



# Synthesis and X-ray crystal structures of dinuclear hydrogen-bonded cadmium and lead 2-aminoethanethiolates

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## Abstract

Under varying conditions the reaction of cysteamine hydrochloride (SHCH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)Cl with stoichiometric amounts of Cd and Pb salts in water gave [Cd<sub>2.5</sub>Cl<sub>5</sub>(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)] (1), [Cd(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>] (2), [Pb<sub>2</sub>Cl(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>] (3) and [Pb<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>](NO<sub>3</sub>)<sub>0.67</sub>(Cl)<sub>0.33</sub> (4). Compound 1 is a molecular solid, one that contains a solid state-like core, but is nevertheless soluble in common organic solvents. The geometry around the Cd atoms in 1 are octahedral with varying numbers of sulfur and chlorine atoms. In contrast the pentacoordinate Cd atoms in 2 possess distorted square pyramidal geometry comprised of cysteamine sulfur and nitrogen atoms. Compounds 3 and 4 are structurally similar despite the presence and involvement of the anion in 4. The Pb atoms in 3 possess both distorted square pyramidal and octahedral geometry, while in 4 the geometry around the Pb atoms is distorted square pyramidal. The NO<sub>3</sub> and Cl anions in 4 participate in more extensive hydrogen bonding by comparison to 3, which has a Cl anion only. The hydrogen bonding in these compounds is not confined to the presence or absence of anions, as it is also observed between the amine of cysteamine with adjacent sulfur and nitrogen atoms. Full characterization of the compounds was achieved using IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, EA, Mass Spectrometry and X-ray crystallography.

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## 1. Introduction

Cysteamine (2-aminoethanethiol, SHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) may be considered a derivative of either cysteine (HSCH<sub>2</sub>CH(NH<sub>2</sub>)COOH) or Penicillamine (SH(CH<sub>3</sub>)<sub>2</sub>CCH(NH<sub>2</sub>)COOH) and its chemistry with transition metals has been studied extensively. The compounds may be used as alkylating agents and as a radiation protectant [1]. Mononuclear and polynuclear complexes of Ni(II) with cysteamine were the first reported examples [2]. Since then a wide range of metal complexes with various stoichiometries have been reported [3,4]. These are

of the formula: M<sub>x</sub>L<sub>y</sub> ( $x = 3-6$ ,  $y = 4-12$ , L = cysteamine and M = Au<sup>+</sup>, Cu<sup>1+/2+</sup>, Cd<sup>2+</sup>, Co<sup>3+</sup>, Fe<sup>3+</sup>, Hg<sup>2+</sup>, Ir<sup>3+</sup>, Mo<sup>3+/4+</sup>, Ni<sup>2+</sup>, Os<sup>3+</sup>, Pb<sup>2+</sup>, Pd<sup>2+</sup>, Pt<sup>2+</sup>, Re<sup>3+</sup>, Rh<sup>3+</sup>, Ru<sup>3+</sup>, Zn<sup>2+</sup>) [1,3-7] and ML<sub>2</sub> for the alkaline earth metals and Bi<sup>3+</sup>, Ag<sup>1+/2+</sup>, Pd<sup>2+</sup>, Zn<sup>2+</sup>, ReO<sup>5+</sup> and Ni<sup>2+</sup> [8-10]. The study of mercaptide ions as donors, especially 2-aminoethanethiol, of mL<sub>2</sub> stoichiometry have not been subjected to detailed study as the complexes obtained are extremely insoluble, bridged and/or even polymeric in nature, making structural studies prohibitively difficult [3]. Recently, Bi<sup>3+</sup> and ReO<sup>5+</sup> cysteamine complexes of ML<sub>2</sub> stoichiometry have been characterized by X-ray structures [10,11]. In recently reported Pb-cysteamine complexes (PbCl<sub>2</sub> · (SCH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)), Pb(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub> · 2PbCl(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) and Pb(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>, the molecules are held together through intermolecular Pb-S bonds, unlike 3

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and **4** reported here [12]. This clearly implies that the reaction conditions affect the structural chemistry.

Our continued interest in aqueous chemistry of heavy metal-thiolates led us to study Cd and Pb-aminoethanethiolates [13,14]. In a previous study with cysteamine [15], we have shown that binding to Hg in water results in a linear S–Hg–S linkage (bond angle 168.53°). This follows the precedent found in other monodentate thiolate ligands such as cysteine [16,17]. There were also some S–H hydrogen bonding, something that has not been observed for Hg containing metalloproteins such as MerR and MerP [18,19]. Here, we describe the cysteamine complexes of Cd(II) and Pb(II) which, in addition to forming unique structures, also possess extensive hydrogen-bonding involving something that has not been reported previously for similar dinuclear complexes.

## 2. Experimental

All the reactions were carried out at room temperature in deionized water. The reagents CdCl<sub>2</sub>, CdCO<sub>3</sub>, Pb(Ac)<sub>2</sub> · 3H<sub>2</sub>O and PbNO<sub>3</sub> (J.T. Baker) and cysteamine hydrochloride (TCI America) were used as received. NMR (<sup>1</sup>H and <sup>13</sup>C) data were obtained with JEOL-GSX-400 and 270 instruments operating at 199.17 and 399.78 MHz using *d*<sup>6</sup>-DMSO and D<sub>2</sub>O as solvents, with tetramethylsilane as the reference. IR data were recorded as KBr pellets on a Matheson Instrument 2020 Galaxy Series spectrometer and are reported in cm<sup>-1</sup>.

X-ray data for **1–4** were collected on a Nonius Kappa-CCD unit using Mo K $\alpha$  radiation and crystallographic data are summarized in Table 1. For bond lengths and bond angles see Tables 3–6. A summary of the IR spectra for compounds **1–4** in tabular form is included in the supplementary information.

### 2.1. Preparation of [Cd<sub>2.5</sub>Cl<sub>5</sub>(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)] (**1**)

Cadmium (II) chloride (0.94 g, 5 mmol) was added to a stirring solution of cysteamine hydrochloride (1.14 g, 10 mmol) in deionized water (20 mL) and the resulting mixture was stirred over 3 days. The solution was then filtered to remove a white precipitate and the filtrate was allowed to stand for 4 weeks in the refrigerator (4 °C), during which colorless crystals were formed. Crystalline yield: 0.29 g (10%), m.p. 222–224 °C (dec). <sup>1</sup>H NMR (*d*<sup>6</sup>-DMSO, 200 MHz, ppm):  $\delta$  2.69 (t, 4H, CH<sub>2</sub>N), 3.14 (t, 4H, CH<sub>2</sub>S), 7.75 (s, 6H, NH<sub>3</sub>). <sup>13</sup>C NMR (*d*<sup>6</sup>-DMSO, 200 MHz, ppm):  $\delta$  33.9 (CH<sub>2</sub>S), 43.1 (CH<sub>2</sub>N). IR (KBr,  $\nu$ /cm<sup>-1</sup>): 657 (C–S), 1230 (C–N, stretching), 1258, 1320, 1376, 1427 (S–CH<sub>2</sub>), 1491, 1561, 1583 (–NH<sub>2</sub> and N–H, bending), 2361, 2938, 3130 (NH<sub>3</sub><sup>+</sup>), 3450 (R–NH<sub>2</sub>, stretching). MS (EI, positive): *m/z* 247 (M + 2)<sup>+</sup>, 171 (M – SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sup>+</sup>, 92 (M – 2(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>))<sup>+</sup>, 76 (SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sup>+</sup>. Anal. Calc. for C<sub>4</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub>Cl<sub>5</sub>Cd<sub>2.5</sub>: C, 7.84; H, 2.30; N, 4.57; S, 10.47. Found: C, 7.65; H, 2.20; N, 4.55; S, 10.43%.

Table 1  
Crystallographic data for compounds **1–4**

Data/compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>4</sub> H <sub>14</sub> N <sub>2</sub> S <sub>2</sub> Cd <sub>2.5</sub> Cl <sub>5</sub>	C <sub>4</sub> H <sub>12</sub> N <sub>2</sub> S <sub>2</sub> Cd	C <sub>6</sub> H <sub>18</sub> N <sub>3</sub> S <sub>3</sub> Pb <sub>2</sub> Cl	C <sub>6</sub> H <sub>18</sub> N <sub>3.67</sub> O <sub>2.02</sub> S <sub>3</sub> Pb <sub>2</sub> Cl <sub>0.33</sub>
Molecular weight	612.54	264.68	678.24	696.15
Temperature (K)	173 (1)	145(2)	145 (2)	206 (2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Unit cell dimensions</i>				
<i>a</i> (Å)	10.4530 (6)	6.2800 (10)	9.1680 (10)	9.3600 (10)
<i>b</i> (Å)	8.1430 (5)	8.2360 (10)	9.5880 (10)	9.5300 (10)
<i>c</i> (Å)	17.5180 (8)	8.5420 (10)	16.707 (2)	17.057 (10)
$\alpha$ (°)	90	92.270 (10)	90	90
$\beta$ (°)	90.426 (3)	99.566 (10)	95.410 (10)	95.860 (10)
$\gamma$ (°)	90	102.563 (10)	90	90
<i>V</i> (Å <sup>3</sup> )	1491.07 (14)	423.92 (10)	1462.1 (3)	1513.5 (3)
<i>Z</i>	4	2	4	4
Absorption coefficient (mm <sup>-1</sup> )	4.694	2.990	23.587	22.685
<i>F</i> (000)	1156	260	1216	1254
Crystal size	0.11 × 0.10 × 0.06	0.08 × 0.08 × 0.08	0.16 × 0.10 × 0.10	0.15 × 0.14 × 0.05
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.050	1.081	0.492	1.049
<i>R</i> <sub>1</sub> (on <i>F</i> , <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0354	0.0154	0.0249	0.0327
<i>R</i> <sub>1</sub> (all data)	0.0513	0.0176	0.0359	0.0453
<i>wR</i> <sub>2</sub> (on <i>F</i> <sup>2</sup> , <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0737	0.0350	0.0625	0.0582
<i>wR</i> <sub>2</sub> (all data)	0.0787	0.0355	0.0686	0.0619

## 2.2. Preparation of $[Cd(SCH_2CH_2NH_2)_2]$ (**2**)

To a stirring solution of cysteamine hydrochloride (1.14 g, 10 mmol) in deionized water (20 mL) sodium hydroxide (0.80 g, 20 mmol) was added followed by addition of cadmium carbonate (0.86 g, 5 mmol). The mixture was stirred over one day and then solution was filtered to isolate a white precipitate. The filtrate was allowed to stand for 3 days in the refrigerator (4 °C), during which colorless crystals formed in near quantitative yield. Crystalline yield: 0.62 g (47%), m.p. 172–174 °C.  $^1H$  NMR ( $D_2O$ , 200 MHz, ppm):  $\delta$  2.73 (t, 4H,  $CH_2N$ ), 3.01 (t, 4H,  $CH_2S$ ).  $^{13}C$  NMR ( $D_2O$ , 200 MHz, ppm):  $\delta$  28.29 ( $CH_2S$ ), 44.02 ( $CH_2N$ ). IR (KBr,  $\nu/cm^{-1}$ ): 622–661 (C–S), 1051, 1064, 1120, 1214, 1228 (C–N, stretching), 1423 (S– $CH_2$ ), 1580 (– $NH_2$  and N–H, bending), 3551 (R– $NH_2$ , stretching). MS (EI, positive):  $m/z$  266 ( $M + 2$ )<sup>+</sup>, 190 ( $M - SCH_2CH_2NH_2$ )<sup>+</sup>, 114 ( $M - 2(SCH_2CH_2NH_2)$ )<sup>+</sup>, 76 ( $SCH_2CH_2NH_2$ )<sup>+</sup>. Anal. Calc. for  $C_4H_{12}N_2S_2Cd$ : C, 18.15; H, 4.57; N, 10.58; S, 24.23. Found: C, 18.00; H, 4.62; N, 10.51; S, 24.05%.

## 2.3. Preparation of $[Pb_2Cl(SCH_2CH_2NH_2)_3]$ (**3**)

To a stirring solution of cysteamine hydrochloride (1.14 g, 10 mmol) in deionized water (20 mL) sodium hydroxide (0.80 g, 20 mmol) was added followed by addition of lead acetate trihydrate (1.90 g, 5 mmol) and the mixture was stirred over one day. The solution was then filtered to remove a yellow precipitate and the filtrate was allowed to stand for 3 days in the refrigerator (4 °C), during which pale yellow crystals formed. Crystalline yield: 0.64 g (19%), m.p.: 120–122 °C.  $^1H$  NMR ( $D_2O$ , 200 MHz, ppm):  $\delta$  2.852 (t, 6H,  $CH_2N$ ), 3.028 (t, 6H,  $CH_2S$ ).  $^{13}C$  NMR ( $D_2O$ , 200 MHz, ppm):  $\delta$  29.1 ( $CH_2S$ ), 48.5 ( $CH_2N$ ). IR (KBr,  $\nu/cm^{-1}$ ): 668–657 (C–S), 1032, 1065, 1105, 1219 (C–N, stretching), 1417 (S– $CH_2$ ), 1596 (– $NH_2$  and N–H, bending), 3463 (R– $NH_2$ , stretching). MS (EI, positive): 359 ( $Pb(SCH_2CH_2NH_2)_2$ )<sup>+</sup>, 282 ( $Pb(SCH_2CH_2NH_2)$ )<sup>+</sup>, 76 ( $SCH_2CH_2NH_2$ )<sup>+</sup>.

( $SCH_2CH_2NH_2$ )<sup>+</sup>. Anal. Calc. for  $C_6H_{18}N_3S_3ClPb_2$ : C, 10.63; H, 2.67; N, 6.20; S, 14.18. Found: C, 10.24; H, 2.48; N, 5.87; S, 13.37%.

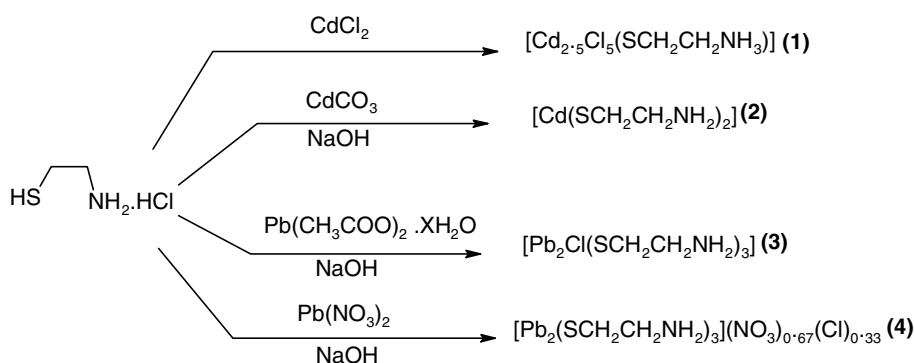
## 2.4. Preparation of $[Pb_2(SCH_2CH_2NH_2)_3](NO_3)_{0.67}(Cl)_{0.33}$ (**4**)

Sodium hydroxide (0.80 g, 20 mmol) was added to a stirring solution of cysteamine hydrochloride (1.14 g, 10 mmol) in deionized water (20 mL) followed by addition lead nitrate (1.66 g, 5 mmol) and the mixture was stirred over a day. The solution was then filtered to remove a white precipitate, and the filtrate was allowed to stand for 10 days in the refrigerator (4 °C), during which colorless crystals formed. Crystalline yield: 0.41 g (24%), m.p. 132–134 °C.  $^1H$  NMR ( $d^6$ -DMSO, 200 MHz, ppm):  $\delta$  2.746 (m, 4H,  $CH_2N$ ), 3.204 (t, 4H,  $CH_2S$ ).  $^{13}C$  NMR ( $d^6$ -DMSO, 200 MHz, ppm):  $\delta$  30.0 ( $CH_2S$ ), 49.3 ( $CH_2N$ ). IR (KBr,  $\nu/cm^{-1}$ ): 628–706 (C–S), 1046–1221 (C–N, stretching), 1430 (S– $CH_2$ ), 1593 (– $NH_2$  and N–H, bending), 3448 (R– $NH_2$ , stretching). MS (EI, positive): 359 ( $Pb(SCH_2CH_2NH_2)_2$ )<sup>+</sup>, 282 ( $Pb(SCH_2CH_2NH_2)$ )<sup>+</sup>, 76 ( $SCH_2CH_2NH_2$ )<sup>+</sup>. Anal. Calc. for  $C_6H_{18}N_{3.67}S_3O_{2.02}Cl_{0.33}Pb_2$ : C, 10.35; H, 2.61; N, 7.38; S, 13.82. Found: C, 10.36; H, 2.57; N, 7.36; S, 13.55%.

## 3. Result and discussion

### 3.1. Synthesis and characterization

Cysteamine hydrochloride and various metal salts were combined in a 1:1 ratio in deionized water to produce compounds **1–4** (Scheme 1). Compounds **1**, **2** and **4** gave white precipitates, while **3** was isolated as a yellow precipitate. The compounds were isolated by filtration in high yields (60–90%) and the supernatants were used to grow X-ray quality crystals at 4 °C. The characterization data (IR, NMR, EA, Mass Spectrometry) were matched for both the precipitates and the crystals. The



Scheme 1. Synthesis of compounds **1–4**.

Table 2  
NMR data for cysteamine hydrochloride and compounds 1–4

<sup>1</sup> H and <sup>13</sup> C NMR/ compounds (in ppm)	Cysteamine hydrochloride	1	2	3	4
<sup>1</sup> H NCH <sub>2</sub>	2.69	2.69	2.73	2.85	2.74
<sup>1</sup> H SCH <sub>2</sub>	2.99	3.14	3.01	3.02	3.20
<sup>13</sup> C NCH <sub>2</sub>	42.8	43.1	44.0	48.5	49.3
<sup>13</sup> C SCH <sub>2</sub>	22.2	33.9	28.2	29.1	30.0

compounds are soluble in hot water but not in common organic solvents.

In the <sup>1</sup>H NMR for 1–4 (Table 2), single peaks were observed for the CH<sub>2</sub>N and CH<sub>2</sub>S groups, which is consistent with symmetrical structures in solution. When bound to the metal ion the ligand hydrogen atoms become more deshielded compared to the free ligand, cysteamine hydrochloride. However, in 1 no change in the chemical shift for CH<sub>2</sub>N confirms the presence of a free amine. The significant shifts in CH<sub>2</sub>S peaks in the <sup>1</sup>H and <sup>13</sup>C spectra for compounds 1–4 indicate a strong metal–sulfur interaction.

In the IR spectra for 1–4 the C–S and S–CH<sub>2</sub> stretches are shifted to lower frequencies when compared to free cysteamine hydrochloride. This implies coordination of the metal to the thiols. The ammonium bands at 2938–3130, 1561–1583 cm<sup>-1</sup> and no change in the C–N stretching in 1 indicate free amine. For 2–4 the NH<sub>2</sub> stretching and bending modes are observed at higher frequencies compared to the free ligand, indicating the presence of a metal–nitrogen contact. In the mass spectrum for 2 the parent peak is observed at 266 (*m/z*) while the successive loss of two cysteamine units is observed for all the complexes.

#### 4. Description of structures

Compound [Cd<sub>2.5</sub>Cl<sub>5</sub>(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)] (1) has three-dimensional connectivity indicative of a solid-state material but it is nevertheless soluble in common solvents. This qualifies 1 as a “molecular solid” [20]. The structure contains layers of (Cd(Cl)SR)<sub>x</sub> perpendicular to one another (Fig. 1). The structure is comprised of alternate opposite open cores of hexacoordinate Cd with Cl and S present at the corners. Similar polymeric chains with hexacoordinate Cd atoms are also observed in [Cd<sub>2</sub>(5-CF<sub>3</sub>-pyS)<sub>4</sub>(DMF)]<sub>n</sub>, where the coordination is completed by S, N of the ligand and solvent, DMF [21]. This is not observed for 1, where the coordination is completed by S and Cl to achieve octahedral geometry. The repeating pattern observed in the unit is Cd1(2S,4Cl)–Cd2(S,5Cl)–Cd1(2S,4Cl) and so on. Cd1 and Cd3 are coordinated to two sulfurs and four chlorines with two chlorides involved in bridging with another unit, whereas Cd2 is bonded to one sulfur, one terminal chlorine and four core bonded chlorine atoms.

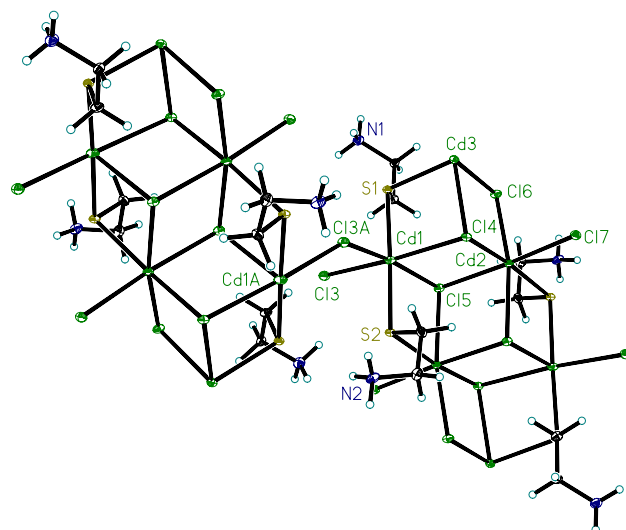


Fig. 1. View of the unique repeating unit of compound 1 at 50% thermal ellipsoids value.

Selected bond lengths and angles are given in Table 3. The Cd–S bond length varies in different cores. For Cd1 and Cd3, the distances are nearly the same (average 2.498 Å) while for Cd2, the bond distance is comparatively higher (2.601 Å). By comparison, [CdBr<sub>2</sub>(C<sub>5</sub>H<sub>13</sub>NS)], which also contains polymeric Cd–S chains has Cd–S distances ranging from 2.515 to 2.520 Å [22].

Variation in the Cd–Cl bond lengths is also observed for different chlorides (terminal, core bonded and bridging) as well as for different Cd atoms. For Cd(1), the distance between Cd and the core bonded chlorine is shorter (average 2.808 Å), compared to the bridging chlorine (2.920 Å). The bond lengths of chloride present in the core are nearly the same with an average distance of 2.790 Å. For Cd(2), Cd–Cl bond distances for core bonded and terminal chloride are nearly the same.

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

Cd(1)–S(1)	2.4825 (14)	Cd(2)–S(2)'	2.6018 (14)
Cd(1)–S(2)	2.4995 (14)	Cd(2)–Cl(2)	2.6679 (14)
Cd(1)–Cl(1)	2.8875 (15)	Cd(2)–Cl(3)	2.6968 (14)
Cd(1)–Cl(2)	2.8276 (14)	Cd(2)–Cl(4)	2.6372 (13)
Cd(1)–Cl(3)	2.7895 (14)	Cd(2)–Cl(5)	2.6060 (14)
Cd(3)–S(1)	2.5417 (14)	Cd(3)–Cl(2)	2.8159 (13)
Cd(3)–Cl(4)	2.7306 (13)		
S(2)–Cd(1)–S(1)	178.22 (5)	S(2)–Cd(1)–Cl(3)	84.70 (4)
S(1)–Cd(1)–Cl(3)	95.85 (4)	S(2)–Cd(1)–Cl(2)	96.23 (5)
S(1)–Cd(1)–Cl(2)	85.52 (5)	Cl(3)–Cd(1)–Cl(2)	82.67 (4)
S(2)–Cd(1)–Cl(1)	91.66 (5)	S(1)–Cd(1)–Cl(1)	86.68 (5)
Cl(3)–Cd(1)–Cl(1)	87.82 (4)	Cl(2)–Cd(1)–Cl(1)	167.01 (4)
S(2)–Cd(1)–Cl(1)'	84.86 (4)	S(1)–Cd(1)–Cl(1)'	94.80 (4)
Cl(3)–Cd(1)–Cl(1)'	167.25 (4)	Cl(2)–Cd(1)–Cl(1)'	91.20 (4)
Cl(1)–Cd(1)–Cl(1)'	99.79 (2)	S(2)–Cd(2)–Cl(5)	90.65 (4)
Cl(5)–Cd(2)–Cl(4)	90.22 (4)	Cl(5)–Cd(2)–Cl(2)	88.05 (4)
Cd(1)–Cl(1)–Cd(1)'	142.52 (5)	Cd(2)–Cl(2)–Cd(1)	94.74 (4)
Cd(2)–Cl(3)–Cd(1)	90.50 (4)	Cd(1)–S(2)–Cd(2)'	101.90 (5)

However a shorter Cd–Cl distance with a terminal chlorine, compared to bridged is observed in the complex  $[\text{Cd}_2\text{Cl}_4(\text{C}_{14}\text{H}_{23}\text{N}_4\text{OPS})_2]$  [23], where the bridging Cd–Cl distance is 2.644 Å, compared to terminal Cd–Cl, 2.387 Å. The S–Cd–S angle in **1** is almost linear (178.2° and 180.0°) due to the presence of a regular structure, when compared to the similar complex  $[\text{CdBr}_2(\text{C}_5\text{H}_{13}\text{NS})]$  (126.9°) [22]. The linear Cl–Cd–Cl angle (range 167–180°) and average angle of 90° signify octahedral geometry around the metal ion, whereas in  $[\text{Cd}_2\text{Cl}_4(\text{C}_{14}\text{H}_{23}\text{N}_4\text{OPS})_2]$  [23] a distorted tetrahedral geometry around Cd is indicated by Cl–Cd–Cl angles, ranging from 89° to 112°. The terminal amine is oriented away from the core with a N1–C2–C1 angle of 111.9° to reduce steric interactions. There are no signs of intramolecular hydrogen-bonding observed within a unit. However, intermolecular hydrogen-bonding involving chlorine with amines on adjacent units is observed. Similar hydrogen-bonding has been observed in  $[\text{CdBr}_2(\text{C}_5\text{H}_{13}\text{NS})]$  [22], where bromine is involved in inter-chain hydrogen-bonding with adjacent ammonium groups.

Compound (**2**) consists of discrete  $[\text{Cd}(\text{SCH}_2\text{CH}_2\text{NH}_2)_2]$  molecules (Fig. 2) that are linked through intermolecular hydrogen bonds (Fig. 3). Selected bond lengths and angles are shown in Table 4. Cd is pentacoordinate, bonded to three sulfur and two nitrogen atoms in a distorted square pyramidal geometry. In the dimeric structure the two cadmium atoms are related by a center of inversion situated at the mid-point of the line between the two metal centers. One of the ligands acts as a terminal chelating unit (S,N) while the other behaves as both a chelate and a bridge through the sulfur. The  $\text{Cd}_2\text{S}_2$  core is nearly planar with average internal angles close to 90°, with two different fused five-membered cysteamine rings (axial, terminal cysteamine unit and equatorial, cysteamine unit attached to the core). The Cd–S

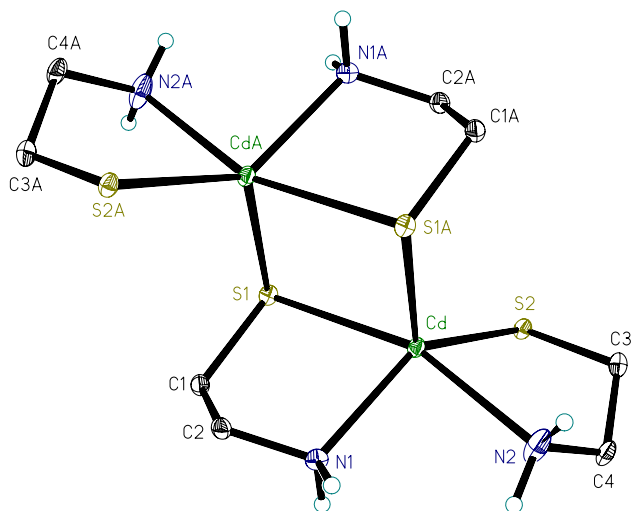


Fig. 2. Molecular structure of compound **2**.

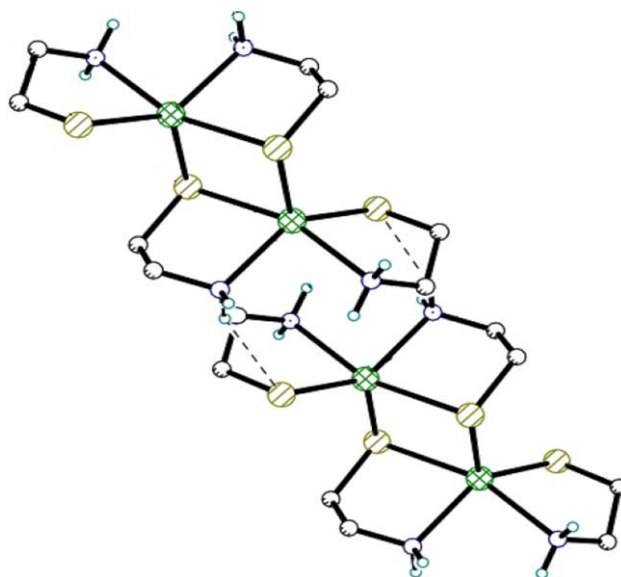


Fig. 3. View of the unit cell of compound **2** emphasizing the intermolecular hydrogen bonding.

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

Cd–N(1)	2.3087 (18)	Cd–N(2)	2.436 (2)
Cd–S(1)	2.7359 (7)	Cd–S(1')	2.5813 (7)
Cd–S(2)	2.4920 (7)	S(1)–Cd'	2.5843 (7)
N(1)–Cd–N(2)	85.54 (7)	N(1)–Cd–S(2)	137.38 (5)
N(2)–Cd–S(2)	81.66 (5)	N(1)–Cd–S(1)	78.22 (5)
N(2)–Cd–S(1)	161.82 (6)	S(2)–Cd–S(1)	104.85 (2)
S(1)'–Cd–S(1)	93.54 (2)	Cd'–S(1)–Cd	86.46 (2)
N(1)–Cd–S(1')	101.85 (5)	N(2)–Cd–S(1')	97.79 (6)

bond distances vary from 2.492 to 2.735 Å in axial, equatorial and the central core but are comparable to related sulfur-bridged compounds (2.537–2.713 Å) as well as those containing S/N ligands (2.466–2.673 Å) [22–24]. The Cd–N bond distances are also different in both four- (2.308 Å) and five-membered fused rings (2.436 Å) but comparable to Cd–N bond distances in similar complexes [23–27].

The Cd–S1 distance is larger than Cd–S2 and Cd–N1 is smaller than Cd–N2 implying a stronger Cd–S bond in the axial position. The Cd–S and Cd–N bond distances show an opposite trend, similarly observed for distorted octahedral  $[\text{Cd}(\text{3-CF}_3\text{-pyS})_2(\text{DMF})_2]$  [21]. The cysteamine units in axial and equatorial positions are neither perpendicular nor parallel to each other (N(1)–Cd–S(1)', 101.8° and C(1)–S(1)–Cd(1)', 102.9°). The deformity is due to the interaction of the sulfur and nitrogen with the amine hydrogen of the equatorial cysteamine molecule of another unit. The presence of the  $\text{M}_2\text{S}_2$  core and intermolecular hydrogen-bonding (N–H–S, N–H 0.92 Å and H–S 2.95 Å) results in the distortion of planarity of the axial cysteamine ring. The equatorial and the axial cysteamine have torsion angles

Cd–S(2)–C(3)–C(4) 48.9° and Cd–S(1)–C(1)–C(2) 28.6°, that minimize strain energy.

In the structure of  $[\text{Pb}_2\text{Cl}(\text{SCH}_2\text{CH}_2\text{NH}_2)_3]$  (**3**), four- and five-coordinate Pb, are observed (Fig. 4). The Pb atoms possess stereochemically active lone pairs giving four-coordinate Pb a distorted square pyramidal geometry and five-coordinate Pb an octahedral geometry. The five-coordinate Pb atoms form a planar four-membered  $\text{M}_2\text{S}_2$  ring with average internal angles of nearly 90°.

The Pb–S distance in the pentacoordinate Pb is larger than the Pb–S distance of tetracoordinate Pb (Table 5). The bridging Pb–S distance (2.897 Å) between tetra and pentacoordinate Pb is in agreement with other related lead–thiolate complexes (2.671–2.960 Å) [28,29]. The Pb–N distance in pentacoordinate Pb is smaller compared to Pb–N in tetracoordinate Pb. These distances are comparable to  $[\text{Pbc}[15]\text{crown-5}](\text{SCN})_2$  [30], where the Pb–N distances range from 2.436 to 2.532 Å. The Pb–S and Pb–N bond distances in different units are opposite with a stronger Pb–S bond in the axial position. This trend is also observed in **2**. When compared to a similar complex  $\text{Pb}(\text{SCH}_2\text{CH}_2\text{NH}_2)_2$  the Pb–S and Pb–N distances are in agreement [12].

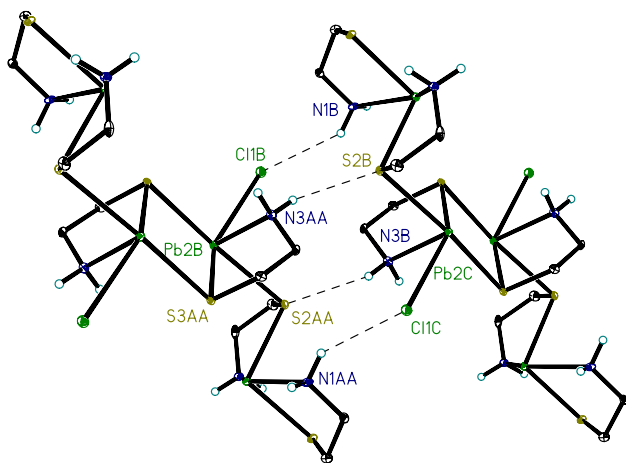


Fig. 4. A view of the repeating units of **3** showing inter-molecular hydrogen-bonding.

Table 5  
Selected bond lengths (Å) and bond angles (°) for **3**

Pb(1)–N(1)	2.629 (6)	Pb(1)–N(2)	2.613 (7)
Pb(1)–S(1)	2.713 (2)	Pb(1)–S(2)	2.673 (2)
Pb(2)–S(2)	2.897 (2)	Pb(2)–N(3)	2.394 (7)
Pb(2)–S(3)	2.7377 (19)	Pb(2)–S(3)′	3.053 (2)
Pb(2)–Cl(1)	3.082 (2)		
N(1)–Pb(1)–S(1)	73.17 (15)	N(1)–Pb(1)–S(2)	86.41 (16)
N(2)–Pb(1)–S(1)	81.08 (16)	N(2)–Pb(1)–S(2)	73.51 (16)
N(3)–Pb(2)–S(2)	83.89 (18)	N(3)–Pb(2)–S(3)	73.61 (17)
S(2)–Pb(1)–S(1)	99.56 (6)	S(3)–Pb(2)–S(2)	83.81 (6)
S(2)–Pb(2)–S(3)′	165.09 (5)	S(3)–Pb(2)–S(3)′	84.35 (6)

The tetra-coordinate Pb unit is linked to the  $\text{M}_2\text{S}_2$  core Pb through one of its sulfur atoms, which is nearly linear (165.0°), very much comparable to the polymer sheet  $\text{Pb}(\text{SCH}_2\text{CH}_2\text{OH})(\text{NO}_3)$  (162.7°) [31] and  $\text{Pb}(\text{SPh})_2$  (158.9°) [29]. The bond angles around the tetra-coordinate Pb are nearly equal within the ring (73°) and between two cysteamine units (83° and 86°). The chloride bonded to the central Pb forms a hydrogen-bond with the  $-\text{NH}_2$  group of the tetracoordinate Pb of another unit (Fig. 4). The NH of the cysteamine attached to the core form a hydrogen-bond with the sulfur of the tetracoordinate Pb of a second unit. Hence the intermolecular hydrogen-bonding is responsible for the stacking of the molecules and making the  $\text{Pb}_2\text{S}_2$  cores parallel to each other. Such stacking is also observed in  $\text{Pb}(\text{SPh})_2$  [29]. The whole molecule is symmetrical with an axis going through the plane of the four membered  $\text{Pb}_2\text{S}_2$  ring.

The crystal structure of  $[\text{Pb}_2(\text{SCH}_2\text{CH}_2\text{NH}_2)_3](\text{NO}_3)_{0.67}(\text{Cl})_{0.33}$  (**4**) reveals two types of Pb, both in a four coordinate geometry (Fig. 5). The  $\text{M}_2\text{S}_2$  core, fused five membered cysteamine above and below the core plane and four coordinate metal linked to the core with sulfur as in **4**, is also observed in **3**. The axial Pb–S bond lengths (average 2.697 Å) are shorter than the Pb–S bond lengths of the core (average 2.989 Å). The bridging Pb–S distance (2.893 Å) connecting the core and the axial unit is nearly the same as the bridging Pb–S bond of **3** (2.987 Å). Like compounds **2** and **3**, Pb–S and Pb–N distances also show opposite trends in axial and the core units. Except for the presence of chloride attached to central Pb in **3**, compounds **3** and **4** are nearly identical and have similar lattice parameters (Table 1). Bond lengths and bond angles for **4** are given in Table 6. The presence of extensive hydrogen-bonding in **4** might explain the higher thermal stability compared to **3**. This

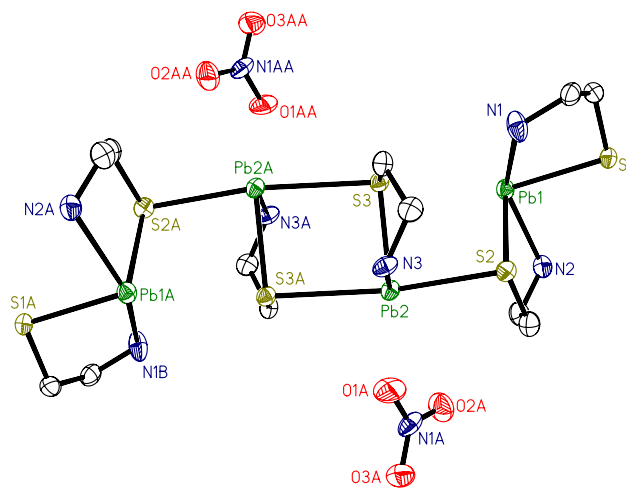


Fig. 5. Molecular structure of compound **4**. The counter anions are 2/3rd  $\text{NO}_3^-$  and 1/3rd  $\text{Cl}^-$  (sitting at the same position). For the sake of clarity, only  $\text{NO}_3^-$  are shown.

Table 6  
Selected bond lengths (Å) and bond angles (°) for **4**

Pb(1)–N(1)	2.604 (7)	Pb(1)–N(2)	2.575 (7)
Pb(1)–S(1)	2.7138 (19)	Pb(1)–S(2)	2.6806 (19)
Pb(2)–S(2)	2.893 (2)	Pb(2)–N(3)	2.411 (7)
Pb(2)–S(3)	2.704 (2)	Pb(2)–S(3)′	3.0857 (19)
N(1)–Pb(1)–S(1)	72.39 (14)	N(1)–Pb(1)–S(2)	84.28 (16)
N(2)–Pb(1)–S(1)	83.32 (14)	N(2)–Pb(1)–S(2)	73.54 (15)
N(3)–Pb(2)–S(2)	84.43 (16)	N(3)–Pb(2)–S(3)	74.15 (17)
S(2)–Pb(1)–S(1)	100.78 (6)	S(2)–Pb(2)–S(3)′	168.83 (6)
S(3)–Pb(2)–S(2)	86.00 (6)	S(3)–Pb(2)–S(3)′	87.00 (6)
Pb(1)–S(2)–Pb(2)	96.11 (6)	Pb(2)–S(3)–Pb(2)′	95.65 (6)

is due to the presence of  $\text{NO}_3^-$  anions, which supplies more hydrogen bonding contacts than single chloride anions. The amine hydrogens are also weakly hydrogen bonded to sulfur and chlorine atoms as observed in **2** and **3**.

## 5. Conclusion

In the present manuscript we have described the Cd(II) and Pb(II) compounds of 2-aminoethanethiol with the help of crystal structures. As the reactions were carried out following the same general procedure the products were similar. Compounds **2**, **3** and **4** show structural similarities involving bridging sulfurs to form a four-membered  $\text{M}_2\text{S}_2$  core. Beside the central core, fused five-membered axial (with tetracoordinate metal) and equatorial (with pentacoordinate metal) cysteamine units are also observed in in **2**, **3** and **4**. It is important to note that the reaction conditions affect the structural chemistry as in **3** and **4** there is no Pb–Pb interaction observed, compared to a similar  $\text{Pb}(\text{SCH}_2\text{CH}_2\text{NH}_2)_2$  complex [12]. A common feature of all the four compounds is intermolecular hydrogen-bonding involving nitrogen/sulfur and the counter anions.

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## Appendix A. Supplementary data

Crystallographic data for the structures analysis for compounds **1–4** have been deposited with the Cam-

bridge Crystallographic Data Center, CCDC Nos. 210040–210043, respectively. Copies of the information may be obtained free from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel.: +44 1223 336408; fax: +44 1223 336033). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.01.019.

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