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A Novel Multi-helical Polymer: Pyridine-2,6-dicarboxylato Plumbum(II) Complex [Pb(dipic)]_n

Yong-qi Qin*, Jin-hui Xue, Zi-feng zhang and Yuan-biao Qiao
Institute of Applied Chemistry, Lvliang University, Lvliang, Shanxi, PR China

RESEARCH ARTICLE

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*For Correspondence

Yong-qi Qin, Institute of Applied Chemistry, Lvliang University, Lvliang, Shanxi 033001, PR China, Tel: 0086-0358-2274301

E-mail: qinyq2003@163.com

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ABSTRACT

Self-assembly of pyridine-2, 6-dicarboxylato dianion (dipic)²⁻ and plumbous nitrate affords a coordination polymer of [Pb(dipic)]_n (1). Its structure was determined by elemental analyzer, IR spectroscopy and single crystal X-ray diffraction, and further characterized by thermal gravity (TG) analysis. Interestingly, this polymer exhibits a novel 2D framework which contains three-type of helical chains with the highest-stranded number of three in the entangled system. The reticular 2D framework is connected through oxo-bridges. When the strong hydrogen bonds in the structure are taken into account, Pb(dipic)]_n forms a 3D layer structure. The hydrogen bonds between these helical chains play important roles in constituting a 3-dimension layer structure from its 2-dimension network.

INTRODUCTION

Designed synthesis of metal-organic frame-works (MOFs) has been a great challenge in solid-state chemistry^[1-5]. Crystal engineering of MOFs is currently of great interest not only because of its tremendous potential applications in gas storage, chemical separations, microelectronics, nonlinear optics, and heterogeneous catalysis, but also because of its intriguing structural diversity, new topologies and intricate entangled motifs^[6-12]. Entangled systems, one of the major themes of supramolecular chemistry, are common in biology (as seen in catenanes, rotaxanes, and molecular knots). Entangled systems have attracted a great deal of attention from chemists not only because of their intrinsic aesthetic appeal^[13-16], but also interesting properties and potential applications ranging from drug delivery vehicles to sensor devices^[17-20]. Interpenetrating network, which have been the most investigated type of entanglement, can be described as polymeric analogues of catenanes and rotaxanes^[21,22]. They have provided a longstanding fascination for chemists, and many appealing interpenetrated frameworks have been constructed and discussed in comprehensive reviews by Batten and Robson^[21,22]. However, the study of self-penetrating network considered as polymeric equivalents of molecular knots remains largely unexplored, as evidenced in a recent review by Ciani *et al.*^[13]. According to Robson, Ciani and Champness^[13,23-27], self-penetration is a single net having the peculiarity that the smallest topological rings are catenated by other smallest rings belonging to the same net. In contrast to the fruitful production of interpenetrating networks, the self-penetration feature is still uncommon within coordination polymers, and only a few elegant examples belonging to this family have been reported so far^[23-27], implying a new challenging issue in coordination chemistry. Particular attention of chemists has recently been devoted to the finding of frames with novel entanglements, such as multiple helices, Borromean architectures, and polyrotaxanes^[13-16], that contribute to our knowledge of the self-assembly processes^[27]. Multiple helices, which are ubiquitous in nature and are the foundation of genetic codes, are attracting increased attention in coordination chemistry and material chemistry originating from their importance in biological systems, optical devices, and asymmetric catalysis^[6,28-32]. Driven by the pioneering work of Lehn and co-workers^[33,34], some appealing coordination polymers containing multiple helices have been constructed^[35-37].

Self-assembly of organic acids form many novel coordination polymers because organic acids can stabilize the coordination

polymers through proton transfer [38,39]. H_2 dipic is an effective tridentate chelating ligand in forming stable complexes with most metal ions and has very intricate coordination environments. Our strategy of employing V-shaped ligand, such as H_2 dipic, was based on the following considerations: employment of V-shaped bridging ligand could improve the helicity of the polymeric chains, which may thus favor the formation of helical and meso helical structure [28-37]. Many coordination polymers of MOFs have been synthesized with pyridine-2, 6-dicarboxylato acid, but it is hardly reported that self-assembly of pyridine-2, 6-dicarboxylato acid affords the examples of coordination polymers of multi-helical structure. In this paper, we report an interesting self-penetration network, namely, $[Pb(dipic)]_n$.

EXPERIMENTAL

Preparation of $[Pb(dipic)]_n$

Hydrothermal treatment of plumbous nitrate (331.2 mg, 1.0 mmol), H_2 dipic (167.0 mg, 1.0 mmol), and EtOH (10 mL) for 5 days at 150°C yields a colorless crystalline suitable for X-ray measurements product. Yield: 85.6% on the basis of lead source. FT-IR (cm^{-1}): 3419 (w), 1609 (s), 1423 (m), 1382 (s), 1271 (s), 1178 (w), 1139 (m), 1070 (m), 1016 (m), 913 (m), 820 (m), 769 (s), 728 (s), 693 (m), 662 (m). Anal. Calcd for $[Pb(dipic)]_n$: C, 22.52; H, 0.81; N, 3.75. Found: C, 22.18; H, 0.91; N, 3.52.

RESULTS AND DISCUSSION

Complex **1** is isomeric with the previously published $[Pb(dipic)]_n$ (**A**) [40]. Similarities and differences of complex **1** and complex **A** are shown in **Table S1** and **S2**, **Figure S1** and **Figure 1**. Although the molecular formula and crystal system for complex **1** and complex **A** are almost identical, their space structures, bond lengths and angles are different. In the complex **A**, each six Pb atoms are bridged by four oxo-bridges and two double oxo-bridges in **Figure S1(b)**. the Pb-Pb distances bridged by the carboxylate groups are 4.864, 4.440 and 5.536 Å for Pb1- Pb1D, Pb1-Pb1B and Pb1- Pb1E, respectively, in **Figure S1(a)**. But, in the structure of complex **1**, each four Pb atoms are bridged by four oxo atoms in **Figure 1**. An eight-atom ring is formed by four O and four Pb atoms in complex **1**. The eight-atom rings interweave each other with a common edge of Pb-O-Pb forming the formation of a 2D infinite network. The distance of two Pb atoms is 4.5647(35) Å by O3-bridge, and 4.9141(33) Å by O2-bridge. Angles of three Pb atoms is 75.514(61)° by O3-bridge, and 69.330(53)° by O2-bridge (see **Figure 1**). Seen from these data, Pb atoms are almost planar. Therefore, we conclude that all Pb atoms of this structure exist in a plane. This can be testified in the **Figure 1**.

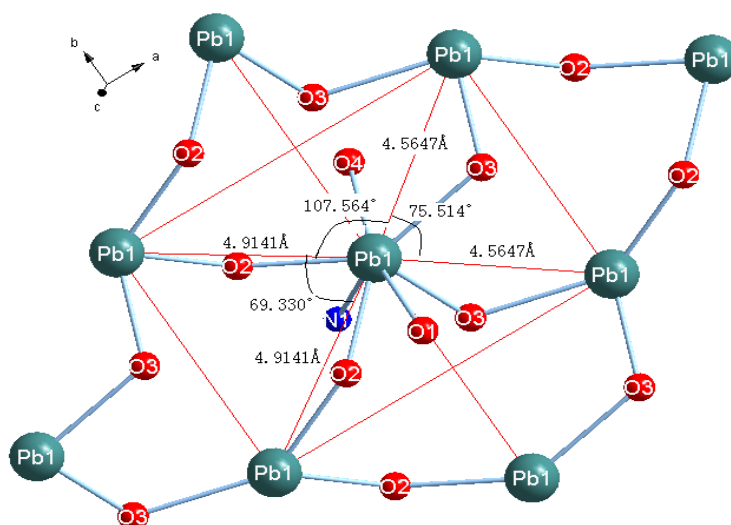


Figure 1. Perspective views of the four-connected (Pb and O atoms) nodes in the title complex.

Single-crystal X-ray diffraction analysis reveals that the complex **1** is a 2D self-penetrating network whose structure contains three types of helices chains. The crystallographically independent Pb atom adopts distorted decahedron geometry, being coordinated with a nitrogen atom and six oxygen atoms from four H_2 dipic ligands in **Scheme S1**. On the basis of this connection mode, Pb atoms are connected by H_2 dipic ligands to generate a scalelike 2D network of composition $[Pb(dipic)]_n$ (see **Figure S2**). The most fascinating and peculiar structural feature of the complex **1** is that three types of helical chains coexist in the 2D network of $[Pb(dipic)]_n$. As depicted in **Figure 2**, the Pb atoms are bridged by dipic ligands to form the triple-stranded helical chains down b axis. Known from the structure of the complex **1**, $[Pb(dipic)]_n$ is an example of a polymeric coordination network containing a triple-stranded helical chains. Similarly, triple-stranded helical chains constructed by pyridine rings, O1 and O3 of dipic ligands bridging with the Pb atoms further intertwines with two neighboring triple-stranded helix chains to give an attractive 5-fold interwoven meso helix (**Figure 3**). The 5-fold meso helix exhibits the structure of entanglement in a self-penetrating system. A double-stranded helix is formed by pyridine rings, O2 and O3 of dipic ligands bridging the Pb atoms down a axis (**Figure S3**). Each double-stranded helical chains further intertwines with two neighboring double-stranded helix chains to construct a two-fold interwoven meso helix (**Figure S4**). In addition, the complex **1** also contains a single-stranded helix that is built from pyridine rings and O3 of dipic ligands that bridge between the Pb atoms down b axis (**Figure S5**).

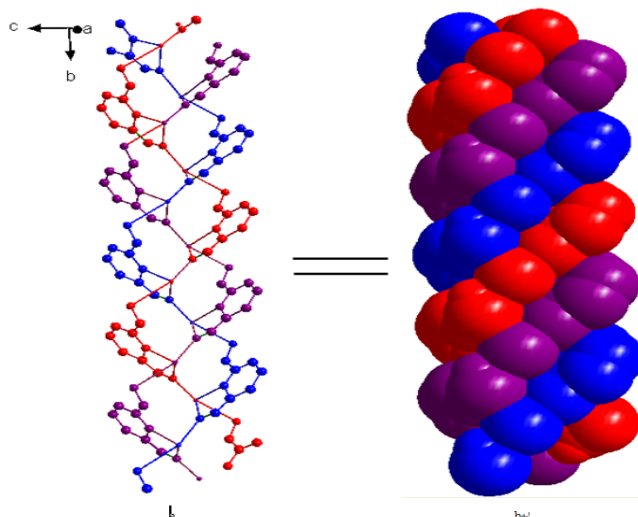


Figure 2. Space-filling views of the triple-stranded the helical chains.

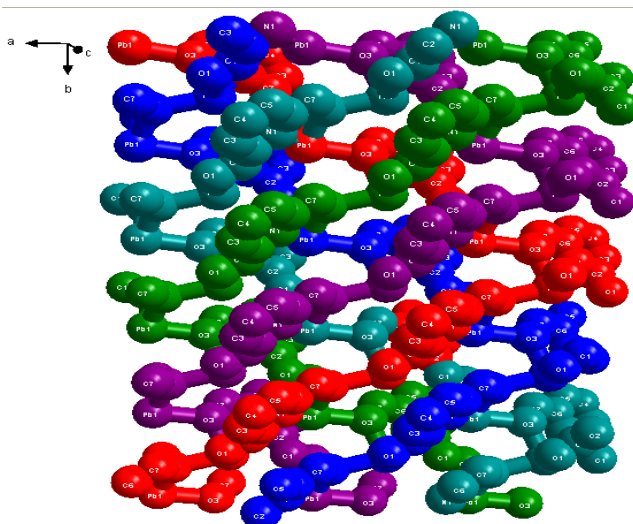


Figure 3. Space-filling views of the 5-fold interwoven meso helix.

In the crystal lattice of the complex **1**, there exist some supermolecular functions, such as potentially weak C-H...O hydrogen bonds intermolecular interactions, π - π stacking interactions and C-H- π supermolecular interactions. The intermolecular hydrogen bonds play important roles in constituting a 3D layer structure from its 2D network (**Figure 4**).

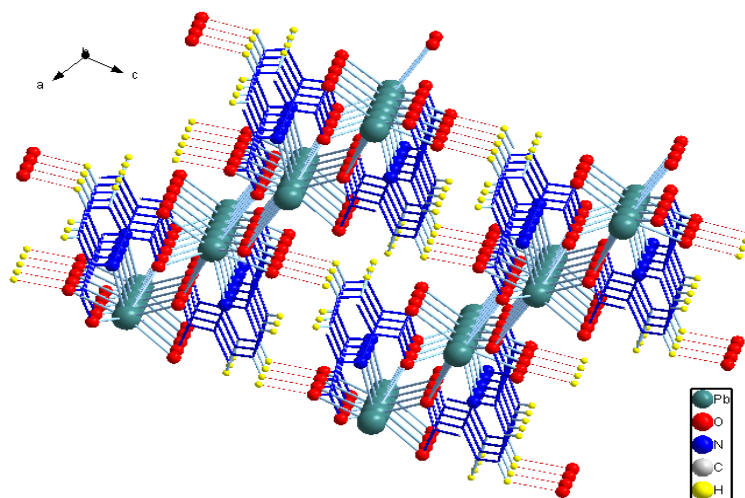


Figure 4. Crystal packing of the title complex: view approximately along the b-axis showing the formation of 3-D layers via C-H...O interaction.

Thermal Studies

The TG/DTC curves of the title compound, $[\text{Pb}(\text{dipic})]_n$, are presented in **Figure S6**. It can be seen that there are two steps of weight loss, and the decomposition event mainly take place at 474.1°C with one heat-absorption peak. On the base of weight

changes, the first process of the weight loss (28.52%) corresponds to the loss of the acyl-pyridine groups with an endothermic phenomenon and the remainder is $(\text{PbCO}_3)_n$ (calc. 28.23%); In the temperature range of 530~900°C, there is a weak endothermic event and about 12.19% weight loss may be related to the loss of carbonate for the second decomposition process and the remainder is $(\text{PbO})_n$ (calc. 11.82%).

A better insight into the nature of this intricate framework can be achieved by the application of diamond software reducing multidimensional structures to simple node- and-connection nets. As discussed above, the structure of the complex 1 is binodal nodes (with Pb atoms and O atoms of H_2dipic ligand). The plumbum atoms through oxo-bridge form double-helices (see Figure 5a). The rotation directions of double-helix chains are just opposite. The double-helix chains crossed-extending form a 2D framework polymer including Pb and O atoms (see Figure 5b). We speculate that the 2D framework may be consistent with the structure of the remainder $(\text{PbO})_n$ after decomposition process.

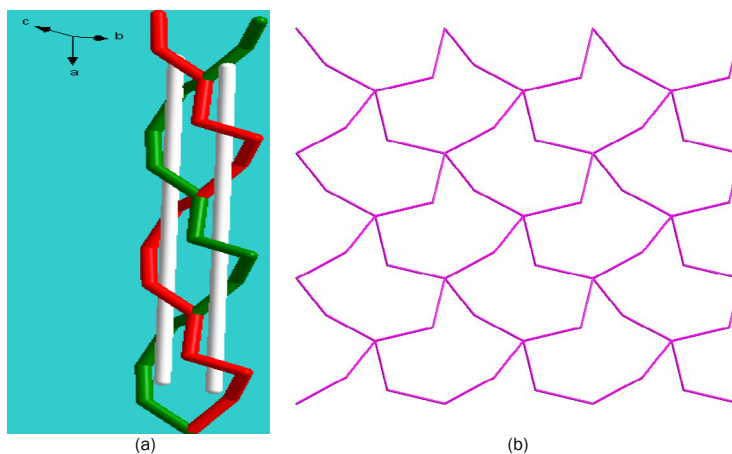


Figure 5. Double-helix structure of $(\text{PbO})_n$.

CONCLUSIONS

In summary, we have prepared and characterized one attractive self-penetrating coordination networks with uncommon entangled motifs. The isolation of the title compound not only provides helix examples of chemical structure but also confirms the aesthetic diversity of coordinative network chemistry.

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