

Solvothermal synthesis a novel hemidirected 2-D (3,3)-net metal-organic framework $[\text{Pb}(\text{HIDC})]_n$ based on the linkages of left- and right-hand helical chains

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Abstract

A novel 2-D hemidirected metal-organic framework $[\text{Pb}(\text{HIDC})]_n$ (**1**, H_3IDC = imidazole-4,5-dicarboxylic acid) has been hydrothermally synthesized and characterized by elemental analyses, IR, TGA, and X-ray single-crystal diffraction. Compound **1** is the first MOF based on Pb(II) and imidazole-4,5-dicarboxylic acid ligand. The 2-D (3,3)-net architecture with a rare $(4 \cdot 8^2)$ topology is built from alternately arranged left- and right-handed helical chains bridged by HIDC^{2-} ligand.

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As we know, lead is a heavy and toxic metal, so the study of Pb(II) model complexes in biological systems and removal of lead by chelating agents through coordination is very important [1]. Lead(II) possesses a large radius, a variable stereochemical activity, and a flexible coordination environment, which provides unique opportunities for the construction of novel metal-organic frameworks (MOFs) [2]. For these reasons, in main group metals, the lead based MOFs are the most in the literature to date [1–8]. Imidazole-4,5-dicarboxylic acid (H_3IDC) is a kind of multidentate N- or O-donor ligand that can be deprotonated to generate H_2IDC^- , HIDC^{2-} , and IDC^{3-} with versatile metal-binding and hydrogen-bonding capabilities, and it has recently drawn extensive attention in the construction of MOFs with fascinating structures [9–32]. However, most of the work has so far focused on the assembly of the d-block [11,15–17] or the lanthanides [31,32] metal-organic open frameworks. The architectures of MOFs or

supramolecular compounds constructed from Pb(II) and the ligand H_3IDC have not been reported to date. Accordingly, our aim is to synthesize novel Pb-based MOF by using the H_3IDC ligand for constructing interesting structure. Herein, we report the synthesis and crystal structure of the first 2-D MOF of lead with left- and right-hand helical chains, namely $[\text{Pb}(\text{HIDC})]_n$ (**1**).

The solvothermal reaction of $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ with H_3IDC , $\text{C}_2\text{H}_5\text{OH}$ and H_2O in molar ratio 0.2:0.2:33.9:222.2 at 140°C for 72 h led to the formation of yellow-block compound **1** [33]. Single-crystal X-ray diffraction analysis [34] reveals that compound **1** possesses a hemidirected 2-D architecture in which the asymmetric unit (Fig. 1) contains one Pb atom and one crystallographically unique HIDC^{2-} ligand. The Pb(II) ion in the asymmetry unit is five-coordinated with one N atom and four O atoms from three different HIDC^{2-} ligands. The distances of Pb–O bonds range from 2.391(10) to 2.712(9) Å, comparable to those in other Pb(II) carboxylate compounds [2,6]. The O–Pb–O bond angles range from $50.5(3)$ to $144.4(3)^\circ$. The H_3IDC is deprotonated to HIDC^{2-} in compound **1**, and five (one N and four O atoms) of the all six potential donor

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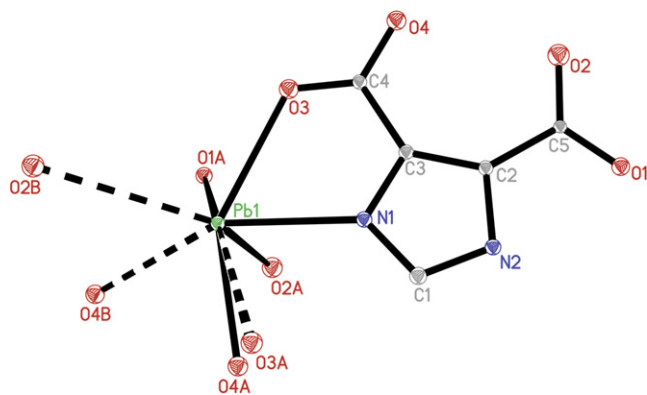
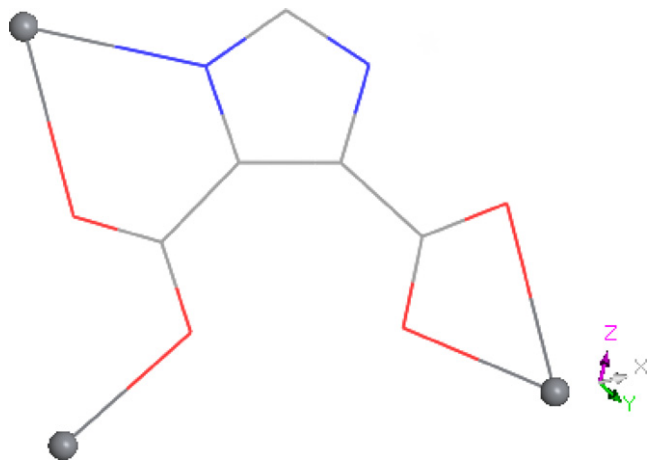


Fig. 1. ORTEP view of the coordination environments of the Pb atom in asymmetric unit of **1** with 30% thermal ellipsoids. All H atoms are omitted for clarity. Pb(1)–O(2A)#1 2.391(10), Pb(1)–O(4A) 2.462(9), Pb(1)–O(3) 2.649(9), Pb(1)–O(1A)#1 2.712(9), Pb(1)–N(1) 2.513(6). Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y - 1/2, -z + 3/2$.

atoms coordinate to three Pb centers through coordination mode $\eta^1:\eta^1:\eta^1:\eta^1:\mu_3$ (Scheme 1), which plays a key role in constructing the 2-D framework of **1**. The coordination mode of the HIDC^{2-} ligand in compound **1** has not been seen in other coordination polymers to the best of our knowledges. The Pb(II) centers are linked up via carboxyl groups of HIDC^{2-} to give rise to two types of helical $-\text{Pb}-\text{O}-\text{C}-\text{O}-$ chains with a pitch of 10.136 Å running along the z_1 -axis (Fig. 2). The left- and right-hand helical chains are further bridged by HIDC^{2-} ligand through one N atom and the other carboxyl group atoms to form a 2-D structure in bc plane (Fig. 3). From the topological point of view, the 2-D layer of **1** is a (3,3)-connected net. Both Pb(II) and HIDC^{2-} function as 3-connected nodes in the ratio 1:1. The (3,3)-connected net is shown schematically in Fig. 4. The Schläfli symbol is $(4 \cdot 8^2)$.

The coordination geometry of Pb(II) complex has close relationship with the 6s electrons. The stereochemical active 6s electrons of Pb usually produce hemidirected coordination geometry, while inactive 6s electrons easily produce



Scheme 1. Coordination mode of the H_3IDC ligand in title compound.

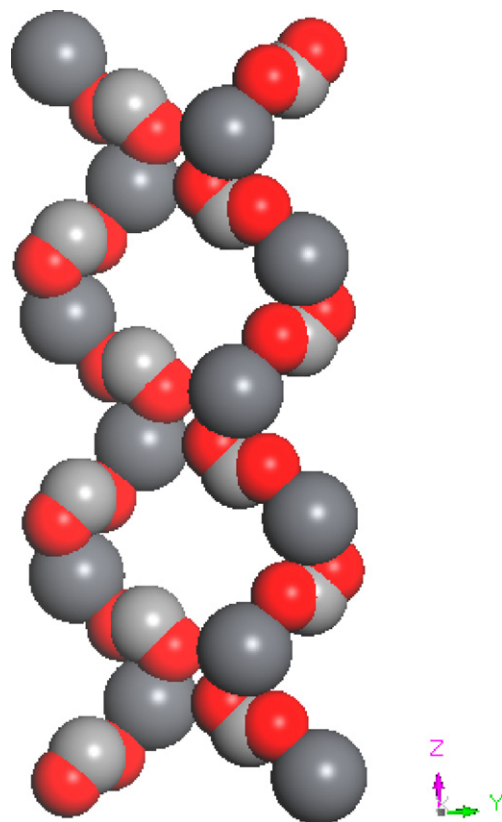


Fig. 2. View of the left- and right-handed helical $-\text{Pb}-\text{O}-\text{C}-\text{O}-$ chains along the z -axis. Color code: Pb, gray; O, red; C, Dark gray. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

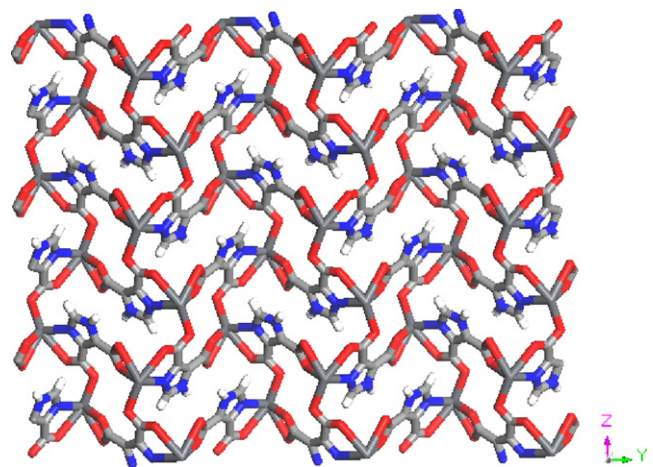


Fig. 3. The 2-D structure built from alternately arranged left- and right-handed helical chains bridged by HIDC^{2-} ligand in bc plane.

holodirected coordination structure. However, the difference between hemidirected and holodirected geometry around Pb(II) is ambiguous sometimes [8]. With the extending of bonding limit, the potential ligands, which are a little far from Pb(II) centre due to the repulsion of the 6s electrons, will be found and the hemidirected coordination sphere will be completed to holodirected. Indeed, **1** exhibits

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