C(1)	102.3(6)		
		Hg(1) Cl(1)−Hg(1)	94.6(3)	Hg(2)−S(2)−C(2)	100.7(7)		
		Hg(2)−Cl(1)−Hg(1a)	119.2(3)	Hg(1)−N(1)−C(3)	121.4(8)		
		Hg(2)−S(1)−C(1)	106(1)	Hg(3)−N(2)−C(6b)	119.9(8)		
				S(1)−Hg(1)−S(1a)	143.9(1)		
				Cl(1)−Hg(2)−Cl(2)	102.0(1)		
				Cl(1)−Hg(2)−S(2)	97.1(1)		
				Cl(2)−Hg(2)−S(2)	113.3(2)		
				S(2)−Hg(3)−N(2)	112.5(1)		
				N(2)−Hg(3)−S(2b)	112.5(1)		
				Cl(1)−Hg(3)−Cl(1b)	177.3(1)		
				Cl(1)−Hg(1)−S(1a)	95.4(1)		
				Cl(1)−Hg(3)−S(2)	88.1(1)		
				Cl(1)−Hg(3)−N(2)	88.6(2)		
				Hg(2)−Cl(1)−Hg(3)	76.0(7)		
				Hg(1)−S(1)−C(1)	102.1(6)		
				Hg(2)−S(2)−Hg(3)	93.7(1)		
				Hg(3)−S(2)−C(3)	103.9(5)		
				Hg(1)−N(1)−C(3a)	121.4(8)		
				Hg(3)−N(2)−C(6)	119.8(8)		

Thermolyses. Samples of the prepared chloromercurythiolate compounds (1.5 g) were placed individually in a flask and heated under vacuum (0.2 Torr) at 200 °C for 4 h. Mercury sulfide was characterized by XRPD. $HgCl_2$ was identified by reaction with an aqueous ammonia solution, which yielded elemental mercury. A test for chloride was carried out by adding silver nitrate solution to a solution of the recovered solid in diluted nitric acid, yielding AgCl. The volatile products were trapped in a flask cooled by liquid nitrogen and subsequently characterized by GC/MS. The thermolysis of $Hg(SBz)_2$ was mentioned 40 years ago.[11]

X-ray Crystallography. Data were taken on Enraf Nonius CAD-4 [ClHgSBz·TMEDA] Siemens P3 {[ClHgS-iso-Pr]$_\infty$} or Siemens P4 {[ClHg(S-neo-Pent)·0.5 Py]$_\infty$;[Hg(SBz)$_2$]$_\infty$} diffractometers. Crystallographic data and refinement details are summarized in Table 1. Programs used during structure solution and refinement were SHELXTL-Plus,[13] SHELXL-**93** (refinement [ClHg(S-neo-Pent)·0.5 Py]$_\infty$ and [Hg(SBz)$_2$]$_\infty$),[14] PLATON,[15] and ORTEP (unit cell of [ClHgS-iso-Pr]$_\infty$).[16]

[ClHgS-iso-Pr]$_\infty$. Crystals suitable for X-ray diffraction were obtained by slowly cooling a saturated solution of the compound in ethanol from 70 to 25 °C overnight. Structural data for this compound have been published previously;[17] however, the compound isolated herein has a different absolute configuration and the present refinement resulted in a considerably lower residual electron density, thus this structure is discussed briefly in the context of this paper. Important interatomic distances and angles are summarized in Table 2 and Table 3, respectively. Sufficient data were collected to ascertain the absolute structure of the molecule. The inverted molecule refined to $R = 4.0$, $R_w = 3.4$. A numerical absorption correction was applied to the raw data. A plot of the unit cell indicates that an alternative assignment in *C*2/*m* is not plausible. Standard indications (statistical analysis of the intensities, anomalous scattering, cell plots, unsuccessful solution and refinement in a centrosymmetric space group) combine to indicate the choice of *C*2.

[ClHg(S-neo-Pent)·0.5Py]$_\infty$. Crystals were obtained by slow evaporation of the solvent from a saturated solution of ClHgS-

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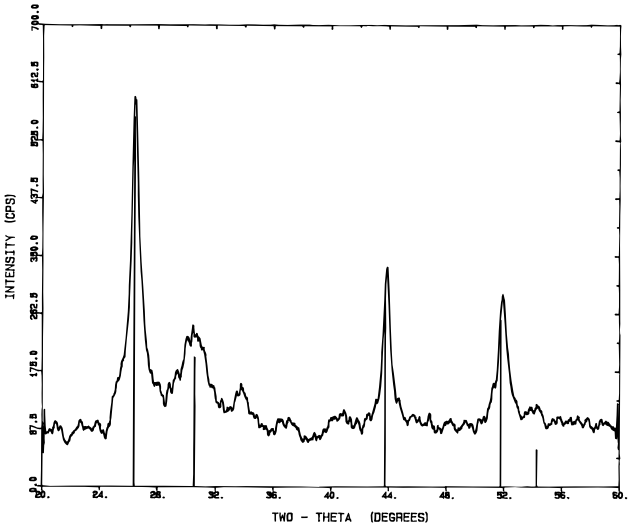

Figure 1. XRPD pattern of HgS obtained from the reaction of $HgCl_2$ and $HSCPh_3$ at ambient temperature in ethanol. The lines represent HgS (Metacinnabar) [JCPDS 6-261].

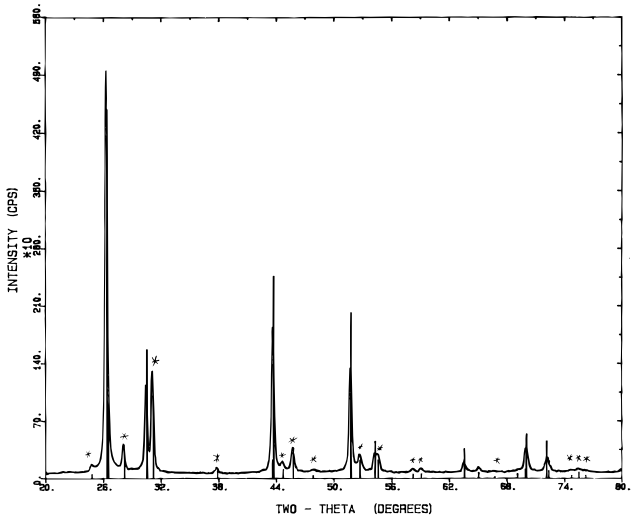

Figure 2. XRPD pattern of HgS obtained from the solid-state decomposition of ClHgSBz (200 °C, 4 h). The lines represent HgS (Metacinnabar, JCPDS 6-261 and Cinnabar *, JCPDS 6-256).

neo-Pent in pyridine overnight. Interatomic distances and angles are summarized in Tables 2 and 3, respectively. Sufficient data were collected to ascertain the absolute structure of the molecule. The Flack parameter has a value of 0.003(14). An empirical absorption correction (ψ scans) was applied to the raw data. A plot of the unit cell indicates that an alternative assignment in *C*2/*m* is not plausible. Standard indications (statistical analysis of the intensities, anomalous scattering, cell plots, unsuccessful solution, and refinement in a centrosymmetric space group) combine to indicate the choice of *C*2.

ClHgSBz·TMEDA. Crystals were obtained by cooling of a saturated solution of ClHgSBz in tetramethylethylenediamine slowly from 70 to 25 °C overnight. Interatomic distances and angles are summarized in Tables 2 and 3, respectively.

[Hg(SBz)$_2$]$_\infty$. Crystals were obtained by slowly cooling a saturated solution of the compound in ethanol from 70 to 25 °C overnight. Interatomic distances and angles are summarized in Tables 2 and 3, respectively.

Results and Discussion

Syntheses and Pyrolyses. Compounds of the general formula ClHgSR (R = iso-Pr, neo-Pent, Bz) as well as the mercury bis(thiolate) compound [Hg(SBz)$_2$]$_\infty$ have been prepared and characterized by single crystal X-ray diffraction of either the unsolvated compounds or, in the cases of ClHgSBz and ClHg(S-neo-Pent), of Lewis base adducts. The prepared chloromercurythiolates form polymeric chains, except for ClHgSBz·TMEDA, which is a monomer. These compounds are white crystalline solids and are soluble in polar and in coordinating solvents. They do not show any sensitivity toward oxygen, even after prolonged exposure. The compound ClHgSBz, as well as its TMEDA adduct, each exhibit sensitivity toward photodecomposition, while the other compounds discussed herein show no pronounced sensitivity toward light.

Attempts to isolate $ClHgSCPh_3$ were thwarted, presumably due to the instability of this compound at ambient conditions. The decomposition products (isolated in a matter of minutes after $HgCl_2$ and triphenylmethylthiol are mixed in ethanol) are mercury sulfide and triphenylmethylchloride, as determined by XRPD and GC/MS, respectively. Figure 1 shows the XRPD pattern of the obtained HgS. It reveals the formation of a relatively crystalline material—which is surprising considering that the preparation occurred at ambient temperature. Triphenylmethyl derivatives containing a C−S bond are known to decompose at mild conditions. It was reported in the first quarter of this century[18] that $(Ph_3C)SS(CPh_3)$ decomposes spontaneously when stirred in benzene at ambient temperature according to eq 3.

$$(Ph_3C)SS(CPh_3) \xrightarrow[25\ °C]{\text{benzene}} Ph_3C^{\bullet} + {}^{\bullet}SSCPh_3 \quad (3)$$

Apparently, the known high stability of the triphenylmethyl radical is the predominate contributor to this decomposition pathway. Incidentally, following the completion of the present project, a similar decomposition was disclosed for a copper(II) thiolato complex containing a triphenylmethylthiolate group.[19]

Chloromercurybenzylthiolate decomposes when heated to 200 °C to form a black solid, identified as HgS (Metacinnabar and cinnabar) by XRPD (JCPDS File #6-261 and 6-256, respectively) (Figure 2) and a colorless liquid which was found to be BzCl by GC/MS (m/e^+ = 126 amu). Thus, the benzyl derivative follows the same decomposition pathway observed for the triphenylmethyl compound, albeit at a somewhat more elevated temperature (eq 4).

$$ClHgSBz \xrightarrow{200\ °C} ClHgS^{\bullet} + {}^{\bullet}Bz \rightarrow BzCl + HgS \quad (4)$$

The chloromercury alkylthiolates [ClHgS-iso-Pr]$_\infty$ and ClHg(S-neo-Pent) also decompose at a temperature of about 200 °C. However, unlike the decomposition of the triphenylmethyl and benzyl derivatives, each of which apparently are initiated by the cleavage of a C−S bond, the thermolyses of [ClHgS-iso-Pr]$_\infty$ and ClHg(S-neo-Pent) proceed by a rupturing of the Hg−S bond. The decomposition products of such a bond scission are Hg_2Cl_2 and organosulfur compounds, the latter being formed presumably by recombination of radicals (eq 5 and Scheme 1). If the alkyl group present in the

$$ClHgSR \xrightarrow{200\ °C} Hg_2Cl_2 + R{-}S{-}S{-}R \qquad R = C_5H_{11}(\text{neo-Pent}) \quad (5)$$

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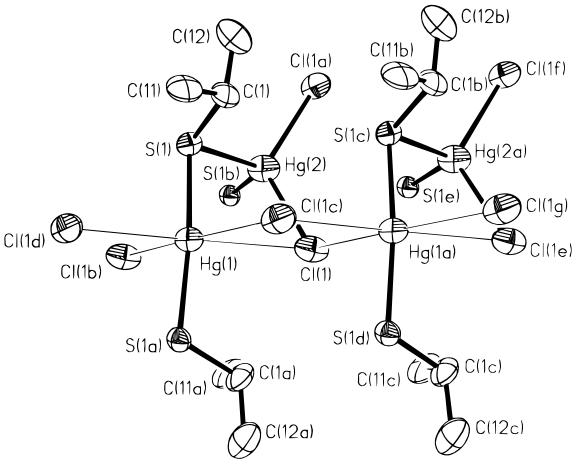
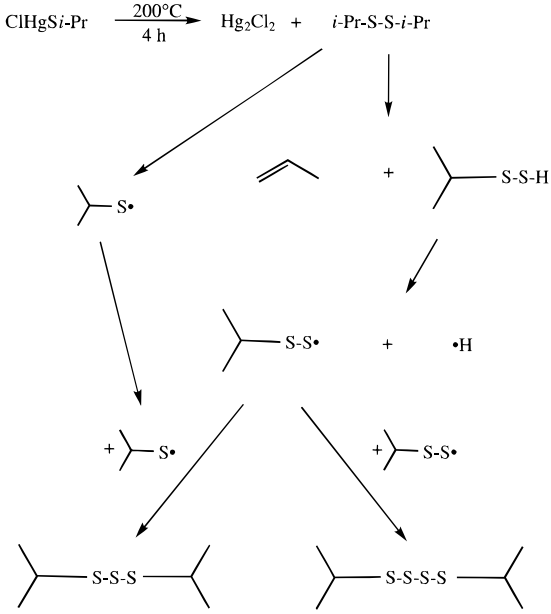


Figure 3. ORTEP representation of the solid-state structure of $[ClHgS\text{-}iso\text{-}Pr]_\infty$.

Scheme 1. Proposed Thermal Decomposition Mechanism for ClHgS-iso-Pr



chloromercury thiolate contains β-hydrogen atoms, the number of organic decomposition products increases due to β-hydride elimination (Scheme 1).

The dialkyldi-, -tri-, and -tetrasulfides each were isolated and characterized by GC/MS (Table 4). However, propene escaped detection as a consequence of the GC/MS instrument available for use in these experiments not being equipped to detect such highly volatile species. In the absence of β-hydrogen atoms, the dialkydisulfide is the only organic decomposition product (eq 5).

Solid-State Structures of the Precursors

Structural Motifs. *$[ClHgS\text{-}iso\text{-}Pr]_\infty$.* The compound is best described by the formula $\{[Hg(S\text{-}iso\text{-}Pr)_2]\cdot HgCl_2\}_\infty$ and forms a two-dimensional polymeric chain (Figure 3). Atom Hg(1) reaches a coordination number of six by coordinating to two sulfur atoms [Hg(1)-S(1), Hg(1)−S(1a) 2.36 Å, S(1)−Hg(1)−S(1a) 176°] and four chlorine atoms. The Hg(1)−Cl interatomic distances are 3.07 and 3.29 Å, as compared to 2.50 Å for the Hg(2)−Cl−interatomic distances. Atom Hg(2) is in a distorted tetrahedral environment and interacts with two sulfur atoms and two chlorine atoms (Figure 3).

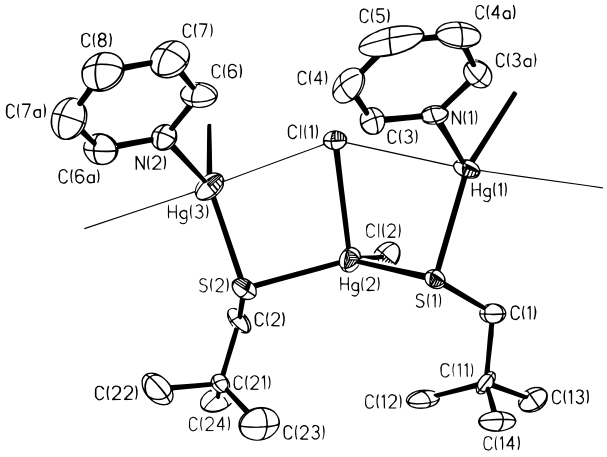


Figure 4. ORTEP representation of the solid-state structure of $[ClHg(S\text{-}neo\text{-}Pent)\cdot 0.5\ Py]_\infty$.

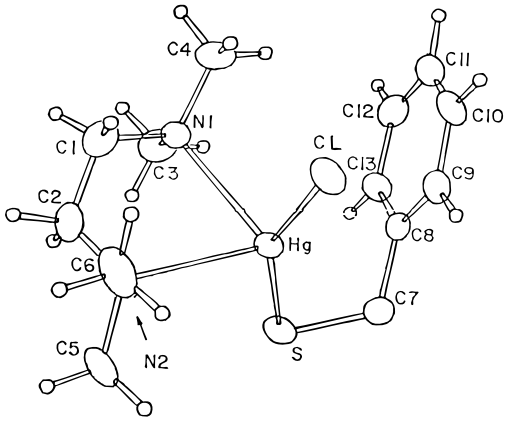


Figure 5. ORTEP representation of the solid-state structure of ClHgSBz·TMEDA.

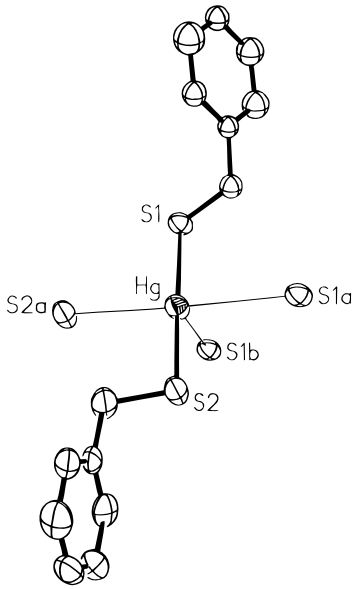


Figure 6. ORTEP representation of the solid-state structure of $[Hg(SBz)_2]_\infty$. All unlabeled atoms are carbon atoms.

$[ClHg(S\text{-}neo\text{-}Pent)\cdot 0.5\ Py]_\infty$. The compound forms a one-dimensional polymer $[(neo\text{-}PentS)_2\ Hg(NC_5H_5)\cdot HgCl_2]_\infty$ (Figure 4). The mercury atoms Hg(1) and Hg(3) are coordinated by two sulfur atoms and two chlorine atoms. Their distorted trigonal bipyramidal environment is completed by coordination to the nitrogen atom of the pyridine ring. The Hg−S interatomic distances (2.43, 2.42 Å) clearly are within the range observed for

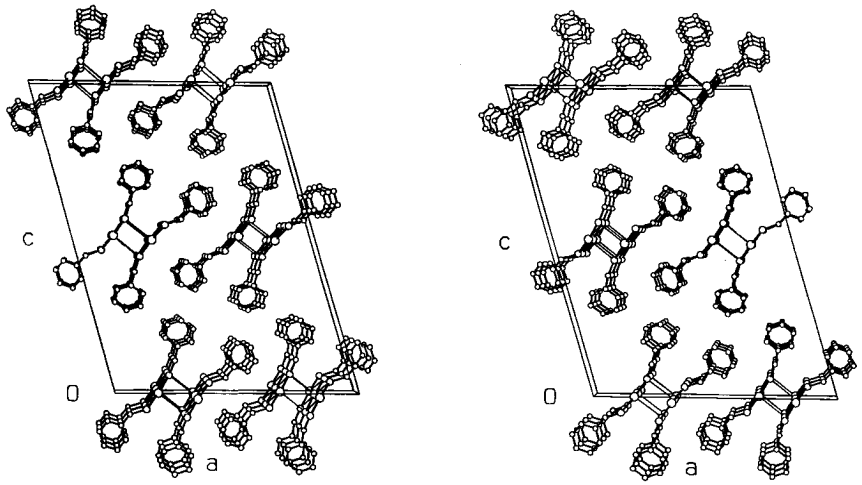


Figure 7. Stereoview of the unit cell of $[Hg(SBz)_2]_\infty$, showing the double chains formed by the extended array of the molecules.

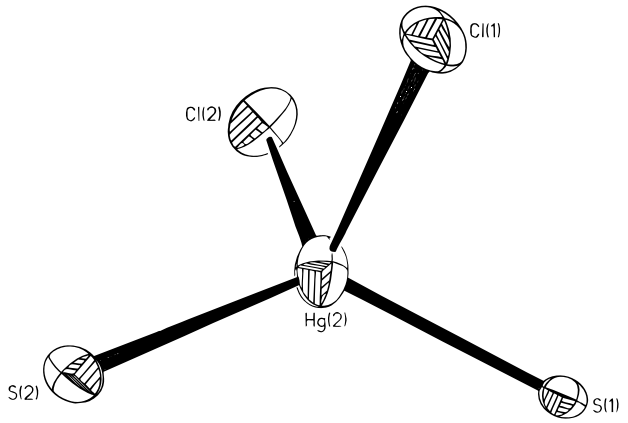


Figure 8. Detail of tetrahedral atomic coordination present around Hg(2) in $[ClHg(S\text{-}neo\text{-}Pent)\cdot 0.5Py]_\infty$.

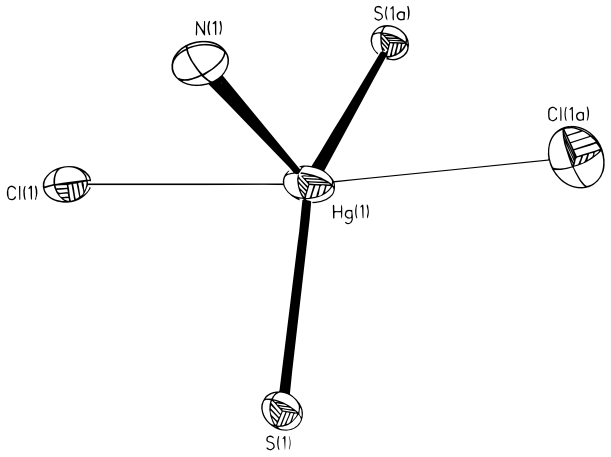


Figure 9. Detail of trigonal bipyramidal atomic coordination present around Hg(1) in $[ClHg(S\text{-}neo\text{-}Pent)\cdot 0.5Py]_\infty$.

other mercury thiolate complexes (2.32−2.43 Å).[2] The separation between Hg(2)−Cl(1) (2.69 Å) is considerably longer than that observed for Hg(2)−Cl(2) (2.47 Å). This presumably is due to the presence of the additional interaction of Cl(1) to Hg(3) and Hg(1) (Figure 4, narrow lines in ORTEP). Atom Hg(2) possesses a coordination number of four, with a tetrahedral (average angle = 108.2°) array of two sulfur and two chlorine atoms.

ClHgSBz·TMEDA. The compound is a monomer and the coordination sphere around the mercury atom is a distorted tetrahedron (Figure 5). The Hg−S distance (2.35 Å) is in the range observed for the other complexes

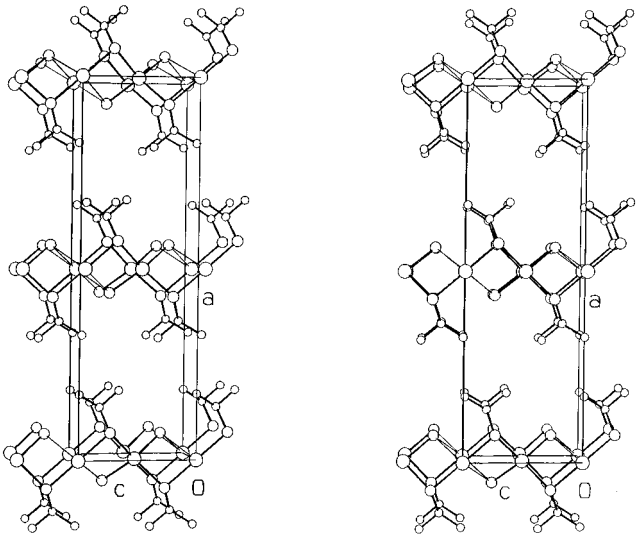


Figure 10. Stereoview of the unit cell of $[ClHgS\text{-}iso\text{-}Pr]_\infty$, showing the two-dimensional planes formed by intermolecular accretion of the two formula units $[Hg(S\text{-}iso\text{-}Pr)_2]$ and $HgCl_2$.

described herein. The Hg−Cl distance (2.39 Å) (Table 2) is shorter than the analogous distances in $[ClHgS\text{-}iso\text{-}Pr]_\infty$ or $[ClHg(S\text{-}neo\text{-}Pent)\cdot 0.5\ Py]_\infty$. This is explained by noting that the chlorine atom in ClHgSBz·TMEDA is interacting exclusively with one mercury atom, while each of the chlorine atoms in the other chloromercury thiolate compounds discussed herein are involved in secondary, bridging interactions between two metal centers, thereby resulting in an observation of an elongation of the distance (2.47−3.29 Å).

$[Hg(SBz)_2]_\infty$. The compound forms a polymeric chain $[Hg(SBz)_2]_\infty$ by intermolecular Hg−S interactions (Hg−S(2a) 3.25 Å; Hg−S(1a) 3.39 Å) (Figures 6 and 7). The chains are connected to each other by short Hg−S interactions (Hg−S(1b) 3.15 Å) leading to the formation of a double chain structure (Figure 7). The coordination environment around the mercury atom is best described as a distorted trigonal bipyramid. The Hg−S distances [Hg−S(1) 2.34 Å; and Hg−S(2) 2.39 Å] are almost identical with those observed in ClHgSBz·TMEDA and are in the range reported for other comparable compounds.[20,21] The angle S(1)−Hg−S(2) is close to 180°, a value observed in many mercury bis(thiolate) com-

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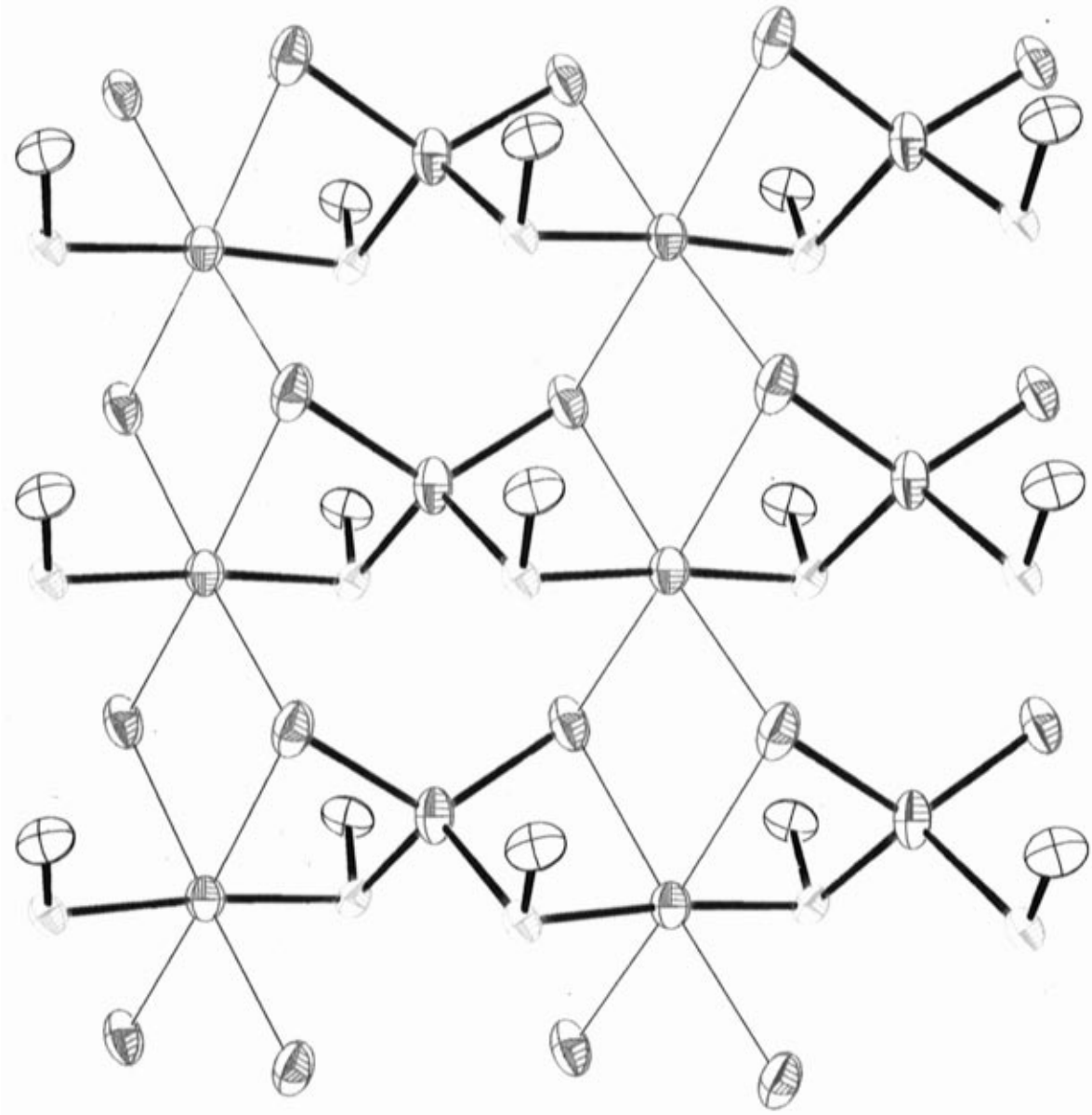

Figure 11. Representation of the layered nature of $[ClHgS\text{-}iso\text{-}Pr]_\infty$ by a partial view of the extended solid-state structure. Key: purple, mercury; green, chlorine; yellow, sulfur; white, ipso-carbon of iso-Pr groups; terminal methyl groups and all hydrogen atoms have been omitted for clarity in viewing of the presentation.

pounds[20,21] and, indeed, in numerous homoleptic divalent mercury compounds in general.[22]

Comments

Atom Hg(2) in $[ClHg(S\text{-}neo\text{-}Pent)\cdot 0.5Py]_\infty$ has a geometry almost identical with that of Hg(2) in $[ClHgS\text{-}iso\text{-}Pr]_\infty$, both being pseudo-tetrahedral (Figure 8). However, the localized geometry around each of the remaining independent mercury atoms for each structure is quite different. While Hg(1) in $[ClHg(S\text{-}neo\text{-}Pent)\cdot 0.5Py]_\infty$ has near TBP geometry, Hg(1) in $[ClHgS\text{-}iso\text{-}Pr]_\infty$ is almost octahedral. The axial arrangement of the two chlorine atoms is completed with two equatorial sulfur atoms and the nitrogen atom of pyridine for $[ClHg(S\text{-}neo\text{-}Pent)\cdot 0.5Py]_\infty$ (Figure 9). An equatorial complement of four chlorine atoms is offset by axial positioning of the two sulfur atoms in $[ClHgS\text{-}iso\text{-}Pr]_\infty$ (Figure 3).

The two-dimensional nature of $[ClHgS\text{-}iso\text{-}Pr]_\infty$ may be gleaned by study of the stereoview of the unit cell (Figure 10). This correlates well with the formation of Hg_2Cl_2 upon thermolysis of the compound. The interlayer connectivities are portrayed as thin lines, while the intralayer connectivities are represented by bold lines to demonstrate the clear layering of this solid-state structure (Figure 11).

The chainlike nature of $[ClHg(S\text{-}neo\text{-}Pent)\cdot 0.5Py]_\infty$ differs substantially from the individual chains present in $[ClHgS\text{-}iso\text{-}Pr]_\infty$. In the absence of an additional Lewis base, the regular ordered array of mercury atoms may be described best by a comb configuration off of a central backbone, with all pendant units pointing in the same direction. The zigzag arrangement (Figure 12) arises upon incorporation of a monodentate Lewis base within the structural formula.

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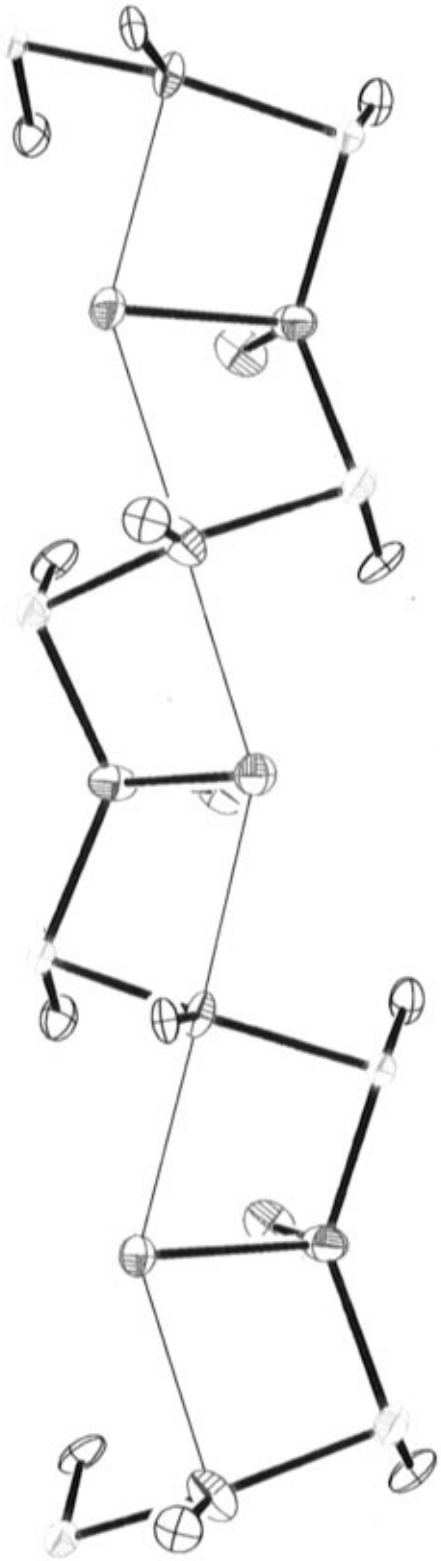

Figure 12. Representation of the zig-zag nature of the structure of [ClHg(S-neo-Pent)·0.5Py]$_\infty$ by a partial view of the extended solid-state structure. Key: purple, mercury; green, chlorine; yellow, sulfur; blue, nitrogen; white, methylene carbon of neo-Pent groups. All hydrogen atoms and terminal alkyl groups have been omitted for clarity in viewing of the presentation; π-ring atoms on pyridine also omitted.

Conclusion

Chloromercury thiolate compounds have been characterized structurally, and the thermal decomposition of these species has been studied. Upon scrutiny of the solid-state motifs displayed by the four compounds structurally characterized in the present single crystal X-ray diffraction investigations, a few universal themes emerge. In the absence of any additional Lewis base, chloromercurythiolate compounds aggregate into infinite sheetlike structures (Figure 3). When a monodentate Lewis base is added, the 2D planes undergo dimensional reduction to form 1D chains (Figure 4). Once chelated with a difunctional Lewis base, a monomeric species results (Figure 5).

Table 4. Volatile Decomposition Products Obtained from the Thermolysis of ClHgS-iso-Pr As Determined by GC/MS

obs mass	abundance	assignment
150 amu	81.4%	iso-PrSS-iso-Pr
182 amu	17.3%	iso-PrSSS-iso-Pr
214 amu	1.3%	iso-PrSSSS-iso-Pr

Table 5. Interatomic Hg−Cl and Hg−S Distances [Å]

compound	Hg−Cl	Hg−S
[ClHgS-iso-Pr]$_\infty$	3.07	2.36
	3.29	
	2.50	
[ClHg(S-neo-Pent)·0.5 Py]$_2$	2.69	2.43
	2.47	2.42
ClHgSBz·TMEDA	2.39	2.35

A comparison of the localized coordination environment present around mercury atoms can be derived (Table 5). The observed geometry of the nearest neighbors ranges from linear (Figure 6) to octahedral (Figure 3), with intermediate examples of tetrahedral (Figures 8 and 11) and trigonal bipyramidal (Figure 9). Thus, as a function of the presence of added external Lewis base, the degree of catenation is reduced, while the metal coordination sphere is observed to portray a diversity of atomic arrays.

The polymeric chloromercuryalkylthiolate compounds which display strong Hg−Cl interactions in their molecular structure decompose to form Hg_2Cl_2, while the absence of these interactions appears to encourage the formation of HgS. A further correlation may be drawn to relate the thermolytic reaction products (HgS or Hg_2Cl_2) with the solid-state structure for chloromercury thiolate compounds. To a first order, the best data fit appears to be related to the stability of the radical formed upon cleavage of the R−S bond (BDE, in kcal/mol for R−H: Ph_3C, <60; Bz, 78; iso-Pr, 94; neo-Pent, 97).[23] This is reinforced by noting that coordinated Lewis bases are lost in the early stages of thermolyses. Noteworthy, TGA data support the identity of the penultimate reaction product in each case as decomplexed ClHgSR. The identified volatile decomposition product distributions also suggest that radical species are formed during the thermolyses. Thus, the decomposition pathway is not only a function of the solid-state molecular structures of the precursors but also, and maybe even more importantly, a function of the stabilities of the radical species prepared during the thermolytic decomposition. By introducing organic groups forming relatively stable radicals, the decomposition route can be designed for the favorable formation of HgS. In the extreme case of chloromercury triphenylmethylthiolate the high stability of the triphenylmethyl radical leads to a spontaneous cleavage of the C−S bond at ambient temperature, thus ensuring the predestined

(23) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 2nd ed.; Allyn and Bacon: Boston, 1966.

formation of moderately crystalline HgS under relatively mild conditions. Exertion of such control over the structure of products prepared via gentle synthetic schemes is an example of the principles of molecular design of materials. Additional examples of these concepts are undergoing active investigations in these laboratories and will be reported in due time.

Acknowledgment. The authors gratefully acknowledge financial support of this project from ONR (W.S.R.) and DFG (G.K., B.N.). The project was initiated while the authors were at FSU, and MARTECH is acknowledged for access to certain analytical facilities.

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