Inorganic Chemistry Communications 35 (2013) 38–41

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Hydrothermal syntheses, crystal structures and luminescence properties of Cd(II) coordination polymers based on 2-(pyridine-2-yl)-1H-imidazole-4,5-dicarboxylic acid

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ARTICLE INFO

Article history:
Received 8 February 2013
Accepted 21 May 2013
Available online 25 May 2013

Keywords:
Hydrothermal synthesis
Helical chain
Hydrogen bonding
$\pi \cdots \pi$ stacking
Luminescence property

ABSTRACT

Two new supramolecular compounds, $[Cd(H_2PIDC)_2(H_2O)]\cdot H_2O$ (**1**) and $\{[Cd(H_2PIDC)_2(H_2O)]\cdot 2H_2O\}_n$ (**2**) (H_3PIDC = 2-(pyridine-2-yl)-1H-imidazole-4,5-dicarboxylic acid), have been synthesized under hydrothermal conditions and structurally characterized by single-crystal X-ray diffraction. Compound **1** contains discrete mononuclear structure, and compound **2** consists of one-dimensional left- and right-helix chains. Both are constructed into high-dimensional supramolecular frameworks by strong non-covalent hydrogen bonding and $\pi \cdots \pi$ stacking interactions. In addition, they were characterized by IR and elemental analysis, and their fluorescence properties in the solid state at room temperature have also been investigated.

During the past decade, considerable efforts have been devoted to construct new metal–organic coordination polymers (MOCPs) not only owing to their enormous varieties of intriguing structural topologies, but also their great potential applications in areas of catalysis, magnetism, separation, luminescence and so on [1–5]. Although the design and synthesis of such materials are highly influenced by many factors, such as the coordination trend of metal centers, the nature of ligands used, the ratio of the metal and ligand, reaction conditions etc., the judicious selection of multifunctional organic ligands is still an effective approach to construct MOCPs with unique structures and properties [6–9]. It is well known that aromatic polycarboxylates, especially the N-heterocyclic aromatic carboxylates, are excellent candidates for preparing novel MOCPs because of their versatile coordination modes [1–4,6,7,10]. Many examples with novel structures and interesting properties have been reported based on the N-heterocyclic carboxylates, such as 4,5-imidazoledicarboxylic acid [11,12], 3,4-pyridinedicarboxylic acid [13,14], 2,3-dicarboxypyrazine [15,16], and so on. Recently, much effort has been devoted to the design and synthesis of supramolecular materials. The low-dimensional crystal structure is generally stabled and directed into a fascinating supramolecular architecture through the non-covalent interactions, such as hydrogen bonding and $\pi \cdots \pi$ stacking interactions, in the construction of supramolecular materials [17,18].

2-(Pyridin-2-yl)-1H-imidazole-4,5-dicarboxylic acid (H_3PIDC) can be used to construct novel frameworks because its potential donor atoms exhibit diverse coordination modes (Scheme S1 modes (a)–(d)) [19,20]. On the one hand, H_3PIDC is endowed with the promising building block 4,5-imidazoledicarboxylic acid (H_3IDC), which has been proved to be a useful ligand, so it may possesses the coordination ability as H_3IDC [21,22]. On the other hand, the additional pyridyl group in H_3PIDC will modulate coordination ability to give more potential coordination modes because the ortho position of pyridine-N enhances the chelating ability in combining with the imidazole-N. In addition, H_3PIDC has not only N–H and C=O groups, but also pyridyl and imidazole groups lead to hydrogen bonding and enlarge the conjugation π-system, so the complexes can be linked into three dimensional supramolecular networks via the hydrogen bonds and $\pi \cdots \pi$ interactions. H_3PIDC may translate to H_2PIDC^-, $HPIDC^{2-}$ or $PIDC^{3-}$ in compounds if its protons in the two carboxylic groups and the imidazole-N were deprotonated, and thus it can potentially generate intriguing frameworks.

In this work, we report two Cd(II) coordination polymers, $[Cd(H_2PIDC)_2(H_2O)] \cdot H_2O$ (**1**) and $\{[Cd(H_2PIDC)_2(H_2O)] \cdot 2H_2O\}_n$ (**2**) [23,24], based on H_3PIDC, as well as their fluorescent properties. When we added $CdCl_2$ and H_3PIDC at a rate of 1:2 in the reaction system, we got the 0D coordination compound **1**. If the amount of $CdCl_2$ was increased, we obtained a 3D coordination polymer $[Cd_4(HPIDC)_4(H_2O)]_n$ which has been reported by Li et al. [19]. When oxalic acid was added in the reaction system, in which the rate of $CdCl_2$ and H_3PIDC was about 4:1, the 1D coordination compound **2** was obtained. The oxalic acid

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http://dx.doi.org/10.1016/j.inoche.2013.05.019

may act as a structure-directing agent in generating compound **2**. In compounds **1** and **2**, two new coordination modes of H_2PIDC^- were reported for the first time (Scheme S1 modes (e) and (f)). Comparing with the reported coordination modes [19,20], the imidazole nitrogen atom and carboxylic oxygen atom in ortho position don't adopt chelate coordination mode in compounds **1** and **2**.

Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the triclinic space group $P-1$. The asymmetric unit contains one crystallographically unique Cd(II) ion, two partially deprotonated H_2PIDC^- ligands, one coordinated water molecule, and one lattice water molecule, as shown in Fig. 1a. The central Cd1 ion is five-coordinated by four nitrogen atoms, N1, N2, N4 and N5, from two individual H_2PIDC^- ligands, and coordinated water molecule O1W, exhibiting a distorted trigonal bipyramid geometry. The equatorial positions are occupied by N2, N5, O1W, while N1 and N4 site the axial positions. The distances of Cd–N [2.223(3)–2.364(3) Å] and Cd–O1W [2.247(3) Å] are in the normal ranges of those observed in reported Cd(II) compounds [25,26]. Though H_2PIDC^- ligand possesses seven coordination points, in **1**, the two H_2PIDC^- ligands chelate the Cd(II) ion into a discrete mononuclear unit only using pyridine-N and imidazole-N (Scheme S1 mode (e)), which leads to the almost coplane of the pyridine and imidazole groups. The type of coordination mode of H_2PIDC^- was reported for the first time here. The hydrogen bonding (Table S3) and $\pi\cdots\pi$ interactions (Table S4) play important roles in stabilizing **1**. As shown in Fig. 1b, the coordinated O1W and carboxylic oxygen O6 atoms acting as hydrogen bond donor and accepter link, respectively, to O6B and O1WB of the neighboring molecule (O1W···O6B = 2.685(4) Å, O1W–H1WA···O6B = 167°; symmetry code: B, 1 − x, 1 − y, 1 − z). Two mononuclear molecules are linked into a binuclear structure through these hydrogen bonds. As shown in Fig. 1c, O2W and O2WA acting as bridges link the neighboring two binuclear structures through hydrogen bonding interactions, forming a 1D chain (O2W···O4 = 2.809(4) Å, O2W–H2WA···O4 = 165°; O2W···O3A = 2.861(4) Å, O2W–H2WB···O3A = 170°; symmetry code: A, 1 − x, 2 − y, 2 − z). The uncoordinated imidazole-N, N3 and N6, acting as hydrogen bond donors link to the carboxylic atom O8E and the lattice water O2WC of the neighboring 1D chains into a 3D supramolecular architecture (N3···O8E = 2.811(4) Å, N3–H3···O8E = 163°; N6···O2WC = 2.770(4) Å, N6–H6···O2WC = 167°; symmetry codes: C, x, −1 + y, z; E, 1 + x, 1 + y, z). There exhibit $\pi\cdots\pi$ stacking interactions between the parallel pyridyl rings of neighboring molecules with the plane-to-plane distances of 3.3420(15) Å and 3.4692(16) Å, respectively (Table S4). All these hydrogen bonding and $\pi\cdots\pi$ stacking interactions play important roles for stabilizing the 3D supramolecular architecture.

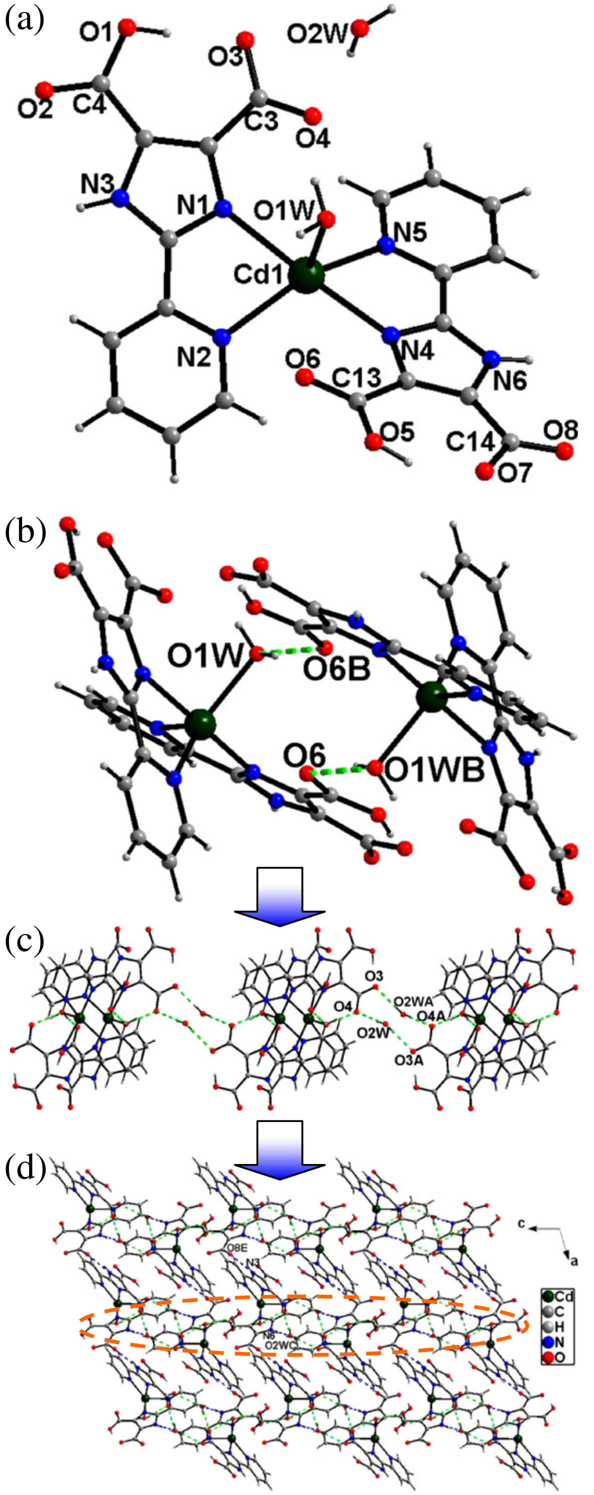

Fig. 1. (a) The asymmetric unit of compound **1**; (b) the mononuclear molecules are linked into binuclear structure by hydrogen bondings; (c) neighboring binuclears are linked into 1D chain through hydrogen bondings; (d) 3D supramolecular architecture of **1**. (Symmetry codes: A, 1 − x, 2 − y, 2 − z, B, 1 − x, 1 − y, 1 − z, C, x, −1 + y, z; E, 1 + x,1 + y, z.).

Single-crystal analysis reveals that compound **2** crystallizes in the monoclinic space group $P2(1)/c$. The asymmetric unit in compound **2** consists of a crystallographically independent Cd(II) atom, two H_2PIDC^- ligands, one coordinated water molecule, and two crystalline water molecules. As shown in Fig. 2a, Cd1 is coordinated by four nitrogen atoms, N1, N2, N5 and N6, from two H_2PIDC^- ligands, one carboxylic atom O1A from the third H_2PIDC^- ligand, and one water oxygen atom O1W to form a distorted octahedral geometry. The distances of Cd–N [2.273(3)–2.379(3) Å] and Cd–O [2.358(3)–2.460(3) Å] are in the normal ranges of those observed in reported Cd(II) compounds [27,28]. In compound **2**, there exist two kinds of H_2PIDC^- ligands. One kind of H_2PIDC^- ligand adopts chelating coordination mode using ortho pyridine-N and imidazole-N (Scheme S1 mode (e)). Another kind adopts μ_2-*k*N, N′: *k*O bridging coordination mode (Scheme S1 mode (g)), in which pyridine-N and imidazole-N chelate one Cd ion, and one carboxylic oxygen atom O1 bridges another Cd ion. μ_2-*k*N, N′: *k*O bridging coordination mode of H_2PIDC^- ligand was reported for the first time. The two kinds of ligands are almost perpendicular to each other with the dihedral angle of 85.6°. Thanks to the coordinating effects between the carboxylic oxygen atoms and Cd ions, μ_2-H_2PIDC^- ligands connect Cd ions into left- and right-handed helical chains with the pitch of 13.1 Å along *b* axis. The neighboring μ_1-H_2PIDC^- ligands of the adjacent two left- and right-handed helical chains are parallel and interdigital to each other with $\pi\cdots\pi$ stacking interaction of about 3.31 Å (Fig. 2b, Table S4). As shown in Fig. 2c, uncoordinated imidazole-N, N3 of μ_2-H_2PIDC^- and N4 of μ_1-H_2PIDC^-, acting as hydrogen bond donors, respectively, bond to carboxylic oxygen atoms O8C of μ_1-H_2PIDC^- and O4E of μ_2-H_2PIDC^- (N3···O8C = 2.737(4) Å, N3–H3···O8C = 163°; N4···O4E = 2.813(4) Å, N4–H4···O4E = 162°; symmetry codes: C, 1 − x, 2 − y, 1 − z; E, −x,