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Article

Structural Diversity within Analogous Compounds: Syntheses and Studies of $M(SCH_2CH_2NH_2)Cl$ ($M = Zn, Cd, Hg$)

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The novel complexes [Zn(L)Cl] (**1**), [Cd(L)Cl] (**2**), [Hg(L)Cl] (**3**), {[Hg(L)Cl]·NaOH·$2H_2O$} (**3**·NaOH·$2H_2O$), and {$[Hg_3(HL)_2Cl_6]\cdot 2H_2O$} (**4**) ($L = {}^{-}SCH_2CH_2NH_2$) were prepared and investigated by means of IR spectroscopy and single-crystal X-ray diffraction. The crystal structures of **1**, **2**, and **3**·NaOH·$2H_2O$ show chelating N,S-coordination of the cysteaminate ligand, bridging S, and terminally coordinating Cl. Apart from these common features, the coordination geometries and modes of intermolecular association are different. **1** forms a cyclic tetramer with a Zn_4S_4 ring, and **3**·NaOH·$2H_2O$ contains one-dimensional $[Hg(L)Cl]_n$ chains with S-bridged Hg atoms. Zn and Hg atoms in **1** and **3**·NaOH·$2H_2O$ are tetracoordinate with a distorted tetrahedral $M(ClNS_2)$ geometry ($M = Zn, Hg$). Each Cd atom of **2** binds to three S atoms and vice versa, such that layers of distorted Cd_3S_3 hexagons are formed. **2** is the first example for a compound exhibiting a group 12–group 16 layer structure, which can be described as an analogue of a graphite layer. Additionally, each Cd atom binds to a chlorine atom and a nitrogen atom from a cysteaminate ligand resulting in pentacoordination with a distorted trigonal bipyramidal $Cd(ClNS_3)$ geometry. **4** contains two differently coordinate Hg atoms. One displays a distorted trans-octahedral $Hg(Cl_4S_2)$ geometry, while the other is coordinated by four Cl atoms and one S atom and additionally forms a long Hg···Cl contact.

Introduction

Much of the interest in metal sulfur chemistry results from the potential relevance of resulting compounds to active sites in metalloenzymes and also to their ability to adopt various nuclearities of significant structural complexity.[1−5] However, in comparison with the coordination chemistry of transition metals, the chemistry of the d^0- and d^{10}-configured metals with sulfur ligands remains much less developed.[6−9] The Zn^{2+} ion is known to have a high affinity toward nitrogen and sulfur donor ligands, as demonstrated by a considerable body of knowledge on Zn(N,S ligand) complexes and zinc enzymes.[6,10] In many cases the interaction of toxic metals with biological systems involves bonding of the metal to the thiolate groups present in enzymes. Hence, an insight into the chemistry of d^{10}-configured heavy metal complexes with N,S-donor ligands is important in terms of understanding the aforementioned interaction. Recently, we investigated the structures of cysteamine, ${}^{+}H_3NCH_2CH_2S^{-}$, HL, and its 2:1 complexes with Zn^{II}, Cd^{II}, Hg^{II}, and Pb^{II}.[11,12] Our own studies as well as those performed by others clearly demonstrated that the type of counteranion(s), concentrations of the specific metal ion and the cysteamine ligand, and the pH value affect the nature of the isolated products.[11,13] While our previous studies covered the above-mentioned 2:1 complexes, we subsequently investigated solutions containing equimolar

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(1) Raper, E. S. *Coord. Chem. Rev.* **1997**, *165*, 475−567.
(2) Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 769.
(3) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.
(4) Blower, P. G.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121.
(5) Sousa-Pedrares, A.; Romero, J.; Garcia-Vazquez, J. A.; Duran, M. L.; Casanova, I.; Sousa, A. *Dalton Trans.* **2003**, 1379−1388.
(6) Fleischer, H. *Coord. Chem. Rev.* **2005**, *249*, 799−827.
(7) Jurkschat, K.; Peveling, K.; Schürmann, M. *Eur. J. Inorg. Chem.* **2003**, 3563−3571.
(8) Englich, U.; Ruhland-Senge, K. *Coord. Chem. Rev.* **2000**, *210*, 135−179.
(9) Briand, G. G.; Burford, N.; Cameron, T. S.; Kwiatkowski, W. *J. Am. Chem. Soc.* **1998**, *120*, 11374−11379.
(10) Libscomb, W.; Sträter, N. *Chem. Rev.* **1996**, *96*, 2375−2433.
(11) Fleischer, H.; Schollmeyer, D. *Inorg. Chem.* **2004**, *43*, 5529−5536.
(12) Fleischer, H.; Dienes, Y.; Mathiasch, B.; Schmitt, V.; Schollmeyer, D. *Inorg. Chem.* **2005**, *44*, 8087−8096.
(13) Bharara, M. S.; Kim, C.-H.; Parkin, S.; Atwood, D. A. *Polyhedron* **2005**, *24*, 865−871.

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Scheme 1. Structural Formulas of Compounds **1**−**4**

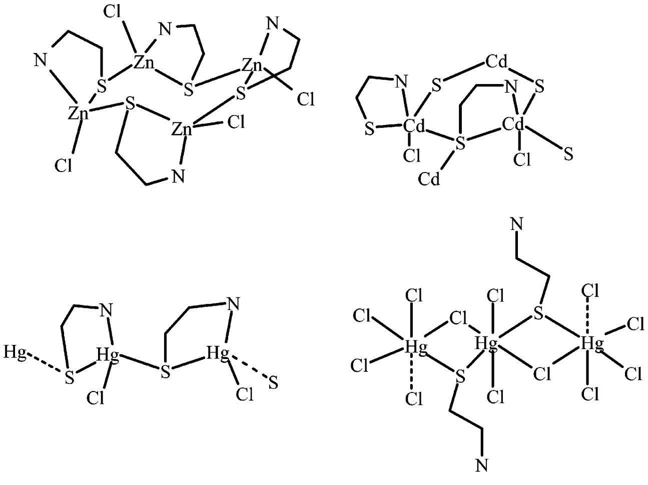

Table 1. Selected Structural Data for **1** from Single-Crystal XRD^a

Zn1−S1	2.368(1)	Zn2−S1	2.323(1)
Zn1−S5	2.312(1)	Zn2−S5	2.360(1)
Zn1−Cl1	2.241(1)	Zn2−Cl2	2.234(1)
Zn1−N4	2.045(3)	Zn2−N8	2.043(3)
N4···Cl2$^{\#1}$	3.387(4)	N8···Cl1$^{\#3}$	3.416(3)
N4···Cl2$^{\#2}$	3.353(3)	N8···Cl1$^{\#4}$	3.512(3)
		N8···S1$^{\#3}$	3.546(3)
S1−Zn1−S5	115.4(1)	S1−Zn2−S5	108.2(1)
S1−Zn1−Cl1	113.4(1)	S5−Zn2−Cl1	118.2(1)
S1−Zn1−N4	88.9(1)	S5−Zn2−N8	89.6(1)
S5$^{\#1-}$Zn1−Cl1	111.1(1)	S1−Zn2−Cl2	114.2(1)
S5$^{\#1-}$Zn1−N4	117.5(1)	S1−Zn2−N8	115.6(1)
Cl1−Zn1−N4	108.9(1)	Cl2−Zn2−N8	108.9(1)
N4−H4A···Cl2$^{\#1}$	136(4)	N8−H8B···Cl1$^{\#3}$	125(4)
N4−H4B···Cl2$^{\#2}$	149(5)	N8−H8B···Cl1$^{\#4}$	144(4)
		N8−H8A···S1$^{\#3}$	171(4)
Zn1−S1−C2−C3	28.6(3)	Zn2−S5−C6−C7	30.0(3)
S1−C2−C3−N4	−56.2(5)	S5−C6−C7−N8	−56.2(4)
C2−C3−N4−Zn1	53.3(4)	C6−C7−N8−Zn2	51.2(4)
C3−N4−Zn1−S1	−27.1(3)	C7−N8−Zn2−S5	−24.9(2)
N4−Zn1−S1−C2	−0.6(2)	N8−Zn2−S5−C6	−2.2(2)

^{a} Distances are given in Å, and angles, in deg. Symmetry transformations used to generate equivalent atoms: #1, $-x + 1/2$, $-y + 1/2$, $-z$; #2, $x + 1/2$, $-y + 1/2$, $z + 1/2$; #3, $-x + 1/2$, $y + 1/2$, $-z - 1/2$; #4, $x - 1/2$, $-y + 1/2$, $z - 1/2$.

Table 2. Selected Structural Data for **2** from Single Crystal XRD^a

Cd1A−S1A	2.656(3)	Cd1B−S1B	2.636(3)
Cd1A−S1B	2.622(3)	Cd1B−S1A$^{\#4}$	2.612(3)
Cd1A−S1A$^{\#1}$	2.660(3)	Cd1B−S1B$^{\#3}$	2.619(3)
Cd1A−Cl1A	2.515(3)	Cd1B−Cl1B	2.545(3)
Cd1A−N4A	2.336(10)	Cd1B−N4B	2.365(10)
N4A···Cl1A$^{\#1}$	3.446(11)	N4B···Cl1B$^{\#3}$	3.423(11)
N4A···Cl1B	3.357(11)	N4B···Cl1A$^{\#4}$	3.334(10)
N4A−Cd1A−Cl1A	167.7(3)	N4B−Cd1B−Cl1B	165.6(2)
S1A−Cd1A−S1B	122.5(1)	S1B−Cd1B−S1B$^{\#3}$	127.0(1)
S1A−Cd1A−S1A$^{\#1}$	123.7(1)	S1B−Cd1B−S1A$^{\#4}$	125.0(1)
S1B−Cd1A−S1A$^{\#1}$	112.4(1)	S1A$^{\#4-}$Cd1B−S1B$^{\#3}$	107.1(1)
τ	0.73	τ	0.68
Cd1A−S1A−Cd1A$^{\#3}$	117.5(1)	Cd1B−S1B−Cd1B$^{\#1}$	118.8(1)
Cd1A−S1A−Cd1B$^{\#2}$	106.6(1)	Cd1B−S1B−Cd1A	109.3(1)
Cd1B$^{\#2-}$S1A−Cd1A$^{\#3}$	121.9(2)	Cd1B$^{\#1-}$S1B−Cd1A	117.0(1)
N4A−H4A···Cl1A$^{\#1}$	167.7	N4B−H4C···Cl1B$^{\#3}$	171.9
N4A−H4B···Cl1B	164.2	N4B−H4D···Cl1A$^{\#4}$	163.4
Cd1A−S1A−C2A−C3A	−33.4(8)	Cd1B−S1B−C2B−C3B	−34.7(8)
S1A−C2A−C3A−N4A	61.2(11)	S1B−C2B−C3B−N4B	58.9(11)
C2A−C3A−N4A−Cd1A	−56.6(11)	C2B−C3B−N4B−Cd1B	−51.4(11)
C3A−N4A−Cd1A−S1A	24.4(7)	C3B−N4B−Cd1B−S1B	21.1(7)
N4A−Cd1A−S1A−C2A	5.5(5)	N4B−Cd1B−S1B−C2B	6.8(5)

^{a} Distances are given in Å, and angles are in deg. Symmetry transformations used to generate equivalent atoms: #1, x, $-y + 1/2$, $z - 1/2$; #2, $x + 1$, y, z; #3, x, $-y + 1/2$, $z + 1/2$; #4, $x - 1$, y, z.

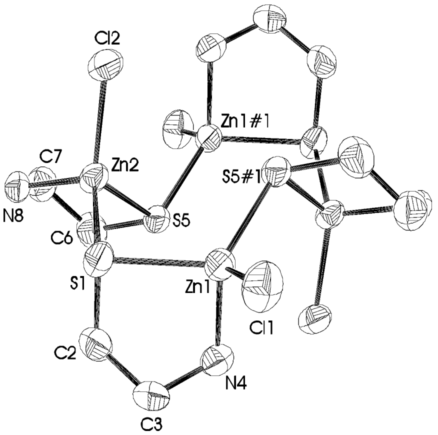

Figure 1. 1. ORTEP diagram of **1**. Displacement ellipsoids are at the 50% probability level.

amounts of M^{2+} and cysteamine. We here report preparation and structural investigation of novel 1:1 complexes of cysteamine with group 12 metal ions.

Results and Discussion

Synthesis and Spectroscopy. [Zn(L)Cl] (**1**), [Cd(L)Cl] (**2**), and [Hg(Cl)L] (**3**) are formed from 1:1:2 solutions of MCl$_2$, [H$_2$L]Cl, and NaOH in methanol or ethanol (see Scheme 1). The composite compound {[Hg(L)Cl]·NaOH·2H$_2$O}$_n$ (=**3**·NaOH·2H$_2$O) formed when thf was condensed into a solution of **3** in dmso and diluted NaOH. While nitrogen and sulfur contents of the precipitate agree well with the formula **3**·NaOH·2H$_2$O, its carbon content was found 1−3% higher than calculated and its hydrogen content was found up to 1% above or below the calculated value. Presently, we cannot give a conclusive explanation for variation and deviation of these results.

While **1** and **2** are well soluble in H$_2$O and dmso, slightly soluble in methanol, chloroform, and acetone, and insoluble in weakly polar solvents, **3** is, apart from the above-mentioned mixture, only soluble in dmso or in hot pyridine. Speciation and stability constants of Zn^{2+} and Cd^{2+} complexes with cysteamine in aqueous solution were investigated by Li and Martell, by means of potentiometric titration.[14] They found complexes [M(L)]$^+$, [M(L)$_2$], and [M(L)OH] for both metal ions and additionally [Cd(HL)]$^{2+}$ for Cd^{2+} to be present at different pH values. No polynuclear complexes were considered by these authors. Thus, the tetrameric form of **1** (see Crystal Structures of **1**−**4** further down) might be present either in very small amounts or only in methanolic but not in aqueous solution. {[Hg$_3$(HL)$_2$Cl$_6$]·2H$_2$O}, **4**, precipitated out of an equimolar aqueous solution of HgCl$_2$ and [H$_2$L]Cl, when—on addition of a 0.1 M NaOH solution—the pH value exceeded 3. Apart from **3** and **4**, the compounds [Hg(HL)$_2$]Cl$_2$,[15] {[Hg(L)Cl]·2H$_2$O}$_n$,[16] [Hg$_3$(HL)$_3$Cl$_5$]Cl,[16]

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(14) Li, Y.; Martell, A. E. *Inorg. Chim. Acta* **1995**, *231*, 159−165.

(15) Kim, C.-H.; Parkin, S.; Bharara, M.; Atwood, D. *Polyhedron* **2002**, *21*, 225−228.

(16) Bharara, M. S.; Thanhhoa, H. B.; Parkin, S.; Atwood, D. A. *Dalton Trans.* **2005**, 3874−3880.

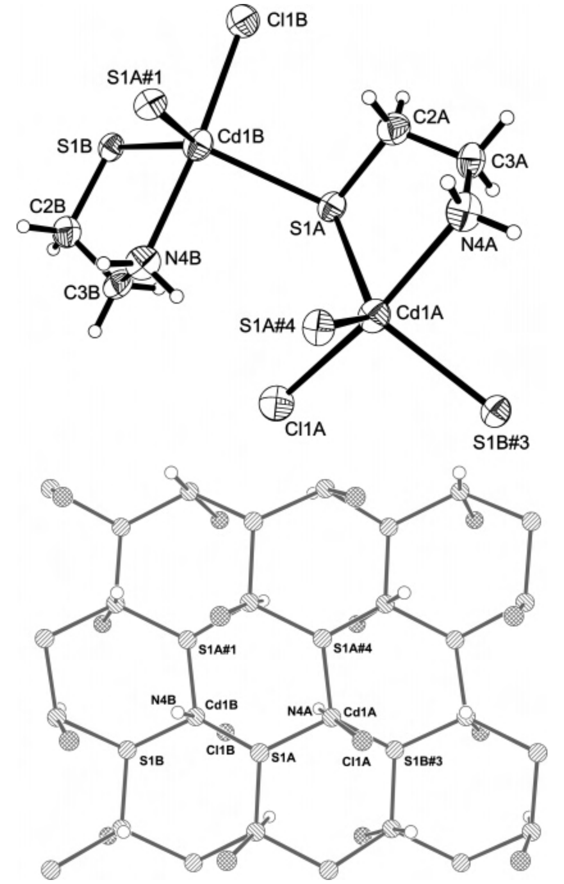

Figure 2. (a) ORTEP diagram of **2** showing the coordination modes of the two crystallographically different Cd atoms. Displacement ellipsoids are at the 50% probability level. (b) Packing diagram of **2**. C and H atoms are omitted for clarity.

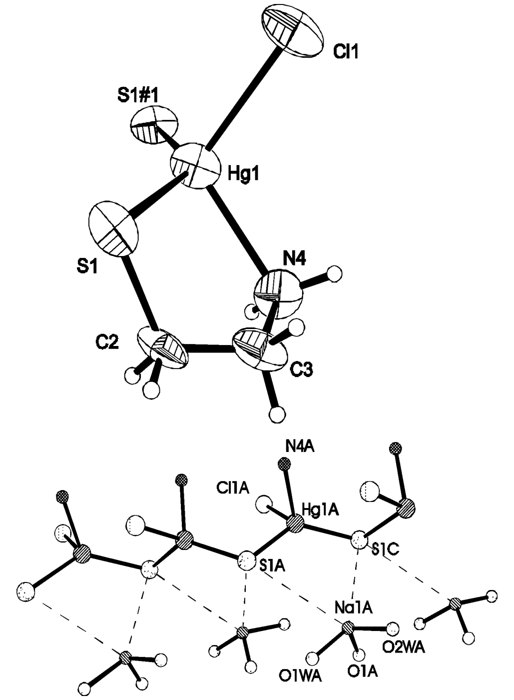

Figure 3. (a) ORTEP diagram of a molecular unit of **3** in **3**·NaOH·2H$_2$O showing the coordination mode of the Hg atom. Displacement ellipsoids are at the 50% probability level. (b) Packing diagram of **3**, also showing the coordination modes of the Na$^+$ ion.

and $\{[Hg_6(HL)_6Cl_8]Cl_4 \cdot 4H_2O\}$[17] are structurally known complexes obtained from aqueous solutions containing Hg^{2+}, Cl$^-$, and L$^-$ (and its protonated forms). The system seems thus to be more complex than its Zn^{2+} and Cd^{2+} analogues.

IR spectra of all compounds were recorded using NaCl windows, to avoid halide exchange reactions, as the may occur with KBr or CsI. The assignment of IR bands was supported by a DFT calculation of vibrational frequencies of a model compound, i.e., an isolated Zn(SCH$_2$CH$_2$NH$_2$)Cl molecule, in which cysteaminate coordinates in a N,S-chelating mode. M−S stretching modes and bending modes involving M were not observed, since their frequencies are outside the spectral range recorded. **1**−**3** exhibit smaller ν(NH$_2$) than H$_3$CSCH$_2$CH$_2$NH$_2$ (3380 cm^{-1})[18] does. Furthermore, ν(NH$_2$) of **1** and **2** are shifted to lower wavenumbers compared to those of **3** and **3**·NaOH·2H$_2$O. A shift of ν(NH$_2$) to lower wavenumbers on coordination of a primary amine to a metal ion is well-known,[19] but hydrogen bonds may also contribute to the observed decrease of ν(NH$_2$). The extended band between 3200 and 2500 cm^{-1} in the IR spectrum of **4** is typical for ammonium groups involved in hydrogen bonds (see Crystal Structures further down).[20] ν_{as}(CH$_2$), ν_s(CH$_2$), δ(NH$_2$), and ν(S−C) do not show any regular trend within complexes **1**−**4**. Ab initio calculations for complexes [ML$_2$] suggested that variations of the frequencies of those modes between Zn, Cd, and Hg are smaller than 10 cm^{-1}.[12] Interestingly, there is little coincidence between band frequencies of **3**, **3**·NaOH·2H$_2$O, and **3**·2H$_2$O, a compound investigated by Atwood and co-workers.[16] According to the number of molecules in the asymmetric unit, four different ν(CH$_2$) should exist for **3**·NaOH·2H$_2$O and eight for **1**, **2**, and **4**. In all cases, only three bands were observed in the ν(CH$_2$) region, a fact that points to a spectral resolution too low to distinguish between the different modes.

Crystal Stuctures of 1−4. Data from crystal structures of compounds **1**−**4** are given in Tables 1−4. Diagrams of molecules or coordination environments of the metal atoms and packing diagrams are given in Figures 1−4. In **1** and **2** the asymmetric unit contains two molecules of M(L)Cl (M = Zn, Cd), differing only slightly in their geometric parameters (see Tables 1 and 2). Despite their analogous constitution, the zinc and the cadmium compounds display different coordination modes at the metal ion, as was already found for the [M(L)$_2$] complexes of these metals.[12] Zn^{2+} is tetracoordinate with a slightly distorted tetrahedral Zn(ClNS$_2$) configuration (see Figure 1), a rare coordination mode with only two prior examples.[21] The basic structural parameters found for **1** agree well with those reported for a bis(mercaptoimidazolyl)(pyrazolyl)borate complex with the

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(17) Bharara, M. S.; Bui, T. H.; Parkin, S.; Atwood, D. A. *Inorg. Chem.* **2005**, *44*, 5753−5760.

(18) Jinachitra, S.; MacLeod, A. J. *Tetrahedron* **1979**, *35*, 1315−1316.

(19) Sen, D. N.; Mizushima, S.-I.; Curran, C.; Quagliano, J. V. *J. Am. Chem. Soc.* **1955**, *77*, 211−212.

(20) Guenzler, H.; Gremlich, H.-U. *An introduction to IR spectroscopy*; Wiley-VCH: Weinheim, Germany, 2004.

(21) Shu, M.; Walz, R.; Wu, B.; Seebacher, J.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **2003**, 2503.

Table 3. Selected Structural Data for **3**·NaOH·2H$_2$O from Single-Crystal XRD[a]

Hg1−S1	2.501(5)	S1$^{\#1}$−Hg1−Cl1	99.7(2)
Hg1−S1$^{\#1}$	2.440(5)	Cl1−Hg1−N4	105.3(5)
Hg1−N4	2.339(17)	Hg1−S1−Hg1$^{\#2}$	100.8(2)
Hg1−Cl1	2.557(6)	O1−Na1−O1W	105.6(11)
Na1−O1	1.416(16)	O1−Na1−O2W	107.0(10)
Na1−O1W	1.76(2)	O1W−Na1−O2W	97.2(11)
Na1−O2W	1.84(3)	N4−H4B···O1	165.3
N4···O1	3.05(3)	N4−H4A···Cl1	146.5
N4···Cl1	3.27(2)	Hg1−S1−C2−C3	43.4(17)
S1−Hg1−S1$^{\#1}$	133.6(3)	S1−C2−C3−N4	−58(2)
S1−Hg1−N4	82.8(4)	C2−C3−N4−Hg1	35(2)
S1−Hg1−Cl1	111.8(2)	C3−N4−Hg1−S1	−6.7(13)
S1$^{\#1}$−Hg1−N4	121.5(5)	N4−Hg1−S1−C2	−16.5(9)

[a] Distances are given in Å, and angles are in deg. Symmetry transformations used to generate equivalent atoms: #1, $-x + 1/2, y - 1/2, z$; #2, $-x + 1/2, y + 1/2, z$.

same coordination mode (see Table 6a). On average, Zn−S bonds are longer and Zn−N distances are shorter for complexes with coordination mode Zn(NS$_2$Cl) than for coordination modes Zn(N$_2$S$_2$) or Zn(NS$_3$).

Cd^{2+} is pentacoordinate with a slightly distorted trigonal bipyramidal Cd(ClNS$_3$) configuration, as can be shown by the structural parameter $\tau = (\alpha - \beta)/60$ (see Table 2), which is a measure for the continuous transition from a trigonal bipyramidal ($\tau = 1$) to a square planar ($\tau = 0$) configuration.[22] Here α and β are the largest and second largest of all X−Cd−Y angles. The S atoms occupy the equatorial positions in the trigonal bipyramid while the Cl, Cd, and N atoms are nearly collinear (see Table 2 and Figure 2a). **2** is the first example for such a coordination mode of Cd^{2+}. In **1** and **2**, cysteaminate acts as an N,S-chelating and S-bridging ligand. The difference in coordination modes of Zn^{2+} and Cd^{2+} arouse from the different types of bridging of the S-atom, i.e. μ^2 for **1** and μ^3 for **2**. In **1** the Zn−S−Zn bridges led to the formation of an eight-membered Zn$_4$S$_4$ ring, a structural motif which is also found in a 1:1 complex of Zn^{2+} with the *N*,*N*-bis(2-mercaptoethyl)benzylamine ligand.[23] In both cases discrete tetrameric units are present in the solid state. The Cl atoms do not form bridges between metal ions but are involved in two N−H···Cl hydrogen bonds each, which in the case of **1**, are formed between different [Zn(L)Cl] tetramers.

Apart from purely inorganic group 12−group 16 compounds with zinc blende or wurzite structure, 74 compounds with an adamantanoidal M$_4$E$_6$ fragment (M = Zn, Cd, Hg; E = S, Se, Te) are known, as was found by a search of the CCDC database.[24] In sharp contrast to that plethora, **2** is the first example for a compound displaying a group 12−group 16 layer structure (see Figure 2b). Each Cd atom binds to three S atoms and vice versa, such that layers of distorted Cd$_3$S$_3$ hexagons with a flat twist boat conformation are formed. The layer can thus be described as a group 12−group 16 analogue of a graphite layer. The layers in **2** are connected to each other via N−H···Cl hydrogen bonds.

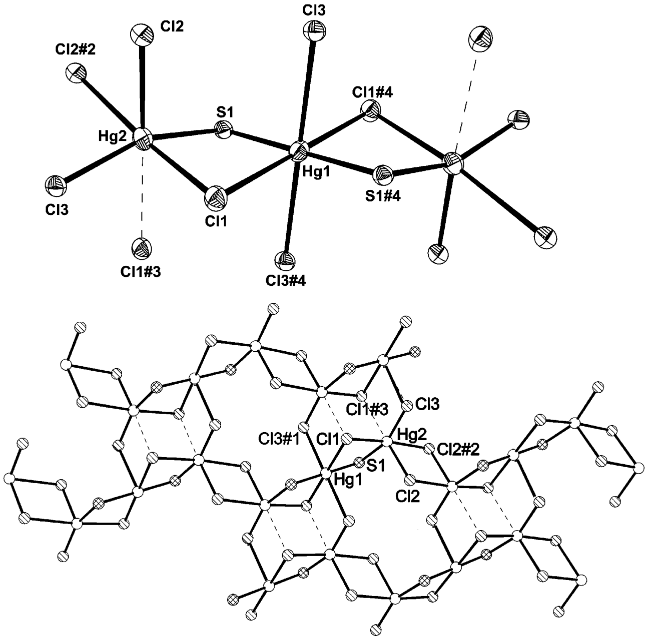

Figure 4. (a) ORTEP diagram of **4**, showing the coordination mode of the two crystallographically different Hg atoms. C, N, and H atoms are omitted for clarity. Displacement ellipsoids are at the 50% probability level. (b) Packing diagram of **4**. C, N, and H atoms are omitted for clarity.

Table 4. Selected Structural Data for **4** from Single-Crystal XRD[a]

Hg1−S1	2.417(3)	S1−Hg1−Cl1	89.1(1)
Hg1−Cl1	2.924(3)	S1−Hg1−Cl3$^{\#1}$	83.3(8)
Hg1−Cl3$^{\#1}$	3.016(3)	Cl1−Hg1−Cl3$^{\#1}$	83.0(1)
Hg2−S1	2.431(3)	S1−Hg2−Cl3	156.9(1)
Hg2−Cl3	2.392(3)	Cl1−Hg2−Cl2$^{\#2}$	172.0(1)
Hg2−Cl2	2.703(3)	Cl2−Hg2−S1	102.0(1)
Hg2−Cl1	2.915(3)	Cl2−Hg2−Cl1	91.7(1)
Hg2−Cl2$^{\#2}$	2.950(3)	Cl2−Hg2−Cl2$^{\#2}$	80.4(1)
Hg2···Cl1$^{\#3}$	3.501(3)	Cl2−Hg2−Cl3	101.1(1)
N4···O1$^{\#4}$	2.858(12)	Hg1−S1−Hg2	100.2(1)
N4···O1$^{\#5}$	2.937(12)	Hg1−Cl1−Hg2	79.2(1)
N4···Cl2$^{\#6}$	3.272(10)	Hg2−Cl2−Hg2$^{\#2}$	99.6(1)
N4···Cl3$^{\#2}$	3.482(9)	N4−H4A···O1$^{\#4}$	138.8
N4···Cl1$^{\#7}$	3.250(9)	N4−H4B···O1$^{\#5}$	121.9
O1···Cl2$^{\#8}$	3.182(8)	N4−H4B···Cl2$^{\#6}$	124.5
O1···Cl1$^{\#9}$	3.249(8)	N4−H4B···Cl3$^{\#2}$	132.1
		N4−H4C ···Cl1$^{\#7}$	171.2
		O1−H1O···Cl2$^{\#8}$	126.0
		O1−H2O···Cl1$^{\#9}$	150.6

[a] Distances are given in Å, and angles are in deg. Symmetry transformations used to generate equivalent atoms: #1. $x + 1, y, z$; #2, $-x, -y, -z + 1$; #3, $-x, -y + 1, -z + 1$; #4, $-x + 1, -y + 1, -z + 1$; #5, $x, y - 1, z + 1$; #6, $-x + 1, -y, -z + 1$; #7, $x + 1, y, z + 1$; #8, $x + 1, y + 1, z$; #9, $-x + 1, -y + 1, -z$.

The sum of all S−Cd−S angles at a given Cd atom (358.6° for Cd1 and 359.1° for Cd2) indicate that the Cd atoms and the three coordinating S atoms are not coplanar, in contrast to what was found for [CdL$_2$] (Table 6a). The distance of the Cd atom to the plane of the three S atoms it is bound to is 0.182(1) Å for Cd1A and 0.142(1) Å for Cd1B. The Cd−N bond vectors and the normal of the S$_3$ plane have angles of 0.9° for Cd1A and 1.6° for Cd1B; i.e., they are nearly collinear. A total of 21 structurally known pentacoordinate Cd^{2+} complexes displaying a Cd(S$_3$XY) coordination mode (X, Y ≠ S) were found by a search of the CCDC database.[24] Apart from **2** and from [CdL$_2$], whose structure was recently reported by us, only two tris(thiobenzoato)cadmium complexes exhibit a trigonal bipyramidal configuration with all

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(22) Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, R.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(23) Spencer, D. J. E.; Blake, A. J.; Parsons, S.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1999**, 1041.

(24) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380−388.

Table 5. Bond Valencies for M−S, M−N, and M−Cl Bonds[a]

	M for 1		M for 2		M for 3	M for 4	
param	Zn1	Zn2	Cd1	Cd2	M for **3**: Hg1	Hg1	Hg2
$\Sigma\nu_{M-S}$	1.004	0.998	1.111	1.183	1.318	1.518	0.731
$\Sigma\nu_{M-N}$	0.472	0.474	0.361	0.334	0.397		
$\Sigma\nu_{M-Cl}$	0.562	0.573	0.445	0.410	0.437	0.574	1.329
$\Sigma\nu_M$[b]	2.038	2.045	1.917	1.927	2.152	2.092	2.060

[a] See paper of O'Keeffe and Brese for a detailed description of the calculation of the valencies.[29] [b] $\Sigma\nu_M$ is the sum of all valencies of a given metal atom.

Table 6. Comparions of Basic Structural Parameters of (a) **1**−**3** and of (b) **4** to Those of Related Compounds (Distances in Å, Angles in deg)

(a) Compounds **1**−**3**

compd	coord mode	Zn−S$_{av}$	Zn−N$_{av}$	S−Zn−S$_{av}$	refs
1	$Zn(NS_2Cl)$	2.341	2.044	111.8	this work
$[ZnL^1]$[a]	$Zn(NS_2Cl)$	2.332	2.041	107.6	21
$[\{\mathit{Zn}(L)\}_4\{Zn(L)_2\}_2](ClO_4)_4$[b]	$Zn(NS_3)$	2.332[f]	2.063		41
$[ZnL^2]_4$[c]	$Zn(NS_3)$	2.337[f]	2.139	109.0[f]	23
$[\{ZnCl_2\}_2\{\mathit{Zn}(L^3)\}_2]$[d]	$Zn(N_2S_2)$	2.285	2.09	148.1	42
ZnL_2	$Zn(N_2S_2)$	2.288	2.054	127.1	12
$[\{Zn(L)\}_4\{\mathit{Zn}(L)_2\}_2](ClO_4)_4$[b]	$Zn(N_2S_2)$	2.313	2.037	122.7	41

compd	coord mode	Cd−S$_{av}$	Cd−N$_{av}$	ΣS−Cd−S	refs
2	$Cd(NS_3Cl)$	2.634	2.351	358.9	this work
CdL_2	$Cd(N_2S_3)$	2.575	2.378	360.0	12
$[AsPh_4][Cd(Ph\text{-}COS)_3]$	$Cd(O_2S_3)$	2.512		360.0	25

compd	coord mode	Hg−S$_{av}$	Hg−N$_{av}$	S−Hg−S	refs
3·NaOH·2H$_2$O	$Hg(NS_2Cl)$	2.471	2.339	133.6	this work
3·2H$_2$O	$Hg(NS_2Cl)$	2.516	2.257	131.4	16
$[\{HgCl_2\}_2\{\mathit{Hg}(L^4)_2\}_2]$[b,e]	$Hg(N_2S_2)$	2.415	2.485	163.6	43
HgL_2	$Hg(N_2S_2)$[g]	2.361	2.591	161.2	12

(b) Compound **4**

compd	coord mode	Hg−S$_{av}$	Hg−Cl$_{av}$	S−Hg−S$_{av}$	refs
4	$Hg1(Cl_4S_2)$	2.417	2.970	180.0	this work
4	$Hg2(Cl_4S)$[h]	2.431	2.740		this work
$[Hg_3(HL)_3Cl_5]Cl$	$Hg1(ClS_2)$	2.390	2.763	167.9	16
$[Hg_3(HL)_3Cl_5]Cl$	$Hg2(ClS_3)$	2.570	2.722	149.3[i]	16
$[Hg_3(HL)_3Cl_5]Cl$	$Hg3(Cl_3S)$	2.450	2.561		16
$[Hg_6Cl_8(HL)_8)]Cl_4\cdot 4H_2O$	$Hg1(Cl_2S_2)$	2.402	2.814	158.1	17
$[Hg_6Cl_8(HL)_8)]Cl_4\cdot 4H_2O$	$Hg2(Cl_2S_2)$	2.368	3.045	171.9	17
$[Hg_6Cl_8(HL)_8)]Cl_4\cdot 4H_2O$	$Hg3(Cl_2S_3)$	2.510	2.863	162.6[i]	17
$[Hg(HL)_2]Cl_2$	$Hg(S_2)$	2.336		168.5	15

[a] L^1 = bis(mercaptoimidazolyl)(pyrazolyl)borate ligand. [b] Data refers to metal atom in italics. [c] $L^2 = BzlN(CH_2CH_2S)_2$. [d] $L^3 = (-CH_2N(Me)CH_2CH_2S)_2$. [e] $L^4 = SCH_2CH_2NMe_2$. [f] Only endocyclic Zn−S bonds and S−Zn−S angles were considered. [g] An additional long Hg···S contact present in the structure is not considered here. [h] An additional long Hg···S contact present in the structure is not considered here. [i] Only the *trans*-S−Hg−S angle was considered here.

three S atoms occupying equatorial positions.[25] In all other cases, either a distorted square pyramidal configuration or a trigonal biypramidal configuration with at least one S atom in an apical position is present. The Cd−S bonds in **2** are distinctly ionic as can be inferred from the bond valencies (see Table 5 and further down for a more detailed discussion) together with the similarity of the distances of the bridging S atom to all three metal ions it coordinates to. The average Cd−S distance is longer and the Cd−N bonds are slightly shorter then those of [CdL$_2$], in accordance with relations found between configurations Zn(NS$_2$Cl) and Zn(N$_2$S$_2$) (see above).

The crystal structure of **3** consists of parallel chains of Hg(L)Cl units between which NaOH(H$_2$O)$_2$ complexes are placed (see Figure 3b). There are already several examples of structures containing a Na(H$_2$O)$_2$(X) unit with Na$^+$ in a trigonal pyramidal coordination environment of three oxygen atoms.[26−28] Presumably due to electrostatic reasons, the distance between the Na$^+$ and the OH$^-$ ion is more than 0.3 Å shorter than the distances between Na$^+$ and the H$_2$O molecules. The coordination of the cations is as one would predict from the HSAB principle; i.e., the hard Na$^+$ ion coordinates to the hardest donors, i.e., the O atoms, while the soft Hg^{2+} ion is coordinated by the softer S atoms. It is interesting to compare the structure of **3**·NaOH·2H$_2$O to that of **3**·2H$_2$O (Table 6).[16] Both contain tetracoordinate Hg atoms

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(25) Vittal, J. J.; Dean, P. A. W. *Inorg. Chem.* **1996**, *35*, 3089.

(26) Yang, W.; Lu, C.; Zhang, Q.; Chen, S.; Zhan, X.; Lin, J. *Inorg. Chem.* **2003**, *42*, 7309.

(27) Rzaczynska, Z.; Bartyzel, A.; Glowiak, T. *J. Coord. Chem.* **2003**, *56*, 77.

(28) Lindsay, A. J.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2723.

Table 7. Crystal Data for Compounds **1**−**4**

param	**1**	**2**	**3**·NaOH·2H$_2$O[a]	**4**
empirical formula	$C_4H_{12}Cl_2N_2S_2Zn_2$	$C_2H_6CdClNS$	$C_2H_6ClHgNS\cdot NaOH\cdot 2H_2O$	$C_2H_7Cl_3Hg_{1.5}NS\cdot H_2O$
fw	353.92	224.01	388.21	502.39
cryst system	monoclinic	monoclinic	orthorhombic	triclinic
space group	*C*2/*c*	*P*2$_1$/*c*	*Pbcn*	*P*1
Z	8	8	8	2
temp/K	295	300	295	193
$\rho_{calcd.}$/g cm^{-3}	1.965	2.620	2.537	3.521
??λ, Å	1.541 78	1.541 78	0.710 69	0.710 69
μ/mm^{-1}	11.94[b]	37.38[c]	15.61[c]	25.30[d]
F(000)	1408	848	1424	520
cryst size/mm^3	0.12 × 0.12 × 0.28	0.02 × 0.20 × 0.20	0.02 × 0.04 × 0.28	0.04 × 0.09 × 0.25
θ-range/deg	$1.5 \leq \theta \leq 74$	$1.5 \leq \theta \leq 74$	$2 \leq \theta \leq 27$	$2 \leq \theta \leq 28.4$
limiting indices	$0 \leq h \leq 29$	$0 \leq h \leq 9$	$-1 \leq h \leq 20$	$-9 \leq h \leq 9$
	$-9 \leq k \leq 0$	$0 \leq k \leq 21$	$-9 \leq k \leq 1$	$-11 \leq k \leq 11$
	$-20 \leq l \leq 16$	$-11 \leq l \leq 11$	$-21 \leq l \leq 1$	$-11 \leq l \leq 11$
a/Å	26.6751(10)	7.4818(14)	15.869(8)	6.8445(3)
b/Å	7.8618(7)	16.9489(25)	7.458(1)	8.7229(3)
c/Å	16.9028(7)	8.9594(24)	17.177(7)	8.9438(4)
α/deg	90.0	90.0	90.0	109.956(2)
β/deg	130.484(2)	91.568(10)	90.0	102.519(2)
γ/deg	90.0	90.0	90.0	99.186(2)
V/Å^3	2392.9(3)	1135.7(4)	2033(1)	473.84(5)
reflcns measd	2480	2568	2895	7597
unique reflcns	2422	2294	2213	2361
reflcns $\lvert F\rvert > 4\sigma(F)$	2220	1881	947	1778
$R\ [\lvert F\rvert > 4\sigma(F)]$[e]	0.0328	0.0783	0.0638	0.0465
goodness-of-fit on F^2	1.062	1.032	0.998	0.967
largest diff peak and hole	−0.81/0.57	−2.90/2.38	−1.590/1.324	−2.59/4.36(near Hg2)

[a] Hydrogen atoms of the two water molecules were not located during the refinement. [b] Absorption correction with ψ-scans using CORINC.[44] [c] Absorption correction with six planes using PLATON.[45] [d] Absorption correction with MULABS.[46] [e] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

with a Hg($ClNS_2$) coordination mode, distorted tetrahedral geometry, and infinite chains resulting from Hg−S bridges between Hg(L)Cl units. While the average Hg−S distances do not differ very much between the two compounds, significant differences of Hg−S bond lengths within and between the chelating rings occur. Hg−S distances within the chelating rings are much longer in **3**·2H$_2$O (2.636 Å) than in **3**·NaOH·2H$_2$O (2.501 Å), and Hg−S bonds between the Hg(L)Cl units are shorter in **3**·2H$_2$O (2.397 Å) than in **3**·NaOH·2H$_2$O (2.440 Å). The coordination of the Hg atoms in **3**·2H$_2$O and in **3**·NaOH·2H$_2$O is analogous to that of the Zn atom in **1**. The most obvious difference between the Zn and the Hg complexes is the mode of aggregation. In contrast to the discrete cyclic tetramers of **1**, infinite chains of alternating Hg and S atoms are present in **3**·NaOH·2H$_2$O. The S−Hg−S angles in **3**·2H$_2$O and in **3**·NaOH·2H$_2$O are approximately 20° wider than the average of the S−Zn−S angles in **1** (Tables 6). This reflects the situation found in [ZnL$_2$] and [HgL$_2$], with S−Zn−S = 127.1(1)° and S−Hg−S = 161.2(1)°.[12] The wide angle is seen as the main reason for the preference of an S−Hg−S−Hg chain over a cyclic structure as found in **1**. Since the Hg atoms are asymmetrically substituted, they can occur in two different configurations. In **3**·NaOH·2H$_2$O and in **3**·2H$_2$O, neighboring units within the chains display opposite configurations. As a consequence, the Hg−S chains do not adopt a helical structure but lay more or less in a plane.

More subtle differences between **1** and **3**·NaOH·2H$_2$O are found, if the bond distances are analyzed in terms of bond valencies, ν_{A-B}, according to O'Keeffe and Brese (see Table 5).[29] Valencies are derived from the standard bond length of an A−B bond, calculated according to the procedure described by O'Keeffe and Brese, and the experimentally found interatomic distance. In all cases, the sum of the valencies of a given central atom (i.e. Zn, Cd, or Hg) is close to a value of 2, which is what one would expect from the charge of the ions. ν_{Hg-S} are substantially bigger than ν_{Zn-S}, while ν_{Hg-Cl} and ν_{Hg-N} are smaller than their Zn analogues. That points to a more covalent character of the Hg−S bonds compared to the Zn−S bonds and Hg−N bonds which are weaker than Zn−N bonds, in accordance with recent findings for ZnL$_2$ and HgL$_2$.[12] Among the four compounds the sum of the bond valencies is smallest for the Cd atoms in **2**, despite its higher coordination number compared to Zn and Hg in compounds **1** and **3**·NaOH·2H$_2$O. Interestingly, the bond valencies of the two Hg atoms in **4** are rather similar, despite their different coordination modes and different values of $\Sigma\nu_{Hg-S}$ and $\Sigma\nu_{Hg-Cl}$.

It is furthermore interesting to note that the S atoms in **1**−**3**·NaOH·2H$_2$O form bridges between the metal atoms, while the Cl atoms are involved in hydrogen bonds.

From the torsion angles given in Tables 1−3, it can be seen that in **1**, **2**, and **3**·NaOH·2H$_2$O, the five-membered chelating rings adopt envelope conformations. In all cases the nitrogen bound C atom is 0.61−0.65 Å above a least-squares plane defined by the other four atoms.

In compound **4** (see Figure 4), the ligand is present as the zwitterionic cysteamine[12] instead of anionic cysteaminate and subsequently coordinates with its S atom only to the Hg^{2+}.

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(29) O'Keeffe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226−3229.

4 contains two differently coordinate Hg atoms. Hg1 is situated on a center of inversion and exhibits a slightly distorted octahedral geometry with a $Hg(Cl_4S_2)$ coordination mode. Hg2 displays a "5 + 1" coordination, with a $Hg(Cl_4S)$ coordination mode and a long Hg···Cl contact, the geometry being best described as a strongly distorted octahedron. While none of the Cl atoms in **1**−**3** coordinates in a bridging mode, all Cl atoms in **4** act either as μ^2 (Cl2 and Cl3) or even μ^3 (Cl1) bridges. Thus, parallel chains of Cl and S bridged Hg atoms are formed which are held together by long Hg···Cl contacts and N−H···Cl hydrogen bonds. Furthermore, O−H···Cl and N−H···O hydrogen bonds are present, by which the two H_2O molecules/$\{[Hg_3(HL)_2Cl_6]$ unit are connected to the latter. The N−H···O hydrogen bonds are longer and more bent than those present in $[Hg_6Cl_8(HL)_8)]Cl_4 \cdot 4H_2O$ ($N \cdots O_{av} = 2.773$ Å, $N-H \cdots O_{av} = 167.9°$).

The bond valencies in Table 5 demonstrate that the bonding situation of Hg1 is best described as a covalent linear S−Hg−S unit to which neighboring chlorine atoms form weak contacts. Similarly, Hg2 forms short bonds to S1 and Cl3, which are trans to each other, while distances to the other chlorine atoms are much longer. The coordination of Hg1 is related to that of the Hg atoms in solid $HgCl_2$, where each Hg atom exhibits a distorted octahedral coordination sphere, with two short (2.28 Å) and four long (3.38 and 3.46 Å) Hg−Cl distances.[30]

A variety of coordination modes is found in three other complexes in the system $Hg^{2+}/Cl^-/HL$ (see Table 6), where due to protonation of the nitrogen atom of the ligand no Hg···N contacts are present. In contrast to **4**, $[Hg_3(HL)_3Cl_5]Cl$, and $[Hg_6(HL)_8Cl_8]Cl_4 \cdot 4H_2O$, no Hg···Cl contacts are present in the solid-state structure of $[Hg(HL)_2]Cl_2$. A linear $Hg(S_2)$ coordination mode with very short Hg−S bonds is found instead.[15]

Conclusion

All compounds [M(L)Cl] (M = Zn, Cd, Hg; L = $SCH_2CH_2NH_2$) exhibit a chelating N,S-coordination mode of the cystaminate ligand, while in $\{[Hg_3(HL)_2Cl_6] \cdot 2H_2O\}$ cystamine binds only via its S atom to the Hg atoms.

Zn^{2+} and Hg^{2+} are tetracoordinate in complexes [M(L)Cl], exhibiting distorted tetrahedral $M(ClNS_2)$ coordination modes. The bigger Cd^{2+} is pentacoordinate by one Cl atom, one N atom, and three S atoms, giving a slightly distorted trigonal bipyramidal geometry with all S atoms in equatorial positions. Due to S atoms acting as μ^2 (M = Zn, Hg) or μ^3 (M = Cd) bridges, the compounds form cyclic tetranuclear complexes (**1**), chain structures (**3**), and sheet structures (**2**). The large S−Hg−S angle in **3** prevents it from having a cyclic structure like **1**. All four compounds presented in this paper crystallize as oligo- or polynuclear instead of mononuclear complexes. This might be a consequence of the ratio of the number of donor atoms, *d*, to those of the metal atoms, *m*, together with the fact that the small cysteaminate ligand does not sterically shield the metal ions. In contrast to $[ZnL_2]$ (mononuclear), $[HgL_2]$ (weakly bound dimer), and $[CdL_2]$ (chain structure) all of which have $d{:}m = 4$, for the M(L)Cl complexes $d{:}m = 3$. In the case of compound **4**, $d{:}m = 2.67$, since the N atoms are protonated and do not act as donor atoms and the O atoms do not coordinate to Hg. Due to ligand bridging, the coordination number of the metal atoms in **1**−**4** is higher than the actual *d*:*m* ratio. As a consequence, the structural dimensionality of **2** and **3** is increased by 1 compared to $[CdL_2]$ and $[HgL_2]$.

Experimental Section

General Procedures. Metal chlorides, $[H_2L]Cl$ (cysteamine hydrochloride), and NaOH were used as purchased. Solvents were purified according to standard procedures. NMR: Bruker DRX 400, $B_1(^1H) = 400.0$, $B_1(^{13}C) = 100.577$. Standard: TMS. IR: Mattson Galaxy 2030 FTIR, resolution 4 cm^{-1}, NaCl pellets, range 4000−600 cm^{-1}. CHNS analysis was performed with an Elemental Vario EL2.

Preparation of Zinc 2-Aminoethanethiolate Chloride, [Zn(L)Cl], 1. 2-Mercaptoethylammonium chloride, $[H_2L]Cl$ (1.14 g, 10.0 mmol), and sodium hydroxide, NaOH (0.80, 10.0 mmol), were dissolved in 15 mL of methanol, and the precipitated NaCl was filtered off. The filtrate was slowly added to a solution of zinc chloride, $ZnCl_2$ (1.36 g, 10.0 mmol), in 40 mL of methanol and the solution refluxed during 4 h. The precipitated NaCl was filtered off and the solution kept at −20 °C. Under these conditions, **1** precipitated as colorless crystals. Yield: 1.13 g (63.8%). Single crystals of **1** suitable for X-ray diffraction were obtained from the precipitate. Anal. Calcd for $C_2H_6ClNSZn$ ($M_r = 176.98$ g mol^{-1}): C, 13.57; H, 3.42; N, 7.92; S 18.12. Found: C, 13.63; H, 3.34; N, 7.88; S, 18.50. ^1H NMR (D_2O): δ 4.6 (broad m, 2 H, NH_2), 2.86 (t, $^3J(H,H) = 5.7$ Hz, 2 H, NCH_2), 2.69 (t, $^3J(H,H) = 5.7$ Hz, 2 H, SCH_2). $^{13}C\{^1H\}$ NMR (D_2O): δ 43.0 (NCH_2), 27.7 (SCH_2). IR: 3273 (w, $\nu(NH_2)$), 3221 (m, $\nu(NH_2)$), 3200 (m, $\nu(NH_2)$), 2990 (vs, $\nu_{as}(CH_2)$), 2959 (vs, $\nu_{as}(CH_2)$), 2910 (sh, $\nu_s(CH_2)$), 2792 (m), 2719 (m), 2599 (m), 2399 (m), 1626 (m, $\delta(NH_2)$), 1600 (s, $\delta(NH_2)$), 1591 (s, $\delta(NH_2)$), 1477 (vs, $\delta(CH_2)$), 1461 (vs, $\delta(CH_2)$), 1422 (m, $\omega(CH_2)$), 1402 (s, $\omega(CH_2)$), 1381 (m, $\omega(CH_2)$), 1336 (m), 1262 (m, $t(CH_2)$), 1242 (m, $t(CH_2)$), 1142 (m), 1096 (s, $\nu(N-C)$), 1064 (m, $\nu(N-C)$), 1028 (m), 946 (m, $\nu(C-C)$), 926 (s, $\nu(C-C)$), 894 (m), 812 (m), 768 cm^{-1} (m).

Preparation of Cadmium 2-Aminoethanethiolate Chloride, [Cd(L)Cl], 2. $CdCl_2$ (1.83 g, 10.0 mmol) and 2-mercaptoethylammonium chloride, $[H_2L]Cl$ (1.14 g, 10.0 mmol), were dissolved in a mixture of 30 mL of methanol and 15 mL of H_2O. A solution of NaOH (0.80 g, 20.0 mmol) in 60 mL of methanol was added, and the resulting solution was heated to reflux for 2 h. **2** precipitated as a colorless powder and was filtered out, washed (2 × 15 mL pf H_2O at 0 °C and 2 × 15 mL of methanol), and dried in vacuo. Yield: 1.87 g (83.5%). Mp: 190 °C (dec). Single crystals of **2** suitable for X-ray diffraction were obtained by vacuum sublimation (150 °C, 2×10^{-3} mbar). Anal. Calcd for $C_2H_6CdClNS$ ($M_r = 224.01$ g mol^{-1}): C, 10.72; H, 2.70; N, 6.25; S 14.31. Found: C, 10.78; H, 2.72; N, 6.24; S, 14.25. IR: 3262 (vs, $\nu_{as}(NH_2)$), 3230 (s, $\nu_s(NH_2)$), 3141 (s, $\nu(NH_2)$), 2964 (m, $\nu_{as}(CH_2)$), 2923 (m, $\nu_s(CH_2)$), 2876 (m, $\nu_s(CH_2)$), 1608 (w, $\delta(NH_2)$), 1587 (m, $\delta(NH_2)$), 1452 (m, $\delta(CH_2)$), 1414 (m, $\omega(CH_2)$), 1382 (w, $\omega(CH_2)$), 1313 (m), 1286 (m, $t(CH_2)$), 1234 (m, $t(CH_2)$), 1095 (s, $\nu(N-C)$), 1055(s, $\nu(N-C)$), 986 (m), 968 (m), 924 (m, $\nu(C-C)$), 825 (m), 659 (m, $\nu(S-C)$), 624 cm^{-1} (m, $\nu(S-C)$).

Preparation of Mercury(II) 2-Aminoethanethiolate Chloride, Hg(L)Cl, 3. 2-Mercaptoethylammonium chloride, $[H_2L]Cl$ (4.45 g, 39.2 mmol), and NaOH (3.12 g, 78.0 mmol) were dissolved in

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[30] Subramanian, V.; Seff, K. *Acta Crystallogr.* **1980**, *B36*, 2131.

100 mL of ethanol, and the precipitated NaCl was filtered off. The solution was added to a solution of $HgCl_2$ (10.68 g, 39.3 mmol) in 50 mL of ethanol which was subsequently heated to reflux for 4 h. A colorless precipitate formed which was filtrated, washed (2 × 15 mL of H_2O at 0 °C and 2 × 15 mL of methanol), and dried in vacuo. Yield: 8.65 g (56.7%). Anal. Calcd for $C_2H_6ClHgNS$ (M_r = 312.19 g mol^{-1}): C, 7.69; H, 1.94; N, 4.49; S 10.27. Found: C, 7.89; H, 1.89; N, 4.04; S, 10.14. IR: 3337 (s, $\nu_{as}(NH_2)$), 3284 (vs, $\nu_s(NH_2)$), 3139 (sh), 2953 (sh, $\nu_{as}(CH_2)$), 2924 (s, $\nu_s(CH_2)$), 2857 (m, $\nu_s(CH_2)$), 1582 (s, δ(NH)), 1452 (m, $\delta(CH_2)$), 1420 (m, ω-(CH_2)), 1363 (s, $\omega(CH_2)$), 1304 (m), 1276 (m, t(CH_2)), 1231 (m, t(CH_2)), 1096 (vs, ν(N−C)), 995 (w, ν(N−C)), 963 (m, ν(C−C)), 916 (m, ν(C−C)), 832 (m), 648 (w, ν(S−C)), 623 cm^{-1} (s, ν(S−C)).

Preparation of Mercury(II) 2-Aminoethanethiolate Chloride Sodium Hydroxide Dihydrate, Hg(L)Cl·NaOH·2H_2O, 3·NaOH·2H_2O. Approximately 0.5 g of **3** was stirred in approximately 10 mL of dmso at room temperature, and diluted (approximately 5%) aqueous NaOH solution was slowly added until the solid was dissolved. Subsequently, thf was condensed onto that solution. Single crystals of **3**·NaOH·2H_2O suitable for X-ray crystallography precipitated from this solution. Anal. Calcd for $C_2H_{11}ClHgNaNO_3S$ (M_r = 388.21 g mol^{-1}): C, 6.19; H, 2.86; N, 3.61; S 8.26. Found: C, 7.27; H, 1.90; N, 3.71; S, 8.52. IR: 3451 (vs, ν(OH)), 3279 (vs, $\nu_{as}(NH_2)$), 3230 (vs, $\nu_s(NH_2)$), 3143 (s, $\nu_s(NH_2)$), 2984 (m, $\nu_{as}(CH_2)$), 2920 (s, $\nu_s(CH_2)$), 2862 (m, $\nu_s(CH_2)$), 1626 (vs, δ(NH)), 1579 (s, δ(NH)), 1449 (m, $\delta(CH_2)$), 1405 (m, $\omega(CH_2)$), 1368 (w, $\omega(CH_2)$), 1302 (m), 1270 (m, t(CH_2)), 1226 (m, t(CH_2)), 1115 (w), 1016 (s, ν(N−C)), 954 (s, ν(C−C)), 917 (s), 829 (m), 647 cm^{-1} (m, ν(S−C)).

Preparation of Tris(mercury(II) chloride) Bis(2-ammoniumylethanethiolate) Dihydrate, {[$Hg_3(HL)_2Cl_6$]·2H_2O}, 4. Solid **4** precipitated from a solution of 1.0 mmol of $HgCl_2$ and 1.0 mmol of [H_2L]Cl in 50 mL of deionized water, when 0.1 M NaOH was added and the pH reached a value of 3. Anal. Calcd for $C_4H_{18}Cl_6Hg_3N_2O_2S_2$ (M_r = 1004.82 g mol^{-1}): C, 4.78; H, 1.81; N, 2.79; S 6.38. Found: C, 4.81; H, 1.92; N, 2.80; S, 6.46.

Crystal Structure Determination. Diffraction experiments were performed on a Turbo CAD4 (Nonius) diffractometer for **1** and **2** and on a SMART CCD (Bruker Nonius) diffractometer for **3** and **4**. The crystal structures were solved by direct methods and the difference Fourier technique (SIR-92);[31] structural refinement was against F^2 (SHELXL-97).[32] Details of the crystal structure determination of **1**−**4** and their crystal data are given in Table 7.

Theoretical Methods. The density functional calculations were performed using the GAUSSIAN98 software package.[33] Geometry optimization, single point energy calculation, and calculation of vibrational frequencies were performed by employing a combination of local, gradient-corrected, and exact exchange functionals according to the prescription of Becke[34] and the gradient-corrected correlation functional of Lee, Yang, and Parr,[35] together with an effective core double-ζ valence basis set designated as LANL2DZ-(d). In these basis sets, relativistic effective core potentials and the corresponding double-ζ valence basis sets for S and Zn,[36,37] augmented by appropriate d-type function for S (with exponents according to Höllwarth et al.),[38] were used. C and N: Dunning's and Hay's [3s2p] contracted valence double-ζ basis,[39] augmented with a set of d-type polarization functions (exponent 0.75 for C and 0.80 for N). H: Huzinaga's (4s) basis contracted to [2s].[40]

Supporting Information Available: X-ray crystallographic files in CIF format for all structures presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435−436.

(32) Sheldrick, G. M. *SHELXL-97 Program for crystal structure refinement*; University of Göttingen: Germany, Göttingen, 1997.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. J. A.; E., S. R.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(34) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(35) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785−789.

(36) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823−2833.

(37) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716−723.

(38) Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237−240.

(39) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4, pp 1−27.

(40) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639−5648.

(41) Friebe, M.; Mahmood, A.; Spies, H.; Berger, R.; Johannsen, B.; Mohammed, A.; Eisenhut, M.; Bolzati, C.; Davison, A.; Jones, A. G. *J. Med. Chem.* **2000**, *43*, 2745.

(42) Albrich, H.; Vahrenkamp, H. *Chem. Ber.* **1994**, *127*, 1223.

(43) Casals, I.; Gonzalez-Duarte, P.; Clegg, W.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M.; Gomez, M.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1991**, 2511.

(44) Dräger, M.; Gattow, G. *Acta Chem. Scand.* **1971**, *25*, 761−762.

(45) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.

(46) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33−38.