

Mercuriphilic interaction in novel polynuclear Hg(II)–2-aminoethanethiolates†

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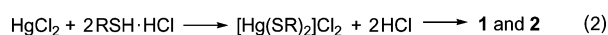
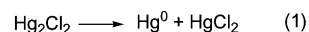
The reaction of 2-aminoethanethiol hydrochloride with Hg₂Cl₂ in water yielded elemental mercury and one-dimensional polynuclear compounds [$\{\text{Hg}_2\text{Cl}_2(\text{SCH}_2\text{CH}_2\text{NH}_3)_3\}\text{Cl}\}_n$ (**1**) and $[\text{HgCl}(\text{SCH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2]_n$ (**2**). The coordination environment around Hg in **1** and **2** is quite variable despite similar reaction conditions. The formation of a five-membered S/N chelate in **2** can be attributed to the use of base to produce a neutral ligand. Three independent types of Hg atoms, both three- and four-coordinate are observed in **1**, whereas in **2**, the Hg atom is tetra-coordinate with S, N and Cl atoms in the primary coordination sphere. Despite distinct structural chemistry, the coordination environments in **1** and **2** are fairly similar with repeating units connected with bridged thiolate S atoms in addition to a terminal Cl attached to Hg. Intermolecular hydrogen-bonding involving amine protons, Cl and water molecules are responsible for a three-dimensional network in both **1** and **2**. A short Hg...Hg distance of 3.564 Å, indicates the presence of a mercuriphilic interaction in **1**. The compounds have been characterized by ¹H and ¹³C NMR, UV-Vis, FT-IR, Raman, mass spectrometry, TGA and single X-ray crystallography.

Introduction

The extreme toxicity of mercury, in its many forms, makes an understanding of the element's coordination chemistry of paramount importance. The organic form of mercury (RHg⁺) is the most problematic due to its bioaccumulation in the food chain. Among the inorganic forms, elemental mercury (Hg(0)) and divalent mercury (Hg(II)) are of toxicological nature. On the other hand the biological affect of mercurous mercury (Hg(I)) is not known, likely due to its redistribution to Hg(II) and Hg(0). However, it has been proposed that Hg(I) may be an intermediate in the redox transformation between Hg(0) and Hg(II) in the body.¹

Mercury-thiolates have attracted much attention in the last few decades because of their importance in the detoxification of mercury by metallothionein,² in a DNA binding-protein,³ and in mercury reductase and related proteins.⁴ Homoleptic mercury-thiolates adopt discrete molecular as well as polymeric structures.⁵⁻⁷ In contrast, heteroleptic mercury-thiolates (containing both thiolate and halide) are generally polymeric.⁸ The stability of the products from the reaction of Hg²⁺ with thiolates leads to the formation of various compounds with similar energy.⁹ Despite the strength of the Hg–S bond many thiolates remain labile and can undergo redistribution.^{10,11} This may be the reason why cysteine alone is not sufficient for detoxification in living systems. In contrast to Hg(II), the reactions of Hg(I) with thiols are practically unknown. The only reference to date describes the formation of a number of bis(organothiolato)mercury(II) complexes.¹² The mechanism proposed indicated that Hg(0), from Hg(I) reacts with disulfide to produce mercury(II)-bis(thiolates).¹³

Here we report the formation of polynuclear Hg(II)-thiolates, when Hg₂Cl₂ is combined with 2-aminoethanethiol in de-ionised (DI) water. The following mechanism is proposed (Scheme 1), as the intermediate $[\text{Hg}(\text{SR})_2]\text{Cl}_2$ ¹⁴ can be obtained from the solution, as soon as the formation of Hg(0) is observed.



Scheme 1 Proposed mechanism for the formation of polynuclear compounds *via* mercury(II)-bis(thiolate).

Compounds **1**, **2** as well as the intermediate can also be obtained by direct addition of HgCl₂ to 2-aminoethanethiol.¹⁵ The compounds were studied by solution NMR, IR and Raman, EI-MS, UV-Vis, TGA and X-ray crystallography.

Experimental

All reactions were carried out at room temperature in deaerated DI water under a flow of nitrogen gas. The ligand 2-aminoethanethiol hydrochloride (TCI America) was dried under vacuum prior to use. The purity was checked by iodometric titration and found to be 99.56 ± 40%. The reagent Hg₂Cl₂ (Fischer Scientific) was used as received. ¹H and ¹³C NMR data were obtained with JEOL-GSX-400 and 270 instruments operating at 200 MHz using d₆-DMSO as a solvent and tetramethylsilane as reference. The IR data were recorded as KBr pellets on a Mattson Galaxy 5200 FT-IR instrument between 400–4000 cm⁻¹. Mass spectral (EI-MS) data were obtained at the University of Kentucky Mass Spectrometry Facility. Raman spectroscopy of the solid samples used a Nicolet FT-Raman 906 Spectrometer ESP between 100–800 cm⁻¹ in the Center for Applied Energy Research at the University of Kentucky. The UV-Vis studies used an Agilent HP 8453 instrument by using a 0.05 mM solution of **1** and **2** in DI water. The thermogravimetric analyses were conducted on a DSC 2950 Thermal Analyzer with TGA 2950 Furnace operating at 10 °C min⁻¹ in an open atmosphere.

Crystallography

Crystals for **1** and **2** were obtained in high yield from the filtrate by slow evaporation at room temperature. X-Ray diffraction data were collected at 90 K on a Nonius Kappa CCD diffractometer unit using Mo-Kα (λ = 0.71073) radiation from colorless regular shaped crystals mounted in Paratone-N oil on glass

† Electronic supplementary information (ESI) available: An additional figure of **2**. See <http://dx.doi.org/10.1039/b509699e>

fibers. Initial cell parameters were obtained using DENZO¹⁶ 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 corrections (SADABS¹⁷) were 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 ref. 18. Crystal data, selected bond distances and angles are provided in Tables 1, and 3–5.

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See <http://dx.doi.org/10.1039/b509699e> for crystallographic data in CIF or other electronic format.

Syntheses

[{Hg₃Cl₅(SCH₂CH₂NH₃)₃}Cl]_n, (1). To a stirring solution of 2-aminoethanethiol hydrochloride (1.14 g, 10 mmol) in deaerated DI water (50 ml) was added mercurous chloride (1.80 g, 5 mmol). The immediate formation of a black precipitate and elemental mercury (Hg⁰) was observed. The resulting solution was stirred for 3 days to obtain a clear solution. The elemental mercury was removed by filtration and the filtrate was partially evaporated to obtain colorless crystals (2.01 gm, 77%) and Hg(0) (0.48 gm, ≈ 50%) (Found C, 6.82; H, 1.99; N, 3.98; C₆H₂₁Cl₆Hg₃N₃S₃ requires: C, 6.89; H, 2.02; N, 4.01%). Mp 204–206 °C. δ_H (DMSO, 200 MHz, ppm): 2.94 (t, 2H, CH₂N), 3.08 (t, 2H, CH₂S) and 6.33 (br, 3H, NH₃). δ_C (DMSO, 200 MHz, ppm): 26.7 (CH₂S), 42.8 (CH₂N). IR (KBr, ν/cm⁻¹): 3444, 2966, 1603, 1467, 1366, 1285, 1029, 807, 629. Raman (solid, ν/cm⁻¹): 189, 215, 225, 269, 351, 391, 477, 559, 621, 686, 763. EI-MS: $m/z = 390$ ([HgCl(SCH₂CH₂NH₃)₂]⁺, 5%); 309 ([Hg(SCH₂CH₂NH₃)₂]⁺, 10%); 277 ([Hg(SCH₂CH₂NH₃)]⁺, 12%); 200 ([Hg]⁰, 25%); 77 ([SCH₂CH₂NH₃]⁺, 25%).

[HgCl(SCH₂CH₂NH₂)(H₂O)₂]_n, (2). To a stirring solution of 2-aminoethanethiol hydrochloride (1.14 g, 10 mmol) in deaerated DI water (50 ml) was added mercurous chloride (3.60 g, 10 mmol). The immediate formation of a black precipitate and elemental mercury (Hg⁰) was observed. The resulting solution was stirred for 3 days to obtain a clear

solution. The elemental mercury was removed by filtration and the filtrate was partially evaporated to obtain colorless crystals (3.61 gm, 78%) and Hg⁰ (0.98 gm, ≈ 50%) (Found C, 7.02; H, 2.21; N, 4.26; C₆H₂₂Cl₁₃Hg₃N₃S₃O₃ requires: C, 7.05; H, 2.28; N, 4.32%). Mp 221–223 °C (decomp. without melting). δ_H NMR (DMSO, 200 MHz, ppm): 2.97–3.09 (m, 4H, CH₂N and CH₂S) and 8.13 (s, 2H, NH₃). δ_C (DMSO, 200 MHz, ppm): 25.6 (CH₂S), 42.9 (CH₂N). IR (KBr, ν/cm⁻¹): 3452, 2966, 2827, 1603, 1262, 1021, 807, 675. Raman (solid, ν/cm⁻¹): 190, 226, 248, 299, 345, 398, 467, 584, 627, 757. EI-MS: $m/z = 624$ ([HgCl(SCH₂CH₂NH₂)₂]⁺, 3%); 388 ([HgCl(SCH₂CH₂NH₂)₂]⁺, 4%); 200 ([Hg]⁰, 26%); 76 ([SCH₂CH₂NH₂]⁺, 75%).

Results and discussion

Spectroscopy

In the ¹H NMR spectra of **1** and **2** a significant downfield shift from the free ligand (2.69 ppm) is observed for the SCH₂ protons (3.08 ppm), which is indicative of an Hg–S contact. The NCH₂ peaks are similar to the free ligand (≈3.00 ppm), which is in contrast to the Hg–N bond observed in **2**. The integration of amine protons indicates the presence of NH₃⁺ and NH₂ in **1** and **2**, respectively.

The IR spectra for both **1** and **2** are quite similar to that of the starting material except for the missing peak at 2500 cm⁻¹, indicating the absence of –SH in the compounds. The stretch at 2966 cm⁻¹ in **1** is assigned to a symmetric NH₃⁺ stretch, whereas the peak at 3450 cm⁻¹ is associated with an N–H stretch in both **1** and **2**. The 1467 and 1603 cm⁻¹ peaks in **1** are assigned to the symmetric deformation and degenerate deformation modes respectively for the –NH₃⁺ group. This is also observed for compounds of mercury with L-cysteine (L-cys) (1487 and 1606 cm⁻¹) and L-cysteine methyl ester (1495 and 1582 cm⁻¹).¹⁹ The involvement of –NH₃⁺ in hydrogen bonding is indicated by shifts (1467 and 1603 cm⁻¹), which are lower than those of free ligand (1484 and 1690 cm⁻¹). The C–N (1099–1366 cm⁻¹) stretch in **1** and **2** do not vary much from the free ligand (1096–1380 cm⁻¹) but a significant change in the C–S stretch is observed. The decrease in C–S distance in **1** and **2** is evident in the lower frequencies found at 629–675 cm⁻¹ compared to that of the free ligand (757 cm⁻¹). In the Raman spectrum for **1** the symmetric and asymmetric frequencies for

Table 1 Crystallographic data for **1** and **2**

	1	2
Empirical formula	C ₆ H ₂₁ Cl ₆ Hg ₃ N ₃ S ₃	C ₆ H ₂₂ Cl ₁₃ Hg ₃ N ₃ S ₃ O ₃
<i>M</i>	1045.91	972.51
<i>T</i> /K	90.0(2)	90.0(2)
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
<i>a</i> /Å	13.7992(3)	21.1255(10)
<i>b</i> /Å	7.7167(2)	7.9607(2)
<i>c</i> /Å	19.6891(4)	22.6473(3)
<i>a</i> /°	90.0	90.0
<i>β</i> /°	93.4(11)	90.0
<i>γ</i> /°	90.0	90.0
<i>V</i> /Å ³	2092.76(8)	3808.68(11)
<i>Z</i>	4	8
<i>D</i> _c /Mg m ⁻³	3.320	3.392
<i>μ</i> /mm ⁻¹	23.014	24.877
<i>F</i> (000)	1872	3472
Reflections collected	21724	8215
Independent reflections	4789 (<i>R</i> (int) = 0.0498)	4375 (<i>R</i> (int) = 0.0289)
Goodness of fit on <i>F</i> ²	1.044	1.049
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0272 <i>wR</i> ₂ = 0.0508	<i>R</i> ₁ = 0.0247 <i>wR</i> ₂ = 0.0542
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0404 <i>wR</i> ₂ = 0.0542	<i>R</i> ₁ = 0.0359 <i>wR</i> ₂ = 0.0573
Largest diff. peak and hole/e Å ⁻³	2.550 and –1.575	1.511 and –1.464

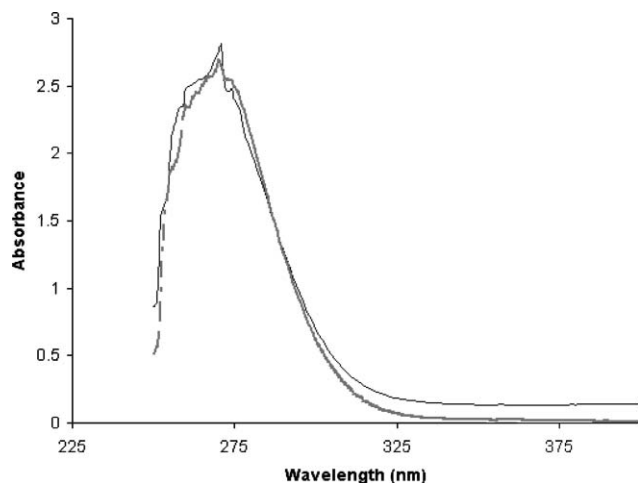
Table 2 Selected vibrational frequencies for **1** and **2** and corresponding frequencies observed for selected Hg(II)-thiolates

Compound	Geometry	$\nu(\text{Hg-S})/\text{cm}^{-1}$	$\nu(\text{Hg-Cl})/\text{cm}^{-1}$	References
1	Distorted Td	269 (s), 351 (as)	225 (t)	This work
2	Distorted Td	299 (s), 345 (as)	226 (t)	This work
$[\text{Hg}_6\text{Cl}_8(\text{SCH}_2\text{CH}_2\text{NH}_3)_8]^{4+}$	Mostly distorted Td	272 (s), 340 (as)	234 (t)	21
$[\text{Hg}_9\text{Br}_{15}(\text{SCH}_2\text{CH}_2\text{NH}_3)_9]^{3+}$	Mostly distorted Td	288 (s), 339 (as)	—	21
$[\text{Hg}(\text{S-n-Bu})_2]$	Td	252 (s)	—	51
$[\text{Hg}(\text{S-t-Bu})_2]$	Td	337 (as)	—	51
$[(\text{NEt}_4)_2\text{Hg}(\text{SMe})_6]$	Bridging Td	260–280	—	52
$[\text{HgCl}_2\{\mu\text{S}(\text{CH}_2)_3\text{NH}(\text{CH}_3)_2\}]_n$	Distorted Td	272 (s), 308 (as)	232 (t)	22
$[\text{HgCl}_2(\text{SCHN}(\text{CH}_3)_2)]_n$	Pseudo Td	270 (s), 308 (as)	225 (t)	23

Td = Tetrahedral, s = symmetric, as = asymmetric, t = terminal.

Hg–S are observed at 269 and 351 cm^{-1} respectively, whereas in **2** the corresponding peaks are observed around 299 and 345 cm^{-1} . Similar frequencies observed for Hg(II)-thiolate with a distorted tetrahedral environment are summarized in Table 2. In **2**, the peak observed at 480 cm^{-1} can be assigned to an Hg–N stretch, which is in the range observed for similar compounds (400–700 cm^{-1}).²⁰ The Hg–Cl frequency for both **1** and **2** fall within the range, 225–248 cm^{-1} , which is also in accord with those reported earlier.^{21–23}

In the UV-Vis spectrum (Fig. 1) the λ_{max} for both **1** and **2** is observed around 270 nm due to the S \rightarrow Hg LMCT, which indicates the presence of a tetrahedral geometry around the Hg center. However, low-energy LMCT bands in the wavelength range 280–310 nm are characteristic of distorted tetrahedral complexes containing a Hg–S bond as observed in $[\text{Hg}(\text{SR})_2]$ (R = Et and Pr),²⁴ Hg-plastocyanin²⁵ and two types of metallothionein.^{26–28} The compounds do not seem to dissociate under the experimental conditions as the λ_{max} for two- and three-coordinate Hg(II)-thiolates, which falls at lower energy levels (228–250 nm), were not observed.²⁴

**Fig. 1** UV-Vis spectra of 2.5 mM solution of **1** (—) and **2** (---) in DI water.

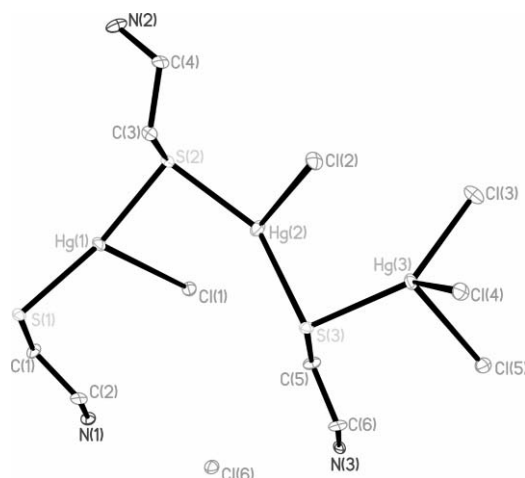
Crystal structures

The repeating unit in **1** is $[\text{Hg}_3\text{Cl}_5(\text{SCH}_2\text{CH}_2\text{NH}_3)]^+$ with a highly distorted coordination around the Hg atoms (Fig. 2). Three independent types of Hg atoms are observed, namely HgS2Cl, HgS3Cl and HgS3Cl3. Hg3 is quite unique as it is bonded to only one S atom, despite the tendency of Hg(II) to maximize bonding with thiolate S atoms. The geometry around Hg1 and Hg3 can be best described as distorted tetrahedral and around Hg2 as slightly distorted 'T' shape. The Hg–S distances within a unit (average 2.442 Å) are comparable to those observed for four-coordinate polynuclear complexes such as $[\text{Hg}(\text{L-cysH})\text{Cl}]_n$ (2.471 Å),²⁹ $[\text{HgCl}_2\{\mu\text{-S}(\text{CH}_2)_3\text{NH}(\text{CH}_3)_2\}]_n$ (2.467 Å),²² and $[\text{Hg}(\text{SMe})(\text{O}_2\text{CCH}_3)(\text{Py})]_n$ (2.451 Å).³⁰ These

Table 3 Selected bond distances (Å) and angles (°) for **1**

Hg(1)–Hg(2)	3.564(3)	Hg(1)–Hg(2)′#1	3.834(3)
Hg(1)–S(1)	2.372(1)	Hg(2)–S(2)	2.479(1)
Hg(1)–S(2)	2.408(1)	Hg(2)–S(3)	2.507(1)
Hg(1)–Cl(1)	2.763(1)	Hg(2)–S(1)′	2.724(1)
Hg(2)–Cl(2)	2.722(1)	Hg(3)–Cl(3)	2.434(1)
Hg(3)–S(3)	2.450(1)	Hg(3)–Cl(4)	2.541(1)
Hg(3)–Cl(5)	2.707(1)	S(1)–Hg(2)′#1	2.724(1)
Hg(2)–Hg(1)–Hg(2)′#1	102.3(7)	Hg(1)–S(2)–Hg(2)	93.6(5)
S(1)–Hg(1)–S(2)	167.9(5)	S(2)–Hg(2)–S(3)	149.3(5)
S(1)–Hg(1)–Cl(1)	106.6(4)	S(2)–Hg(2)–Cl(2)	94.8(4)
S(2)–Hg(1)–Cl(1)	85.35(4)	S(1)–Hg(1)–Hg(2)	143.3(3)
S(2)–Hg(1)–Hg(2)	43.97(3)	S(3)–Hg(2)–Cl(2)	90.90(4)
S(2)–Hg(2)–S(1)′#2	116.9(4)	S(3)–Hg(2)–S(1)′#2	91.85(4)

#1 = $-x + 5/2, y - 1/2, -z + 1/2$; #2 = $-x + 5/2, y + 1/2, -z + 1/2$.

**Fig. 2** The trinuclear repeating unit of **1** with 50% thermal ellipsoids. The additional Hg–S contact to Hg2 is not shown and the hydrogen atoms are omitted for clarity.

distances are, however, shorter than the sum of covalent radii of tetrahedral Hg and S (2.52 Å) indicating a strong bond.^{30,31} The Hg–S distance connecting trinuclear units is larger (2.794 Å) than the corresponding Hg–S distance observed within the trinuclear unit but comparable to those observed in $[\text{Hg}_2(\text{SCH}_2\text{CH}_2\text{S})_3]_n$ (2.723 Å).³²

The average Hg–Cl distance around Hg1 and Hg2 (2.743 Å) is longer than the terminal Hg–Cl distance observed in $[\text{HgCl}_2(\text{C}_3\text{H}_4\text{N}_2\text{S})_2]$ (2.642 Å),³³ $[(\text{Bu}^t\text{S})_4\text{HgCl}_4(\text{C}_6\text{H}_7\text{N})_2]$ and $[(\text{Bu}^t\text{S})_4\text{HgCl}_4(\text{C}_3\text{H}_5\text{N})_2]$ (average 2.46 Å),³⁴ $[(\mu\text{-Cl})\{\text{HgSC}(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{COO}\}_3]^{2+}$, (2.37 Å),³⁵ $[\text{HgCl}_2(\text{SCHN}(\text{CH}_3)_2)_2]$ (average 2.480 Å),²⁵ and $[\text{Hg}(\text{Stpp})\text{Cl}]$ (Stpp = tetraphenyl-21-thiaporphyrin) (2.318 Å).³⁶ These longer distances are indicative of weak Hg–Cl bonding. The Hg–Cl distances around Hg3 are quite variable in the range 2.434–2.707 Å. The longer distance may be attributed to the groups involved in intermolecular hydrogen bonding. In contrast, the long Hg1–Cl1 bond is not

involved in any kind of secondary interaction, which may be attributed to the fact that Hg1 is three-coordinate compared to four-coordinate Hg2 and Hg3.

The smallest and largest bond angles around the Hg atoms are 167° , 85° (Hg1), 149° , 90° (Hg2) and 142° , 93° (Hg3). The more obtuse angles are associated with S compared to bonding with Cl atoms in the order $S-Hg-S > S-Hg-Cl > Cl-Hg-Cl$. The effective angular distortion of $S-Hg-S$ is directly related to the presence of secondary contacts and asymmetric primary coordination. This is evident in the presence of a linear angle around Hg1 ($S-Hg-S = 167^\circ$) compared to Hg2 ($S-Hg-S = 149^\circ$). The Hg1 environment is quite unusual as compounds with $[Hg(SR)_2Cl]^+$ moieties are not known. However it can be compared to $[Hg\{SCH_2CH(NH_3)COO\}\{SCH_2CH(NH_3)COOH\}]Cl$, where the Cl atom is not bonded directly but present as chloride ion in close proximity ($S-Hg-S = 169.8^\circ$ and $Hg-Cl = 3.232 \text{ \AA}$).²⁹ The 'T' shape geometry around Hg1 is common for three-coordinate Hg as observed in $[HgXL_2]$ ($X = I, N; L = N, N, N, N'$ -tetraethylthiuram disulfide, $HSC_6H_2(CMe_3)_3$).^{37,38} The linearity of the $S-Hg-Cl$ angle is also susceptible to distortion by

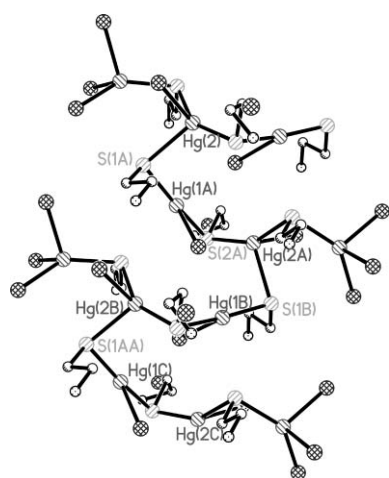


Fig. 3 The polymeric unit of **1** with only Hg and S labelled. The hydrogen and free Cl atoms are not shown for clarity.

secondary interactions with other ions.³⁵ The $S-Hg-Cl$ angles around Hg3 are more linear compared to the almost perpendicular $S-Hg-Cl$ angles around Hg1 and Hg2. The distortion around Hg2 and Hg3 can be attributed to vibronic coupling mechanism leading to d-orbital contribution in the bonds,³⁹ giving rise to distortion usually observed in $[HgX_2(SR)_2]$ type compounds.²³ Hg1, however, acts as a linear bis-mercury thiolate due to the absence of weak interactions associated with the Cl atom.

In the one-dimensional chain, shown in Fig. 3, the $HgSCl_3$ moieties are present on the opposite side of the chain, which is similar to the $HgSBr_3$ moiety observed in $[Hg_9Br_{15}(SCH_2CH_2NH_3)_9]^{3+}$.²¹ The amine units are pointing away from the plane containing Hg, S and Cl to avoid any kind of steric intramolecular interactions. All the Cl atoms, except Cl1, are involved in intermolecular hydrogen bonding with amine protons of a second chain to acquire a three-dimensional structure (Fig. 4). The $NH-Cl$ distances (average 3.222 \AA) are slightly longer than those observed in $Hg(II)$ -thiolates with N and Cl atoms (average 3.15 \AA ²² and 3.16 \AA ³³) but comparable to those observed in the free ligand (average 3.2 \AA ¹⁴).

The geometry around Hg in the repeating unit ($[HgCl(SCH_2CH_2NH_2)(H_2O)_2]$) of **2** is distorted tetrahedral with the coordination sphere consisting of S, N and Cl atoms (Fig. 5). The coordination sphere of Hg is completed by an additional $Hg-N$ bond instead of weak $Hg-Cl$ or $Hg-S$ contacts

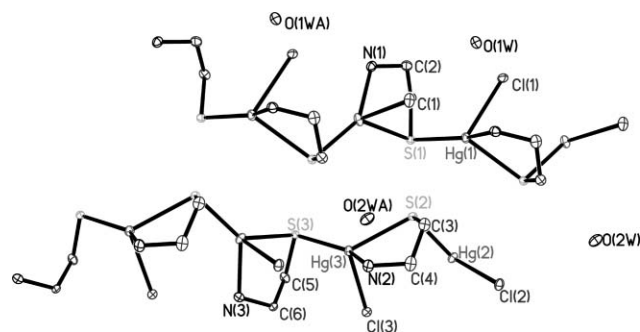


Fig. 5 Polymeric structure of **2**. Thermal ellipsoids are shown at the 50% probability level. Only Hg, S and N atoms are labelled. The hydrogen atoms are not shown for clarity.

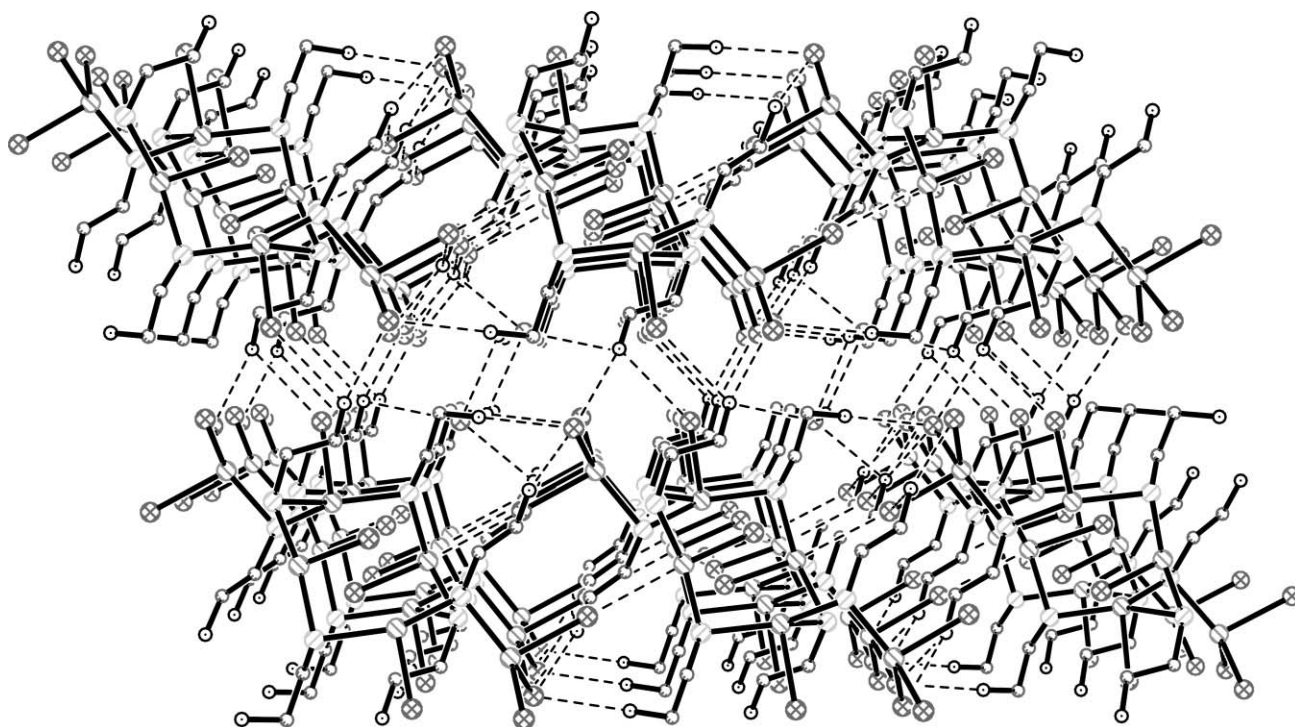


Fig. 4 Packing diagram of **1** along the *b*-axis emphasizing the intermolecular hydrogen bonding (shown with dotted lines).

Table 4 Selected bond distances (Å) and angles (°) for **2**

Hg(1)–S(1)	2.393(1)	Hg(2)–S(2)	2.400(1)
Hg(1)–S(1) ^{#1}	2.692(1)	Hg(2)–S(3) ^{#3}	2.580(1)
Hg(1)–N(1) ^{#1}	2.236(4)	Hg(2)–N(3) ^{#3}	2.277(4)
Hg(1)–Cl(1)	2.719(1)	Hg(2)–Cl(2)	2.717(1)
Hg(1) ^{#1} –S(1) ^{#2}	2.692(1)	Hg(2) ^{#1} –S(3)	2.580(1)
Hg(1) ^{#1} –N(1)	2.236(4)	Hg(2) ^{#1} –N(3) ^{#4}	2.277(4)
Hg(1)–S(1)–Hg(1) ^{#2}	104.0(5)	Hg(2)–S(2)–Hg(3)	105.2(5)
Hg(3)–S(3)–Hg(2) ^{#4}	104.7(5)	S(1)–Hg(1)–S(1) ^{#1}	125.7(5)
S(2)–Hg(2)–S(3) ^{#3}	137.1(4)	N(1) ^{#1} –Hg(1)–S(1) ^{#1}	147.2(1)
N(3) ^{#1} –Hg(2)–S(2) ^{#3}	135.2(1)	N(1) ^{#1} –Hg(1)–S(1) ^{#1}	80.78(1)
N(3) ^{#1} –Hg(2)–S(3) ^{#3}	82.11(1)	S(1) ^{#1} –Hg(1)–Cl(1) ^{#1}	92.16(4)
S(2)–Hg(2)–Cl(2)	103.1(4)	N(1) ^{#1} –Hg(1)–Cl(1) ^{#1}	86.42(1)
S(3) ^{#1} –Hg(2)–Cl(2) ^{#3}	97.38(4)	S(3)–Hg(3)–S(2)	128.11(4)

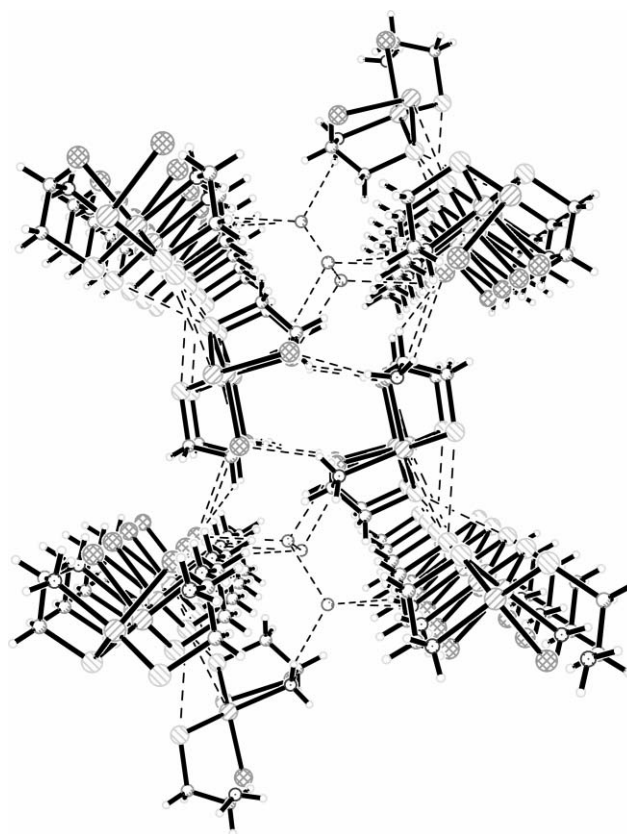
#1 = $-x + 3/2, y - 1/2, z$; #2 = $-x + 3/2, y + 1/2, z$; #3 = $x, y - 1/2, z$; #4 = $x, y + 1/2, z$.

(as seen in **1**). It is quite interesting to observe that the additional Hg–N contact leads to a dramatically different structure. The repeating units are attached through bridging S atoms in a unidirectional fashion. However, intermolecular hydrogen bonding involving an NH₂ group, Cl and water molecules generates a three-dimensional structure. The five-membered rings are neither parallel nor perpendicular to each other (N–Hg–S–C torsion angle $\approx 100^\circ$). This distortion might be due to the hydrogen bonding of amine with Cl atoms from alternate chains in order to avoid any kind of steric interaction among five-membered rings.

In five-membered chelate rings the average Hg–S (2.652 Å) distance is much longer and the Hg–N distance (2.268 Å) is much shorter than the corresponding distances observed in Hg(II)-thiolates with S/N chelates such as [Hg₄Cl₄(SCH₂CH₂N(CH₃)₂)] (3) (average Hg–S = 2.414 Å and Hg–N = 2.485 Å),⁴⁰ [Hg(meimt)₂] (meimt = 1-methyl-1,3-imidazole-2-thione) (average Hg–S = 2.430 Å and Hg–N = 2.451 Å).⁴¹ These distances are indicative of weaker Hg–S and stronger Hg–N bonds. When one bond length in a [Hg(SR)_x] compound increases, the remaining bonds counterbalance by becoming shorter. The chelate Hg–S distance (2.652 Å) is much longer than the bridging Hg–S bond (2.423 Å), which is in contrast to the observations made in **3**, where the S/N chelating Hg–S distances are shorter than the non-chelating Hg–S distances (2.414 and 2.495 Å respectively). The Hg–N distances are also shorter than those observed in Hg(II)-thiolates with additional N donor ligands such as [HgO₂CCH₂(RS)(L)] (R = Me, Et, and L = C₆H₇N and C₅H₅N) (average Hg–N = 2.48 Å),^{30,34} [Hg(Am4DM)X]₂ (Am4DM = 2-pyridineformamide *N*(4)-dimethylthiosemicarbazone) (average Hg–N = 2.393 Å).⁴² The distances observed are, however, in agreement with the sum of the covalent radii of tetrahedral Hg with S and N atoms (2.52 and 2.23 Å respectively).⁴³ The bridging Hg–S distances (average 2.408 Å), present between repeating units, are slightly shorter than the bridging distance observed in **1** as well as in polynuclear Hg(II)-thiolates such as [HgBr(MeS)]_n (2.44 Å),³⁴ [HgCl₂{μ-S(CH₂)₃NH(CH₃)₂}]_n (2.467 Å),²² and [HgCl₂(L-cysH)]_n (2.471 Å).²⁹ This can be attributed to a larger Hg–S bond present in the chelate.

The terminal Hg–Cl distances are quite variable, with Hg1–Cl1, 2.719 Å, Hg2–Cl2, 2.717 Å and Hg3–Cl3, 2.630 Å, but longer than the sum of covalent radii of tetrahedral Hg and Cl (2.47 Å).^{31,44} The contribution of Cl atoms in intermolecular hydrogen bonding makes the Hg–Cl length elongated to some extent, which is found in the upper limit range (2.31–2.83 Å) observed in Hg(II)-compounds with terminal Cl atoms.^{22,35,36}

The one-dimensional polymeric chains are held together *via* intermolecular hydrogen bonding involving NH₃⁺, Cl and water molecules (Fig. 6). The NH–Cl and NH–O_w distances (average 3.446 and 3.034 Å respectively) are in accordance with those observed in complexes such as [HgCl₂{μ-S(CH₂)₃NH(CH₃)₂}] (3.15 Å),²² [HgCl₂(C₃H₄N₂S₂)]

**Fig. 6** Packing diagram of **2** along the *b*-axis showing intermolecular hydrogen bonding.

(3.121 and 3.188 Å),³³ [HgBr₂(1,3-thiazolidine-2-thione)]₂ and [HgBr₂(benzo-1,3-thiazolidine-2-thione)]₂ (3.297 and 3.335 Å),⁴⁵ and [HgBr₂(1,3-imidazole-2-thione)]₂ (3.286 and 3.406 Å).⁴¹ The NH–O distances in **2** are, however, larger than the mean NH–O distance of 2.840 Å cited in the literature.⁴⁶

The Hg–Hg interaction (Hg1–Hg2, 3.564 Å) (Fig. 7) in **1** is longer than the Hg–Hg distances reported for metallic mercury (3 Å),⁴⁷ and the [HgMe₂]₂ dimer, (3.41 Å)⁴⁸ but smaller than those observed in [Hg(SR)X] type compounds such as [Hg(Am4DM)X]₂ (Am4DM = 2-pyridineformamide *N*(4)-dimethylthiosemicarbazone and X = Cl or Br) (3.667 and 3.660 Å)⁴² and [(Bu^tS)₄Cl₄Hg₂(C₆H₇N)₂] (3.648–3.852 Å).^{30,34} This distance is however close to that observed in [(*o*-C₆F₄Hg)₃-μ₃-acetone] (3.512 Å).⁴⁹ The intermolecular Hg–Hg distances (>3.8 Å) are within the range observed for Hg(II)-thiolates. The unprecedentedly short distance between Hg1 and Hg2 can be attributed to the narrow angle of 93.6° observed for Hg2–S2–Hg1. It can be argued that **1** is perhaps the first example of a [Hg(SR)X] (X = halide) type compound to involve a short Hg–Hg mercurophilic contact. In **2**, the Hg–Hg interaction within the chain is quite weak with an average distance of 4 Å and around 4.5 Å between chains. These distances rule out any kind of mercurophilic interaction as observed in **1**, which may be due to the steric effects exerted by the formation of the chelate.

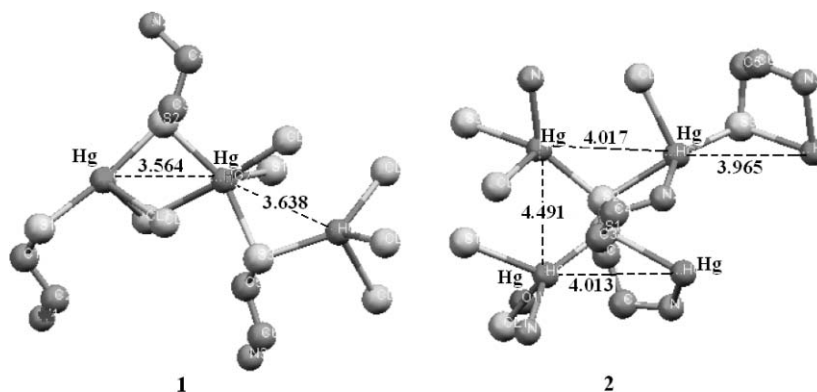
TGA Studies

Thermograms of **1** in air indicate that total degradation of the sample takes place around 600 °C. Weight loss occurs in three steps with 62%, 28% and 6.0% loss (surface water molecules account for the remaining 2%). The trinuclear unit breaks down *via* one of the bridging S atoms to form [HgCl(SCH₂CH₂NH₃)₂]⁺ which account for 37% of the molecules, very close to the calculated value of 36%. In the second step the loss of [HgCl(SCH₂CH₂NH₃)₂]⁺ is in agreement with the calculated as well as observed values.

Table 5 Hydrogen bond geometry in **1** and **2**

D–H...A	D–H/Å	H...A/Å	D...A/Å	DHA/°
1				
N(1)–H(1C)...Cl(2)#3	0.91	2.36	3.230(4)	160.3
N(1)–H(1D)...Cl6	0.91	2.44	3.248(4)	148.7
N(1)–H(1E)...Cl(2)#1	0.91	2.34	3.242(5)	169.4
N(2)–H(2C)...Cl(6)#1	0.91	2.31	3.220(5)	174.2
N(2)–H(2D)...Cl(6)#2	0.91	2.26	3.151(5)	165.6
N(2)–H(2E)...Cl(5)#3	0.91	2.63	3.516(5)	164.5
N(3)–H(3C)...Cl(6)	0.91	2.23	3.132(4)	170.9
N(3)–H(3D)...Cl(4)#4	0.91	2.43	3.130(5)	133.5
N(3)–H(3E)...Cl(5)#5	0.91	2.38	3.256(5)	160.6
2				
N(1)–H(1A)...O(2W)#7	0.92	2.15	2.956(6)	145.1
N(1)–H(1B)...Cl(3)#8	0.92	2.98	3.744(5)	141.2
N(2)–H(2A)...O(2W)#6	0.92	2.34	3.113(6)	142.1
N(2)–H(2B)...Cl(3)#9	0.92	2.60	3.356(5)	140.3
N(3)–H(3A)...Cl(2)#9	0.92	2.52	3.414(5)	165.0
N(3)–H(3B)...Cl(3)#6	0.92	2.68	3.163(4)	113.9
N(3)–H(3B)...Cl(1)#10	0.92	2.89	3.555(4)	130.0

Symmetry transformations used to generate equivalent atoms: #1 $-x + 5/2, y + 1/2, -z + 1/2$; #2 $x - 1, y, z$; #3 $x - 1/2, -y + 1/2, z - 1/2$; #4 $-x + 3, -y, -z + 1$; #5 $-x + 3, -y + 1, -z + 1$; #6 $x, y + 1, z$; #7 $x + 1/2, y + 1, -z + 1/2$; #8 $-x + 3/2, -y + 1, z + 1/2$; #9 $-x + 1, -y + 1, -z$; #10 $-x + 3/2, -y + 1, z - 1/2$.

**Fig. 7** The distances (Å) involved in weak Hg–Hg interactions in **1** and **2**.

The degradation of **2** also occurs in three steps very similar to that of **1**. However a high decomposition temperature (above 1000 °C) compared to **1** is observed despite similar melting temperatures. The formation of $[\text{Hg}_2\text{Cl}_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]^+$ (56%) is observed around 340 °C quite close to the experimental value of 55%. The ligand along with Hg and Cl are lost to obtain HgX_2 (X = Cl or S) with a theoretical value of 27%, which does not differ much from the observed value of 28%. The thermogravimetric studies of heteroleptic Hg(II)-thiolates are rare and there is more to be done as it is observed that it was quite difficult to exactly match the theoretical as well as the experimental values. However, the few selected data reported earlier suggest a similar pattern of degradation.⁵⁰ It should be noted that the formation of HgS as a final product has not been observed.

Conclusion

Novel polynuclear Hg(II)-thiolates have been reported from the reaction of mercurous chloride and 2-aminoethanethiol. The one-dimensional polymeric chain held through $[\text{Hg}-\text{S}]_n$ contacts is extended to a three-dimensional structure via intermolecular hydrogen bonding. The short Hg–Hg contact observed in **1** is a mercurophilic interaction, whereas the corresponding distances in **2** are within the range observed for secondary contacts typical of Hg(II)-thiolates.

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