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Note

Two-dimensional network acquired by Pb(II)–2-aminoethanethiolate

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Abstract

The combination of an equivalent amount of $Pb(NO_3)_2$ and 2-aminoethanethiol hydrochloride in the presence of a base yielded a two-dimensional network consisting of $[PbCl(SCH_2CH_2NH_3)](NO_3)$ (**1**) units. The network is further extended to a three-dimensional framework with intermolecular hydrogen bonding involving NO_3^- and Cl^-. The geometry around Pb in **1** can be best described as distorted pentagonal bipyrimidal with the axial positions occupied by Cl atoms. Due to the presence of a weak Pb—Cl bond, the two-dimensional network can be considered to be formed of PbS_2Cl units with an additional Cl acting as bridging atom.

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1. Introduction

In metal-mediated supramolecular frameworks, the molecular configuration depends on the type of metal as well as the structure of the organic ligand [1–4]. The p-block elements, due in part to their extensive Lewis acid properties, exhibit interesting coordination numbers [5]. More specifically, lead(II) with a lone pair and empty p-orbitals has attracted much attention due to its potentially extensive array of coordination geometries [6,7]. However, due to the lack of suitable lead compounds, structural studies have been limited. Organolead(II)–thiolates are unstable and disproportionate to $R_3Pb—PbR_3$ and elemental Pb unless attached to bulky ligands [8]. Lead(II)–thiolates, on the other hand, are stable with respect to disproportion and hydrolysis but are typically insoluble in non-coordinating solvents which prevents the isolation of crystalline material. Compared to conventional monodentate thiols, aminothiols typically form soluble metal compounds. 2-Aminoethanethiol (AET), in particular has been extensively studied in the formation of self-assembled molecular frameworks [9–12].

2. Experimentals

The reaction was carried out at room temperature in deaerated DI water under N_2. The ligand 2-aminoethanethiol hydrochloride (TCI America) was dried under vacuum prior to the use. The reagent $Pb(NO_3)_2$ (Sigma–Aldrich) was used as received. ^1H and ^{13}C NMR data was obtained with JEOL-GSX-400 and 270 instruments operating at 200 MHz using d_6-DMSO as a solvent and tetramethylsilane as reference. The IR data was recorded as KBr pellets on a Mattson Galaxy 5200 FT-IR instrument between 400 and 4000 cm^{-1}. Mass spectral (EI-MS) data were obtained at the University of Kentucky Mass Spectrometry. The UV–Vis studies were done on Agilent HP 8453 instrument by using 0.05 mM solution of **1** in DI water and DMSO. Crystals for **1** could be obtained from the filtrate by slow evaporation at room temperature and also by recrystallization of precipitate in DI water. For X-ray data, the crystals obtained from slow evaporation were used. X-ray diffraction data were collected at 90 K on the Nonius Kappa CCD diffractometer unit using

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Mo-Kα radiation from regular shaped crystals mounted in Paratone-N oil on glass fibers.

2.1. Synthesis of [PbCl(SCH$_2$CH$_2$NH$_3$)](NO$_3$) (1)

To a stirring solution of 2-aminoethanethiol hydrochloride (10 mm, 1.14 g) NaOH (10 mm, 0.4 g) was added in 30 mL of DI water and stirred for few minutes. To the clear solution $Pb(NO_3)_2$ (10 mm, 3.31 g) was added and stirred for 24 h. The resulting precipitate was washed with cold DI water and methanol and dried well. The filtrate was slowly evaporated to yield light yellow crystals. Yield: 3.5 g (81%), Mp = 190 °C. ^{1}H NMR(d_6-DMSO, 200 MHz, ppm): 3.06 (m, 4H, CH_2CH_2) and 7.36 (br, 3H, NH_3). ^{13}C NMR (d_6-DMSO, 200 MHz, ppm): 25.1 (CS) and 44.6 (CN). IR (KBr, v/cm^{-1}): 3137, 1596, 1475, 1390, 1335, 1091, 1033, 881, 819, 656. EIMS (m/z): 427 (M$^+$, 2), 357 (M−2Cl$^+$, 2). *Anal.* Calc. for [PbCl(SCH$_2$CH$_2$NH$_3$)](NO$_3$): C, 6.291; H, 1.848; N, 7.373. Found: C, 6.289; H, 1.805; N, 7.367%.

3. Results and discussion

The combination of Pb(II) salts with AET · HCl in alcohol yields discrete molecular compounds held together through weak Pb···S or Pb···N interactions [13]. Similar reactions in water, however, yield dinuclear Pb(II)–AET compounds, where the formation of an S/N chelate around Pb is observed (Table 1 and Fig. 1) [14]. In an effort to manipulate the coordination around Pb by preventing polymerization through weak Pb···S/N interactions, we here report the 1:1 combination of $Pb(NO_3)_2$ and AET · HCl in the presence of an equimolar amount of base (NaOH). X-ray quality crystals can be obtained by slow evaporation of filtrate as well as recrystallization of the precipitate from water.

Table 1
Formation of Pb(II)–aminoethanethiolates

Product	Pb^{2+}:AET:NaOH	Reference
[PbCl(SCH$_2$CH$_2$NH$_3$)]$^+$ (**1**)	1:1:1	this work
[PbCl$_2$(SCH$_2$CH$_2$NH$_3$)] (**2**)	1:2:2	[13]
[Pb(SCH$_2$CH$_2$NH$_2$)$_2$] (**3**)	1:2.5:2.5	[13]
[Pb$_2$X(SCH$_2$CH$_2$NH$_2$)$_3$] (**4**)	1:2:4	[14]
[Pb(SCH$_2$CH$_2$NH$_2$)$_2$] · 2[PbCl(SCH$_2$CH$_2$NH$_2$)] (**5**)	1:2:5 or 1:2:7	[13]

X = Cl and/or NO$_3$$^-$.

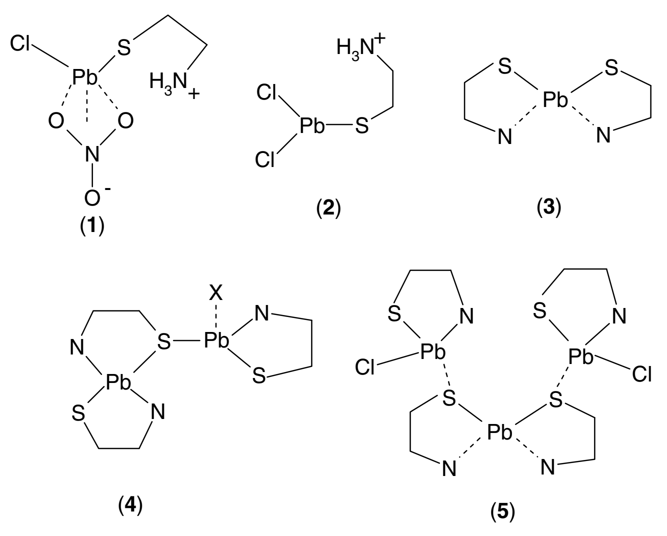

Fig. 1. Structural formula of compounds **1**–**5** (X = Cl or NO$_3$) [13,14].

4. Spectroscopy

In the ^{1}H NMR a single peak is observed for the CH$_2$N and CH$_2$S groups, which is consistent with symmetrical structures in solution. No significant change in the chemical shift for CH$_2$N confirms the presence of a NH$_3$$^+$ group. In the IR spectra the C—S and S—CH$_2$ stretches are shifted to lower frequencies when compared to free ligand, indicating a Pb—S bond. Also, the absence of a –SH peak at 2550 cm^{-1} indicates a Pb—S contact. The ammonium bands at 2938–3130, 1561–1583 cm^{-1} and no change in the C—N stretching further confirms the presence of the NH$_3$$^+$ group. In the UV–Vis, the λ_{max} for **1** in water is observed at 260 nm, which is due to S → Pb LMCT and fall in the range usually observed for lead(II)–thiolates (250–400 nm). This indicates retention of the geometry around Pb [15]. In a similar study with **3** and **5**, the λ_{max} around 201 nm due to free Pb^{2+} indicated dissociation of the compounds. In DMSO the λ_{max} for **1** is shifted to 275 nm with an additional weak shoulder at 315 nm suggesting partial formation of a DMSO adduct. A similar spectrum has been observed for [Pb$_{10}${*S*-2,6-(CH$_3$)$_2$-C$_6$H$_3$}$_{20}$] (333 and 258 nm) [16].

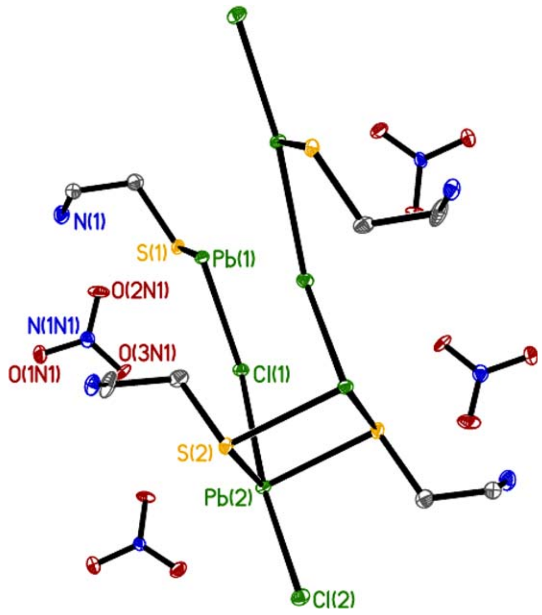

Fig. 2. Polymeric unit of **1** along the '*c*' axis. Additional Pb—S contacts and hydrogen atoms are not shown for clarity. Selected bond distances and angles are Pb1—S1, 2.7383(1); Pb2—S2, 2.7275(1); Pb1—Cl1, 2.8031(1); Pb1—S2″, 2.8399(1); Pb1—Cl2″, 2.9879(1); S1—Pb1—S2″, 83.92(5); S1—Pb1—Cl1, 84.53(5); Cl1—Pb1—Cl2″, 170.48(3); S2—Pb2—S1″, 84.01(5), Cl2—Pb2—Cl1, 172.96(3).

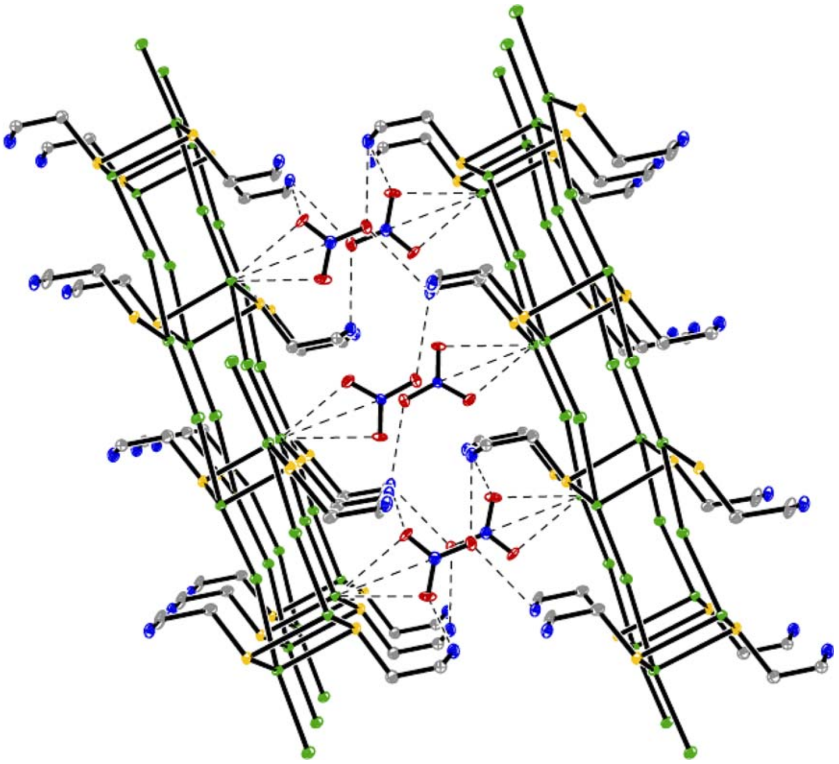

Fig. 3. Three-dimensional network observed in **1** showing intermolecular hydrogen bonding with dotted lines.

5. Crystal structure

The Pb in **1** is tetracoordinate with bridging S and Cl atoms (Fig. 2). The absence of a Pb—N_{AET} bond in **1** can be attributed to the protonation of the amine group. The angle spanning Cl—Pb—Cl is quite linear, 170–173°, while the Cl—Pb—S angles range from 81° to 90° creating a "see-saw" structure. Taking into account weak interactions with nitrate O and N atoms (2.867 Å), the environment around Pb can be considered as $PbS_2Cl_2O_2N$ (CN = 7). Since the lone pair on Pb is stereochemically active, the Pb exhibits a distorted pentagonal bipyrimidal configuration with Cl occupying axial positions. The strain in the four membered Pb_2S_2 ring is evident in the S—Pb—S angle of 84°, which is comparable to that observed in **4** (83–87°) [14]. The Pb···Pb distance observed in the Pb_2S_2 core (4.145 Å) is slightly larger than the sum of the Van der Waals radii of two Pb(II) atoms (4.04 Å) [17] but falls in the range observed for related Pb(II)–thiolates (3.994–4.612 Å) [18]. The S···S distances in the Pb_2S_2 core (3.371 Å) are much smaller than the sum of Van der Waals radii of two S atoms (3.70 Å) [19] but in the range observed in similar Pb–thiolates (3.103–3.836 Å) [20]. The closest possible interactions between the chains are through pairs of Pb···Pb (4.320 Å) and Cl···Cl interactions (3.952), which are comparable to those observed in similar Pb(II)–thiolates [8].

The presence of unsymmetrical Pb—S distances (2.734 and 2.841 Å) relieves the strain caused by the four-membered Pb_2S_2 ring [21]. These distances are, however, much larger than the corresponding distances observed for tetracoordinate Pb in **3**–**5** (2.63–2.71 Å). Such observation in Pb—S distance is in contrast to the fact that exchange of N with Cl (as in **3** and **5**) as an additional donor atom leads to the formation of a stronger Pb—S bonds [13]. The Pb—Cl distances (2.784 and 3.034 Å) fall between those observed for tetracoordinate Pb (2.791 Å in **4**) and pentacoordinate Pb (3.082 Å in **2**). The two-dimensional network can be considered to be formed of PbS_2Cl units with bridging Cl atoms in one direction and the Pb_2S_2 core in the other. Polymeric chains connected through the ligand are also known, for example in, $\{[HB(pz)_3]Pb(\mu\text{-}NCS)\}_n$ (HB(pz) = pyrazolyl borate) [22].

The $-CH_2CH_2NH_3$ groups in the core are present above and below the Pb_2S_2 plane and involved in hydrogen bonding with bridging Cl and nitrate. The two-dimensional network is extended to a three-dimensional framework by intermolecular hydrogen bonding involving NH_3, NO_3^- and Cl (Fig. 3). The NH···Cl distances of 3.311 Å are much smaller than those observed in **4** (3.403–3.571 Å) indicating a stronger interaction. The nitrate ions, present within the chains are weakly bonded to the amine groups with distances in the range 2.884–3.009 Å. The Pb···O(nitrate) (2.867 and 3.187 Å) and Pb—N(nitrate) (3.444 Å) distances are within the range observed for similar interactions of Pb with nitrate or perchlorate [23].

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Appendix A. Supplementary data

Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 293552. Experimental section, additional figures of **1**, selected bond distances and angles and UV–Vis of **1** in DMSO are provided in supplementary data section. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.03.037.

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