Mercury(II) 2-Aminoethanethiolate Clusters: Intramolecular Transformations and Mechanisms

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The combination of HgF₂ and 2-aminoethanethiol (AET, with some AET-HCl present) yielded a cyclic tetranuclear thiolate, [H₄Cl₄(SCH₂CH₂NH₃)₄] (1), with alternating Hg and S atoms. The Cl from the reaction mixture led to the formation of Hg–Cl bonds with no Hg–F in the final product. In contrast, similar reactions with HgBr₂ yielded a nonanuclear cluster, [H₃Br₃(SCH₂CH₂NH₃)₃] (2), and the disulfide salt ([H₄Br₄][NH₄(H₂SCH₂S–H)] (3). Despite similar reactions, the AET groups in 2 are protonated compared to the nonprotonated amine groups in 1, which allows the ligand to chelate the Hg atom in the latter compound. The reaction with HgI₂ yielded a cyclic tetranuclear compound, [H₄I₄(SCH₂CH₂NH₂)₄(SCH₂CH₂NH₃)₂(H₂O/EtOH)] (4), containing protonated and nonprotonated AET groups. Compound 4 at room temperature irreversibly rearranges to [H₄I₄(SCH₂CH₂NH₂)₄] (5), which is isosstructural to 1. A systematic pathway for the formation of 1 along with the intramolecular conversion of 4 to 5 is proposed. These compounds demonstrate that very diverse Hg–S compounds form under similar reaction conditions.

Introduction

Mercury thiolates have received much attention in the last few decades because of their importance in biological Hg toxicity. Mercury thiolates have been implicated in the detoxification of Hg by metallothioneins, DNA binding proteins, and mercury reductase. Homoleptic mercury(II) thiolates adopt discrete molecular as well as polymeric structures with bridging S atoms. On the other hand, heteroleptic mercury(II) thiolates usually adopt discrete molecular as well as polymeric structures containing bridging S atoms. However, higher nuclearity heteroleptic mercury(II) thiolates are fairly common and include (Ph₄P)[(μ-SEt)(μ-Br)[HgBr₄]₄], (Et₄N)[(μ-1)(μ-SPr')(HgI₂)], (Bu₄N)₂[H₄(SR)₂X₄] (R = SEt, SPr), [H₄(SCH₂)₂N(CH₃)₂]₃X₄], and [H₄(SC₆H₄)₂]₃X₄], where X = Cl, Br, or I. The structures of heteroleptic mercury(II) thiolate clusters are usually independent of the halide present; however, the geometry around Hg is affected by the type of halide. For instance, the deviation from the tetrahedral geometry in [Hg(SR)₂X₂] is more pronounced for Cl than for Br and I, which has been attributed to a vibronic coupling mechanism with d-orbital involvement. The deformation is more evident in the Cl than the I derivatives because of the smaller difference in donor strength between S and Cl.

Despite the strong bonds between Hg and S, mercury(II) thiolates are typically labile and undergo ligand exchange, which is more pronounced in low-(two- and three-)coordinate compounds. Intra- and intermolecular exchange leads to the formation of complicated structures because the energy barrier for the exchange is low and often influenced by the nature of the solvent and the counterions. Intermolecular...
exchange induced by the addition of an external reagent or a change in the reaction conditions has been reported for few heteroleptic mercury(II) thiolates. For instance, the addition of excess Na$_2$S$_2$ to trinuclear [Ph$_4$P][Hg$_2$(SCH$_2$CH$_2$S)$_3$] yields polymeric $\{[\text{Ph}_2\text{P}][\text{Hg}_2(\text{SCH}_2\text{CH}_2\text{S})]\}_n$. Similarly, polymeric [HgCl$_2$(SCH$_2$CH(NH$_3$)COO)] in hot water rearranges to the linear bisthiolate [Hg(SCH$_2$CH(NH$_3$)COO)$-$(SCH$_2$CH(NH$_3$)COOH)]. Most probably by dissociation followed by rearrangement.

Here we report the syntheses of mercury(II) thiolates containing an S/N ligand and proposed mechanistic pathways for the intramolecular ligand exchanges observed in the compounds. Because of the structural similarity between AET and L-cysteine, this exchange might be of importance in understanding how Hg$^{II}$-L-cysteine bonds are made and broken in biological systems. Also, the exchange might be useful in understanding the conversion of heteroleptic mercury(II) thiolates (RSH$_2$X) to homoleptic mercury(II) thiolates [Hg(SR)$_2$] in biological systems.

Experimental Section

General Procedure. All reactions were carried out at room temperature in deionized water under N$_2$. The reagents 2-aminooethanethiol hydrochloride (TCI America), HgF$_2$ (Aldrich), HgBr$_2$ (Mallinckrodt), and HgI$_2$ (Alfa Aesar) were used as received.

2-Aminoethanethiol (AET) was obtained from the recrystallization of precipitate from water. Yield (crystals + ppt): 0.66 g (10%). Mp: 170–172 °C (dec). $^1$H NMR (DMSO-d$_6$, 200 MHz, ppm): $\delta$ 2.91–2.93 (m, 4H, NCH$_3$), 3.82 (2H, NH$_2$). $^1$C NMR (DMSO-d$_6$, 200 MHz, ppm): $\delta$ 30.9 (CH$_3$), 41.8 (CH$_2$N), IR/Raman (KBr, v/cm$^{-1}$): 3444, 3242, 3157, 2966, 1627, 1592, 1421, 1386, 1021, 916, 468, 483, 345, 280, 225, MS (EI, +ve): 311 ([M$^+$]), 279 ([311 - S$^-$]), 265 ([279 - CH$_3$$^+$]), 251 ([265 - CH$_3$$^+$]), 235 ([251 - NH$_3$$^+$]), 200 ([235 - Cl$^-$]), 76 ([SCH$_2$CH$_2$NH$_3$]). Anal. Calcd for Hg$_2$(SCH$_2$CH$_2$N$^+$)H$_2$: C, 7.694; H, 1.937; N, 4.480. Found: C, 7.793; H, 1.986; N, 4.450.

Synthesis of [HgBr$_2$(SCH$_2$CH(NH$_3$)COO)] (1). AET (10 mmol, 0.77 g) was dissolved in deionized water (70 mL) under a flow of N$_2$; to this was added HgBr$_2$ (5 mmol, 1.19 g) as a suspension in methanol (30 mL), and the resulting solution was stirred for 48 h. The resulting white precipitate was filtered, washed with deionized water and methanol, and dried. The filtrate at room temperature yielded X-ray-quality crystals. Colorless crystals could also be obtained from the recrystallization of precipitate from water. Yield (crystals + ppt): 0.66 g (10%). Mp: 170–172 °C (dec). $^1$H NMR (DMSO-d$_6$, 200 MHz, ppm): $\delta$ 2.91–2.93 (m, 4H, NCH$_3$), 3.82 (2H, NH$_2$). $^1$C NMR (DMSO-d$_6$, 200 MHz, ppm): $\delta$ 30.9 (CH$_3$), 41.8 (CH$_2$N), IR/Raman (KBr, v/cm$^{-1}$): 3444, 3242, 3157, 2966, 1627, 1592, 1421, 1386, 1021, 916, 468, 483, 345, 280, 225, MS (EI, +ve): 311 ([M$^+$]), 279 ([311 - S$^-$]), 265 ([279 - CH$_3$$^+$]), 251 ([265 - CH$_3$$^+$]), 235 ([251 - NH$_3$$^+$]), 200 ([235 - Cl$^-$]), 76 ([SCH$_2$CH$_2$NH$_3$]). Anal. Calcd for Hg$_2$(SCH$_2$CH$_2$N$^+$)H$_2$: C, 7.694; H, 1.937; N, 4.480. Found: C, 7.793; H, 1.986; N, 4.450.

Synthesis of [HgBr$_2$(SCH$_2$CH$_2$N$^+$)H$_2$] (2). AET (10 mmol, 0.77 g) was dissolved in deionized water (70 mL) under a flow of N$_2$; to this was added HgBr$_2$ (5 mmol, 1.8 g) as a suspension in methanol (30 mL), and the resulting solution was stirred for 48 h. The resulting white precipitate was filtered, washed with deionized water and methanol, and dried (1.74 g). Recrystallization of the precipitate from water yielded crystals of [HgBr$_2$(SCH$_2$CH$_2$N$^+$)H$_2$] (2). Colorless crystals of 3 were obtained from the supernatant at room temperature. Crystalline yield: 0.37 g (10%). Mp: 225–227 °C (dec). $^1$H NMR (DMSO-d$_6$, 200 MHz, ppm): $\delta$ 2.99 (t, 2H, CH$_3$), 3.10 (t, 2H, CH$_2$N), 7.92 (b, 3H, NH$_3$). $^1$C NMR (DMSO-d$_6$, 200 MHz, ppm): $\delta$ 33.9 (CH$_3$), 42.9 (CH$_2$N), IR/Raman (KBr, v/cm$^{-1}$): 3440, 3009, 2718, 1634, 1588, 1475, 1456, 1382, 819, 765, 656, 466, 165. Anal. Calcd for HgBr$_2$(SCH$_2$CH$_2$N$^+$)H$_2$: C, 7.122; H, 2.092; N, 4.153. Found: C, 7.099; H, 2.046; N, 4.145.

Synthesis of [Hg$_4$L$_2$(SCH$_2$CH$_2$N$^+$)H$_2$] (4). To a stirring solution of AET (10 mmol, 0.77 g) in deionized water (70 mL) was HgI$_2$ (5 mmol, 2.27 g) dissolved in ethanol (30 mL), and the resulting solution was stirred for 3 days.

The light-yellow precipitate was removed by filtration, washed with water and ethanol, and vacuum-dried. The supernatant cooled to 4 °C yielded light-yellow crystals. Yield (crystals) and C, 6.218; H, 1.617; N, 2.900. Found: C, 6.199; H, 1.596; N, 3.011 (crystals) and C, 6.189; H, 1.560; N, 3.017 (precipitate).

**Result and Discussion**

The combination of AET with HgF₂ in a mixture of deionized water and methanol (70:30) yielded 1 in low yield, where the Cl originated as an impurity in AET (AET contained a small amount of AET-HCl). A similar reaction with HgBr₂ precipitates a nonanuclear compound, \([\text{Hg}_9\text{Br}_{15}(\text{SC}_2\text{H}_4\text{NH}_3)_3]^{2+}\) (2), which was reported previously. However, the supernatant at room temperature yielded colorless crystals of 3. A similar reaction with HgI₂ in a mixture of water and ethanol (70:30) yielded a light-yellow precipitate of 4. The light-yellow crystals of 4, obtained from the supernatant at 4 °C, irreversibly yielded \([\text{Hg}_4\text{I}_6(\text{SC}_2\text{H}_4\text{NH}_3)_3]^{2+}\) (5) at room temperature. Compound 5 could also be obtained from the direct combination of HgI₂ and AET·HCl in the presence of an equivalent amount of NaOH. The conversion of 4 to 5 at room temperature did not occur in DMSO as shown in \(^{199}\text{Hg}\) NMR. The conversion of 5 to 4 is not observed in either water or DMSO. The reactions are summarized in Scheme 1.

Crystallographic data for structural analysis of compounds 1, 3, and 4 have been deposited with the Cambridge Crystallographic Data Center as CCDC Nos. 606889, 606890, and 606891, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (phone +44 1223 336408; fax +44 1223 336033).

**Spectroscopy.** The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra for compounds 1, 3, and 4 indicate symmetrical solution structures.

In the ¹H NMR, the peaks for the SCH₂ protons in 1 and 4 show slight downfield shifts from the free ligand (2.69 ppm) due to the presence of the Hg–S bonds. Despite the Hg–N bonds, the NCH₂ protons do not show significant shifts in 1 and 4. For 3, the peak for the ammonium group is observed at 8 ppm. In the ¹³C NMR for 1, the peak due to C–S is observed at 29 ppm, similar to that observed in 5. However, in 4, this peak is slightly downfield and appears at 32 ppm. The peak for C–N in both 1 and 4 appears at 41 ppm and is comparable to that of 5 (42 ppm). In the ¹⁹⁹Hg NMR spectrum of 1, a single broad peak is observed at ~704 ppm, indicating a tetrahedral coordination environment around Hg. The coupling between Hg and N atoms is responsible for the broadness of the peak. A similar broad peak is observed in 3, indicating a tetrahedral coordination environment around Hg.

The broadness of the peak could be attributed to the strained S/N chelate (Hg1–S2) (~659 ppm). The ¹⁹⁹Hg NMR for 4 in DMSO-δ6 shows two distinct peaks at ~2983 and ~1928 ppm, which could be assigned to [HgI₂S₂] and [HgIS₂N] coordination environments, respectively. The deshielding present in the first peak is due to the presence of two Hg–I bonds (free HgI₂ = ~3435 ppm). Despite a [HgIS₂N] environment similar to that in 5, a broad peak around ~600 ppm is not observed in 4. Such upfield shielding in [HgIS₂N] could be attributed to the strained octagonal ring in 4 compared to 5 (Figure 4).

The IR spectra for 1 and 4 are quite similar, with the absence of the –SH peak around 2500 cm⁻¹. A weak peak observed at 600 cm⁻¹ in 3 indicates the presence of the disulfide group. In 1 and 4, peaks in the range 3000–3400 cm⁻¹ could be assigned to symmetric and asymmetric –NH₂ stretches. In 3, peaks around 2900 and 1400–1500 cm⁻¹ could be assigned to symmetric –NH₃ stretches and symmetric deformation and degenerate deformation modes, respectively. Similar peaks are also observed for 4 because of the presence of both –NH₂ and –NH₃ groups. In the Raman spectra, symmetric and asymmetric stretching frequencies for Hg–S are observed around 250 and 340 cm⁻¹ for 1 and 289 and 345 cm⁻¹ for 4 (see the Supporting Information). In both 1 and 4, the stretch due to Hg–N could be assigned to peaks around 483 and 460 cm⁻¹, respectively, and are in the range observed for mercury(II) thiocyanates with Hg–N bonds (400–700 cm⁻¹).

The stretch around 220 cm⁻¹ in 1 could be assigned to the Hg–Cl bond, which is in accord with the stretch observed in mercury(II) thiocyanates with terminal Cl atoms (220–235 cm⁻¹). In 3, the stretch due to terminal Hg–Br appears at 165 cm⁻¹, close to that observed in [HgBr₃]²⁻ (150 cm⁻¹). The terminal Hg–Cl frequency for 4 can be assigned to the peak observed around 129 cm⁻¹, which is similar to that observed in 5 (127 cm⁻¹) as well as frequencies reported in the literature.

**Figure 1.** Structure of 1. H atoms are not shown for clarity.

Mercury(II) 2-Aminoethanethiolate Clusters

Å and Hg2–S2 = 2.468 Å) are longer compared to the nonchelate Hg–S bonds (Hg1–S2″ = 2.408 Å and Hg2–S1 = 2.412 Å; Table 2). This is due to the strain in the five-membered ring. These distances, in general, fall in the range observed for tetrahedral mercury(II) thiolates (2.410–2.606 Å). However, the distances are much shorter than the corresponding distances observed in polymeric [HgCl(SCH2CH2NH2)2]n (6) (2.652 Å), which contains a similar Hg environment, namely, an S/N chelate and bridging S and terminal Cl atoms. The shorter bonds in 1 imply a stable cyclic structure compared to the open chain observed in 6. Compound 1 is closely related to [Hg6Cl4(S(CH2)2-NMe2)4] (7), which contains an octagonal ring and five-membered S/N chelates. However, two independent Hg centers are observed in 7, with HgS2Cl2 and HgS2N2 coordination environments. The average Hg–S distances in 7 (2.414 Å) are intermediate to those observed in 1. In 1, the Hg–N distance associated with Hg1 (2.293 Å) is much shorter compared to the corresponding distance associated with Hg2 (2.449 Å), indicating a stronger bond associated with Hg1. Despite similar environments, the difference in the Hg–N bonds in 1 (0.156 Å) is much larger compared to those in 6 (0.009 Å) and 7 (0.042 Å). Unsymmetrical bonds in mercury(II) thiolates are not unusual and provide overall synergic stability to the molecule. The terminal Hg–Cl distances (2.686 and 2.656 Å) in 1 are smaller than those observed in 6 (average 2.718 Å) but comparable to those in mercury(II) thiolates containing terminal Cl atoms (2.58–2.81 Å).

The S–Hg–S angles spanning Hg1 (132°) and Hg2 (146°) are in accordance with the corresponding angles observed for 6 (125°–137°) but shorter compared to the most obtuse S–Hg–S angle observed in 7 (163°). The latter is most probably due to a symmetrical environment around Hg. The S–Hg–N chelate angles spanning Hg1 and Hg2 (average 81°) are similar to those observed for 6 (81°) and 7 (82°) despite the considerable differences observed in the bond distances. The Hg–S–C angles in the chelate are similar for 1 (average 94°) and 6 (average 94°) but more narrow than that for 7 (103°), indicating a more strained five-membered ring in the previous two compounds.

Compound 2 has been described previously in detail. The nonnuclear cluster consists of four independent Hg centers, namely, HgS2(μ-Br)2, HgS2(μ-Br)Br, HgSBr2, and HgS2Br with variable geometry around the Hg atoms. As shown in Figure 2, the structure of 3 consists of [HgBr2]2− and a disulfide of two AET molecules containing ammonium groups. It is interesting to observe that the environment around Hg is distorted tetrahedral with Br–Hg–Br angles in the range 99°–126°, rather than perfectly tetrahedral, as might have been expected. This distortion can be attributed

similarly to that of $5$ compared to that of $4$. The Hg-1 distances associated with the HgS$_2$I$_2$ units are unsymmetrical (average 2.837 Å) and longer compared to the sum of covalent radii of tetrahedral Hg and I (2.81 Å). The angles associated with the HgS$_2$I$_2$ unit (107°–110°) show less distortion from ideal tetrahedral geometry compared to those associated with the HgIS$_2$N unit (82°–135°). The distortion in the HgIS$_2$N unit is due to the formation of the five-membered chelate. The S1–Hg2–S1′ angle in 4 (136°) is more linear compared to the corresponding angle observed in 5 (123°), due to the unsymmetrical environment around Hg2.

**Intermolecular Interactions.** The shortest Hg- - -Hg interactions observed in 1 and 4 are those observed between Hgl and Hg2 [3.782 Å (1) and 3.924 Å (4)]. These distances indicate no mercurophilic interaction and are in the range usually observed for heteroleptic mercury(II) thiolates (3.648–3.852 Å). Despite having similar octagonal frameworks, the Hg- - -Hg interactions are variable and shorter for 1 compared to those observed in 4 and 5 (average 3.901 Å).

The individual molecules in 1, 3, and 4 are connected through weak intermolecular H bonding involving N and X (Cl, Br, or I), yielding a unidirectional chain (see the Supporting Information). The NH- -Cl distances (average 3.4 Å) in 1 are comparable to those in 6 (average 3.4 Å) but smaller than those observed in [HgCl$_2$(μ-S(CH$_2$)$_2$)NH(CH$_3$)$_3$] (3.15 Å) and [HgCl$_2$(C$_3$H$_2$N)$_2$] (average 3.154 Å). The NH–I (average 3.60 Å) distances in 3 are shorter compared to those observed in 5 (average 3.80 Å) but in the range observed for [HgI$_2$(SR)$_2$] compounds [SR = benzo-$1,3$-imidazole-2-thione (average 3.59 Å); 1-methyl-imidazoline-2(3H)-thione (average 3.59 Å)]. In contrast to 1, weak NH- -S interactions are observed in 3 (3.70 Å) and 4 (3.55 Å). These distances are comparable to tetrahedral mercury(II) thiolates with similar interactions (3.39–3.73 Å). The nonplanarity of the octagonal ring in both 1 and 4 is most probably due to the weak interactions as well as the steric effects of the halide. As shown in Figure 4, the deformation observed in the chair configuration acquired by 1 is more distinct compared to that of 4 or 5. This is most probably due to the symmetrically packed I atoms, resulting in restricted vibrational motion in the crystal.

**Mechanistic Pathways.** A mechanistic pathway for the formation of 1 (Scheme 2) and 4 (Scheme 3) can be proposed similarly to that of 5. Because of more ionic character, HgF$_2$ will dissociate completely and the free Hg$^{2+}$ react with AET to form a two-coordinate intermediate [Hg(S/N)]$^+$. This intermediate can further combine with either F$^−$ or a second I equiv of AET to form [HgF(S/N)] and [Hg(S/N)$_2$], respectively. However, the formation of an Hg–F bond is highly unlikely because of the mismatch in soft Hg$^{2+}$ and hard F$^−$ ions. The formation of [Hg(S/N)$_2$] has been reported from less polar solvents without the presence of halide ions. Hence, it can be argued that the structure adopted by a mercury(II) thiolate cluster depends on the halide present in the solution. The three-coordinate intermediate [Hg(S/N)$_2$Cl] is not known to exist because it is highly unstable and readily forms a four-coordinate compound. This is achieved by the formation of an additional Hg–S bond in preference to an Hg–Cl bond, which is evident from the bond energies (Hg–S = 217 kJ/mol and Hg–Cl = 100 kJ/mol). The [HgCl(S/N)] species can react sideways to form polymeric or rearrange to form a cyclic structure (1). The formation of a cyclic cluster is preferred over the linear polymeric chain to achieve overall stability, which is also evident from the shorter bridging Hg–S bonds observed in the former compound.

In the formation of 4, the first step involves the two three-coordinate intermediates, [HgI$_2$(SR)$_2$] and [HgI(S/N)]. This is possible because of the presence of AET as a zwitterion in solution. The [HgI$_2$S] intermediate has been reported
earlier for mercury(II) thiolates containing relatively large ligands such as 1,3-thiazolidine-2-thione and 1,3-imidazole-2-thione. Similarly, [HgIS/N] intermediates have been reported in solution for mercury(II) thiolates with S/N chelates. The stability around the three-coordinate intermediate is achieved by forming a stable fourth bond, Hg−S bridging, in preference to an Hg−I bond (bond energies 217 and 35 kJ/mol, respectively), similar to that observed for [Hg(S/N)Cl] in 1. This is evident from the crystal structure, where the bridging Hg−S bond is shorter than the chelated Hg−S bond. For the formation of 4, the [HgI(S/N)] intermediate combines with the [HgI2S] intermediate to form the dinuclear species, [HgI(S/N)]2+. The intramolecular conversion of 4 to 5 can be postulated to proceed through either three- or five-coordinate intermediates, namely, [HgIS2]+ or [HgI2S2N]3−. The H+ in the solution removes I from the [HgI2S2] unit to form an [HgIS2]−, a three-coordinate intermediate. This might be due to the longer Hg−I bond associated with the [HgI2S2] unit compared to the [HgI(S/N)] unit. The −NH3 groups are deprotonated to form −NH2 through nucleophilic attack of OH−, which is a better nucleophile in the presence of HI. The fourth coordination around Hg is further completed by the formation of an Hg−N bond to form [HgIS2N]2−, a five-coordinate intermediate. In the next step the H+ in the solution removes I from the [HgI2S2N]2− intermediate to form [HgIS2N]− and yield 5. The transformation through a five-coordinate intermediate is more likely because Hg can increase its coordination, and the transformation proceeds via a dissociative mechanism.

Conclusion

Novel mercury(II) thiolate clusters have been synthesized and characterized. A mechanistic pathway for the formation of these clusters through low-coordinate mercury(II) thiolate intermediates is proposed. The intramolecular exchange observed in 4 to 5 is the first for a mercury(II) thiolate, where the ligand exchange is observed in four-coordinate Hg without varying the reaction conditions. This exchange process has been reported earlier but with variable counteranions and varying reaction conditions. This exchange might be useful in understanding the conversion of heteroleptic mercury(II) thiolates to homoleptic mercury(II) thiolates in

\[ \text{Scheme 3. Systematic Pathway for the Formation of 4 along with the Intramolecular Transformation to 5} \]
biological systems. One important conclusion from this work is the structure-directing influence of the halide in these systems, a feature that had not been identified in the previous literature.

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Supporting Information Available: Syntheses, characterization information, additional figures, extensive tables, thermograms, crystal data, and $^{199}$Hg NMR of 1 and 4. This material is available free of charge via the Internet at http://www.pubs.acs.org.