1D-3D Pb(II)-Organic Lattice Assemblies through Chemical Reactivity and Pb(II)-Assisted Ligand Transformations

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Abstract

pH-variable hydrothermal reactions of Pb(II) with dicarboxylic acids in the presence of 1,10-phenanthroline led to new solid-state compounds [Pb₄(C₁₂H₈N₂)₄(C₄H₂O₄)₂(NO₃)₂] (1), [Pb₂(C₁₂H₈N₂)(CO₃)(C₄H₂O₄)]₆nH₂O (2), [Pb₂(C₁₂H₈N₂)(C₄H₂O₄)₉]n (3), and [Pb(C₁₂H₈N₂)(C₄H₂O₄)]n·2nH₂O (4). All compounds were characterized by elemental analysis, FT-IR, CP-MAS-NMR, and single crystal X-ray diffraction. The collective chemical reactivity in the ternary Pb(II)-phenanthroline-dicarboxylate systems unravels seldom seen metal-assisted ligand malate/maleate to fumarate transformations, which in the presence of Pb(II) and 1,10-phenanthroline contribute to the assembly of 2D (2) and 3D lattice networks (3-4). All distinct assemblies in 1-4 reveal interwoven crystal lattice connections, reflecting unique physicochemical properties.

Keywords: Lead, maleic acid, malic acid, fumaric acid, plant toxicity

1. Introduction

Lead (Pb) is one of the major heavy metals that have gained considerable importance as potent environmental pollutants. Apart from natural weathering processes, Pb(II) contamination of the environment occurs through mining and smelting activities, lead-containing paints, gasoline, explosives and the disposal of municipal sewage sludge enriched in lead [1]. As many forms of lead pollutants are frequently used in modern human life, soil contamination with Pb is not likely to decrease in the near future [2]. A significant increase in the Pb content of cultivated soils has also been observed near industrial areas. Pb tends to accumulate on the surface ground layer and its concentration decreases with soil depth [3]. Pb(II) is easily taken up by plants from the soil and is accumulated in different organs. Pb is considered a general protoplasmic poison, which is cumulative, slow acting and subtle.

Soils contaminated with Pb cause a decrease in crop productivity, thereby posing a serious problem for agriculture [4]. On the other hand, Pb is very harmful to human health. Lead is a very strong poison. When a person swallows a Pb-containing object or inhales lead dust, some of the poison can stay in the body and cause serious health problems. A single high, toxic dose of lead can cause severe pathological symptoms. However, it is more common for lead to build up in the human body slowly over time. This occurs through repeated exposure to small amounts of lead. In this case, there may not be any obvious symptoms, but lead can still cause serious health problems in the long term, such as sleeping disorders or low IQ in children. Lead is much more harmful to children than adults because it can affect children's developing nervous system and brain. The younger the child, the more harmful lead can be. Unborn children are the most vulnerable.
Children get lead in their bodies when they put lead objects in their mouth, especially if they swallow the lead object. They can even get lead poisoning evident on their fingers by touching a dusty or peeling lead object, and then putting their fingers in their mouth or eating food afterward. Tiny amounts of lead can also be inhaled [5,6].

Encouraged by successful efforts in our lab to employ hydrothermal synthesis for the assembly of crystalline materials containing Pb(II), we pursued the synthesis, isolation and crystallization of new binary and ternary compounds of Pb(II) with variable nature O,N-containing aromatic and carboxylic acid ligands. Hence, we herein report research efforts on ternary Pb(II)-malic, maleic and fumaric acid systems containing phen, in which employment of well-designed hydrothermal synthesis led in a unique way to the formation, isolation and crystallization of four new compounds containing Pb(II)-fumarate and phen. In this regard, several types of 1D, 2D or 3D supramolecular architectures, assembled from Pb(II) centers with dicarboxylates and phen, arose with discrete structural features, reflecting a wide and interwoven diversity of uniquely defined solid-state lattices.

2. Materials and methods

All experiments were carried out under aerobic conditions. Nanopure quality water was used for all synthetic reactions. Pb(NO$_3$)$_2$, Pb(CH$_3$COO)$_2$·3H$_2$O, maleic acid and sodium hydroxide were purchased from Fluka. Fumaric acid was supplied by Merk. Malic acid and 1,10 phenanthroline were supplied by Aldrich.

3. Results and Discussion

Synthesis. The hydrothermal synthesis of compound 1 was expeditiously pursued through a facile reaction between lead nitrate and malic or maleic acid in aqueous solutions. The pH, at which the reaction was carried out, was 8.5-9. The adjustment of pH was made by addition of phen and aqueous sodium hydroxide. The stoichiometric reaction leading to the formation of the title compound is shown below (Reactions 1 and 2):

$$2 \text{Pb(NO}_3)_2 + \text{(malic or maleic acid)} + 4 \text{phen} \rightarrow [\text{Pb}_2(\text{phen})_4(C_4H_2O_2)_2](\text{NO}_3)_2 \ + 2 \text{NaNO}_3 + 3 \text{H}_2\text{O}$$

Reaction 1
In a similar reaction, Pb(CH$_3$COO)$_2$ and maleic acid reacted in water at pH~9, with phen and aqueous sodium hydroxide, and led to the isolation of crystalline compound 2. Due to the complexity of the reaction and its products, a non-stoichiometric reaction leading to the formation of the 2 is depicted below (Reaction 3):

Compound 3 was the product of the aqueous reaction between Pb(CH$_3$COO)$_2$ or Pb(NO$_3$)$_2$ and fumaric acid, at pH 3.5 (method A) and 4.5 (method C), in the presence of phen (method A and C) and NaOH (method C). In an alternative way, 3 was obtained through the aqueous reaction between Pb(CH$_3$COO)$_2$ and malic acid at pH 4.5 in the presence of phen (method B). The stoichiometric reaction leading to the formation of compound 3 is shown below (Reactions 4-6):

Compound 4 was the product of the aqueous reaction between Pb(CH$_3$COO)$_2$ and maleic acid, at pH~9, in the presence of phen and sodium hydroxide. The stoichiometric reaction leading to the isolation of compound 4 is shown below (Reaction 7):
The derived Pb(II)-fumarate materials were easily retrieved in pure crystalline form through hydrothermal synthesis. Elemental analysis of the isolated colorless crystalline products projected the molecular formulation $[\text{Pb}_2(\text{C}_{12}\text{H}_8\text{N}_2)\text{4(C}_4\text{H}_2\text{O}_4])\text{NO}_3\text{2}]$, $[\text{Pb}_2(\text{C}_{12}\text{H}_8\text{N}_2)\text{4(C}_4\text{H}_2\text{O}_4)\text{CO}_3]\text{C}_4\text{H}_2\text{O}_4\text{H}_2\text{O}$, $[\text{Pb}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_4\text{H}_2\text{O}_4)\text{2H}_2\text{O}]$ and $[\text{Pb}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_4\text{H}_2\text{O}_4)\text{H}_2\text{O}]\text{2H}_2\text{O}$ reflected in 1-4, respectively. Further spectroscopic evaluation of the crystalline products by FT-IR confirmed the presence of fumarate bound to Pb(II), thus being in line with the proposed molecular formulations. Finally, X-ray crystallography confirmed the analytical and spectroscopic results by rendering the lattice molecular formulation of the crystalline products in all four cases. Variable reaction conditions leading to new binary and ternary Pb(II) complex species of fumarate, maleate and malate are currently being investigated.

Compounds 1-4 are insoluble in water and are stable in the crystalline form in the air at room temperature for long periods of time.

**Description of structures.** The structure of complex 1 consists of centrosymmetric dinuclear cations $[\text{Pb}_2(\text{phen})\text{4(fum)}]\text{2+}$ (phen = 1,10-phenanthroline, fum = fumarate) and nitrate counterions in the crystal lattice (Figure 1).

![Figure 1. Partially labeled plot of the cation in $[\text{Pb}_2(\text{C}_{12}\text{H}_8\text{N}_2)\text{4(C}_4\text{H}_2\text{O}_4)]\text{NO}_3\text{2}$ (1) with thermal ellipsoids at the 30% probability level.](image1)

The molecular lattice structure of complex 2 reveals a 1D coordination polymer. The monomeric unit can be described as generated by dinuclear cations $[\text{Pb}_2(\text{phen})\text{4(fum)}]\text{2+}$, in much the same way as those in 1, and bridging carbonato(-2) ligands (Figure 2).

![Figure 2. Partially labeled plot of a very small fragment of the structure of $[\text{Pb}_2(\text{C}_{12}\text{H}_8\text{N}_2)\text{4(C}_4\text{H}_2\text{O}_4)]\text{6nH}_2\text{O}$ (2) with thermal ellipsoids at the 30% probability level.](image2)

The molecular structure of complex 3 reveals a 2D coordination polymer. The monomeric unit consists of two Pb(II) metal ions, one phen molecule and two fumarate ligands (Figure 3).

![Figure 3. Partially labeled plot of a very small fragment of the 2D structure of $[\text{Pb}_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_4\text{H}_2\text{O}_4)\text{2}]\text{n}$ (3) with thermal ellipsoids at the 30% probability level.](image3)

The molecular lattice structure of complex 4 reveals a 2D coordination polymer. The monomeric unit consists of one Pb(II) metal ion, one phen and one fumarato(-2) ligand in the lattice asymmetric unit. Each Pb(II) metal ion is six-coordinate and bound to the two nitrogen atoms of the phen ligand and to four carboxylato oxygen atoms from three fumarato(-2) ligands (Figure 4).

![Figure 4. Partially labeled plot of a very small fragment of the 2D structure of $[\text{Pb}_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_4\text{H}_2\text{O}_4)\text{2}]\text{n}$ (4) with thermal ellipsoids at the 30% probability level.](image4)
4. Conclusion

pH-Specific hydrothermal synthetic reactions of malic, phen, maleic and fumaric acid with Pb(II) salts afforded four new metal-organic framework species 1-4. Compound 1 is a dimer of Pb(II), fumarate and phen, whereas complex 2 is a 1D coordination polymer based on the dinuclear unit of 1 linked through bridging carbonato(-2) ligands. The other two compounds are 2D polymers based on dinuclear and mononuclear repeating units extending to three dimensional assemblies through π-π interactions. The investigated chemical reactivity of Pb(II) at the binary and ternary level toward the three (hydroxy)carboxylic acids revealed a metal-linked transformation process turning malic and maleic acids into fumaric acid. The nature of the metal, Pb(II), may be a significant reason for which the starting ligands transformed finally into fumaric acid, bound to the metal center and promoted formation and assembly of lattices in 1-4. All compounds a) display unique crystal lattice composition, b) support the idea of metal-assisted transformation of the initial ligand to its final metal-bound form, c) exhibit structural features reflecting the significance of π-π interactions in assembling 3D lattice architectures, and d) exemplify the diversity of lattice structure, composition and properties originating in similar binary and ternary aqueous systems of the same metal ion (i.e. Pb(II)) reacting under specific conditions.

As a consequence of the present work, further a) perusal targeting the rationalization of the diverse chemical reactivity observed for Pb(II) in the presence of organic (hydroxy)carboxylic acids, leading to metal-assisted ligand transformation and synthesis, b) in-depth understanding the factors governing metal-linked (poly)carboxylic acid promotion of lattice formation through metal complexation, and c) research on rational design and construction of binary and ternary Pb(II) π-π containing lattices, displaying unique supramolecular structures as well as physicochemical properties (e.g. luminescence), are currently ongoing in our laboratory.

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