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In situ hydrothermal synthesis of two novel Cd(II) coordination compounds

Guo-Jie Yin ^{a, b, c}, Bao-Ming Ji ^b, Chen-Xia Du ^{a,*}

^a Department of Chemistry, Zhengzhou University, Zhengzhou 450052, PR China

^b College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, PR China

^c Department of environment engineering and Chemistry, Luoyang Institute of Science and Technology, Luoyang 471023, PR China

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ABSTRACT

Hydrothermal in-situ reactions of 4,4'-bis(3,3'-dicyano)pyridine (pydcy) with Cd(NO₃)₂·6H₂O under the similar reaction condition but different solvent media result in two new compounds $[C_{48}H_{32}Cd_2N_8O_{18}](1)$ and $[C_{17}H_{13}CdN_3O_5](2)$. Compound **1** features a new dimeric carboxylate bridged structure, while compound **2** gives a 3D framework with large hexagon channels embodied with water molecules. Topology analysis of **2** defines a type of {8³} etb topology. TGA and XRPD analysis indicated that the guest water molecules in **2** can be removed to result in a nanoporous network. Both compounds exhibit intense fluorescence at room temperature, which may originate from the ligand-to-metal charge transfer (LMCT) state.

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Design and synthesis of functional metal-organic frameworks (MOFs) with desired properties is a hard and challenging problem, while introduction of the mechanism of hydro(solvo)thermal in-situ metal/ligand reactions shades light on this scientific problem [1], and this method has been proved to be a promising technique in the preparation of highly stable materials that are inaccessible or not easily obtainable by conventional methods. For example, Lin and co-workers have synthesized a series of acentric MOFs of metal carboxylates with second-order nonlinear optic properties based on in-situ metal/ligand reactions, which may not be accessible from their corresponding carboxylic acids [2]. Arshad Aijaz et al. reported a number of interesting MOFs by using tripodal ligand 3,5-di(1Himidazol-1-vl)benzoxvlate in situ generated from a CN-containing precursor [3]. Also, in situ generated donor groups via slow hydrolysis of precursor ligands under hydro(solvo)thermal conditions can provide more intriguing network topologies than the direct reaction of metal ions with the corresponding carboxylic acids [4].

The carboxylate functional group has been extensively used for constructing polynuclear complexes due to its versatile coordination modes and ability to generate metal-oxygen chains [5]. Other bridging ligands, such as 4,4'-bipyridine, also have strong ability to form polynuclear compounds [6]. Therefore, the combination of carboxylate and pyridine donor moieties in a ligand may lead to more interesting network topologies [7]. Considering these in mind, we choose, 4,4'-bis (3,3'-dicyano)pyridine (pydcy) [8] as a precursor ligand. Hydro(solvo) thermal reaction of pydcy with cadmium(II) salt resulted in the formation of compounds $[C_{48}H_{32}Cd_2N_8O_{18}](1)$ and $[C_{17}H_{13}CdN_3O_5](2)$ with

different topologies and properties depending on whether the solvent is H₂O or H₂O/pyridine/ethanol. The solvent media used in the assembling processes was found to significantly influence the structures and properties of the resultant coordination compounds.

The ligand 4,4'-bis(3,3'-dicyano)pyridine (pydcy) was prepared according to the procedure shown in Scheme 1.

4,4-bipyridine-N,N-dioxide was obtained according to the reference [9]. The 4,4'-bis(3,3'-dicyano)pyridine (pydcy) ligand was easily synthesized from the reaction of 4,4-bipyridine-N,N-dioxide, Me₃SiCN and PhCOCl in CH₂Cl₂ solvent under a dry nitrogen atmosphere [10]. Yellow solid was obtained with a yield of 96%. Anal. Calc. For C₁₂H₆N₄: C, 69.90; H, 2.93; N, 27.17%. Found: C, 69.89; H, 2.94; N, 27.16%. 1H NMR (400 MHz, CDCl₃): δ = 8.919(d, J = 4.8 Hz, 2H), 7.932 (s, 2H), 7.749(d, J = 2 Hz, 2H).

Synthesis of compound $[C_{48}H_{32}Cd_2N_8O_{18}]$ (1). A mixture of pydcy ligand (20.6 mg, 0.10 mmol), Cd(NO₃)₂·4H₂O (30.9 mg, 0.10 mmol) and distilled water(5 ml) was sealed in a Teflon-lined reactor and heated at 130 °C for 3 days. After slow cooling to room temperature, block colorless crystals were collected and dried in air (yield: 42%



Scheme 1. Schematic drawing for the synthetic route of pydcy.

^{*} Corresponding author. Tel.: +86 371 67767896; fax: +86 371 67763390. *E-mail address*: dcx@zzu.edu.cn (C.-X. Du).

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Fig. 1. The coordination environment of the Cd(II) atom in compound 1. Hydrogen atoms are omitted for clarity.

yield based on Cd). Anal. Calc. For C₄₈H₃₂Cd₂N₈O₁₈: C, 46.68; H, 2.61; Cd, 18.21; N, 9.06%. Found: C, 46.64; H, 2.64; Cd, 18.17; N, 9.02%.

Compound $[C_{17}H_{13}CdN_3O_5]$ (2) was obtained under the same reaction condition as that of compound **1** except that the solvent used was H₂O/pyridine/ EtOH (5 ml, 1:2:2, v/v). Colorless acicular crystals were collected and dried in air (yield: 62% yield based on Cd). Anal. Calc. For C₁₇H₁₃CdN₃O₅: C, 45.20; H, 2.91; Cd, 24.89; N, 9.32%. Found: C, 45.16; H, 2.95; Cd, 24.84; N, 9.25%.

The single crystal X-ray structural analysis reveals that the cyanogen moieties of the ligand was hydrolyzed to carboxylic acid through in-situ ligand reaction (Hpydca⁻ or $pydca^{2-}$, $pydca^{2-} = 4,4'$ -bis (3,3'-dicarboxyl)pyridine). The solvent media is said to play a crucial role in the assembling processes of the resulting complexes [11].

Compound 1 crystallizes in triclinic with space group P^{-1} . As shown in Fig. 1, each Cd(II) atom is six-coordinated by three carboxylate oxygen atoms (Cd1-O1 2.269(2) Å, Cd1-O5 2.429(2) Å, Cd1-O6 2.3225(18) Å), two pyridyl nitrogen atoms (Cd1-N1 2.276(3), Cd1-N3 2.293(2) Å) of the ligands and one oxygen atom of water (Cd1-O9 2.299(2) Å). The overall geometry around the Cd(II) center is a distorted octahedron. A typical feature of 1 is the dimeric carboxylate bridged unit, of which eight carboxylate groups adopt three different chelating modes. 03-04 carboxylate group is free, while 01-02 carboxylate group is in a semi-chelating fashion and O5-O6 carboxylate group adopts a syn-anti μ_2 - η^1 : η^2 bridge to link two metal atoms to form a dimetal linkage. As shown in Fig. 2, each dicaryon was interlinked via hydrogen bonds {O(9)-H(2 W)...O(1)[O/O 2.676(3)A, H...O 1.99 Å, ∠OHO, 148(8)°], O(4)-H(4)...O(7) [O/O 2.890(4)Å, H...O 2.11 Å, \angle OHO, 159(4)°]} to form a two dimensional supramolecular structure. Furthermore, the two pyridyl rings of the ligand are almost coplanar, the aromatic π - π stacking interaction between adjacent ligands not only leads to increased thermodynamic stability but also effectively fills the void space of this two dimensional



Fig. 2. Perspective view of the network of compound 1 along *a* axis.



Fig. 3. The coordination environment of the Cd(II) atom as well as coordination mode of pydca²⁻ ligand in compound **2.** Free water molecules and H atoms are omitted for clarity.

structure. As a result, no free solvent molecules are enclathrated in compound **1**.

Compound **2** crystallizes in the Rhombohedral with space group R^{-3} . There are one unique Cd(II) atom, one pydca²⁻ ligand, one pyridine and two free water molecules in the asymmetric unit of compound **2**. As illustrated in Fig. 3, each Cd(II) atom is six-coordinated by three carboxylate oxygen atoms (Cd1-O1 2.369(5) Å, Cd1-O2 2.278(5) Å, Cd1-O3 2.296(5) Å), two nitrogen atoms (Cd1-N1 2.370 (6) Å, Cd1-N2 2.297(6) Å) from the ligand and one nitrogen atom (Cd1-N3 2.319(6) Å) from pyridine to furnish a distorted octahedral coordination geometry.

The two carboxylate groups of pydca^{2–} ligand adopt different chelating modes. O3–O4 carboxylate group is in a semi-chelating mode, while O1–O2 carboxylate group adopts a syn-anti μ^2 - η^1 : η^2 bridge to link adjacent two Cd(II) atoms. The dihedral angle between the two pyridyl rings of pydca²– ligand is 71.5°. First, one-dimensional (1D) helical chain subunit is formed by the operation of a threefold screw along c-axis. The distance between adjacent Cd(II) atoms bridged by O1–O2 carboxylate group is 5.370 Å. (Fig. 4a). The 1D helical chains are further joined together by O3 N2 chelating atoms (Fig. 4b) to result in a 3D framework with large hexagon channels (Fig. 4c), and water molecules are embodied in the hexagon channels via hydrogen bonds.

In order to get a better insight into the nature of this complicated 3D framework, the topology approach can be used. From the topological view, each Cd(II) atom coordinated with three pydca^{2–} ligands together with its adjacent pyridine can be considered as a 3-connecting node, and each pydca^{2–} ligand linked three Cd(II) atoms can be defined as another 3-connecting nodal point (Fig. 5). Thus compound **2** possesses a 3D 3-connected net with the ratio of these two 3-connecting nodes of 1:1. The topology analysis by the TOPOS4.0 program suggests that it is a 3-connected net with a Schläfli symbol of {8³}. It can be seen from the Fig. 5b that the minimum loop through each node was a chair like eight-membered ring configuration. The net of compound **2** defines a type of etb topological framework which is earliest observed by Nathaniel L. Rosi [12].

Considering the possibility of generating porous network by removing the guest molecules, the thermal stability of compound **2**



Fig. 4. Perspective view of the 1D helical chain structure along c-axis (a) and the 3D framework of **2** extended along the ab plane by the connection of adjacent helical chains with O3, N2 chelating atoms (b) 3D framework of **2** showing trapped water molecules inside the large hexagon channels (c).



Fig. 5. View of the 3D framework of **2** along c-axis (a) and {8³} net topology (b), the chair like eight-membered ring defined by the green line shows the minimum loop through each node.

has been investigated. The TGA curve of compound **2** showed that guest molecules can be easily removed by heating under nitrogen atmosphere (Fig. 1S). The first stage weight loss of 4.017% in the temperature range 54–160 °C corresponded to the release of H_2O guest molecules (expected 3.988%). Interestingly, XRPD pattern for the sample of compound **2** after removal of the included water molecules remains essentially identical with that of pristine solids (Fig. 2S). Moreover, guest water molecules can be readily reintroduced into the porous network of compound **2** by exposure to the water vapor at room temperature, which can be confirmed by TGA analysis. This result conclusively demonstrated that the guest molecules in compound **2** can be successfully removed to result in a porous network with hexagon channels. As shown in Fig. 1S, the framework structure of compound **2** is stable up to 300 °C.

It has been established that coordination polymers with conjugated organic ligands are promising candidates for photoactive materials due to their luminescent properties. Consequently, solid state fluorescent properties of these two compounds have been investigated at room temperature. As shown in Fig. 6, Na₂pydca shows a very broad weak emission band centered at 445 nm upon excitation at 400 nm, which can be attributed to the $\pi^*-\pi$ intraligand transition. However, compounds **1** and **2** display apparent red-shifted strong emissions compared with that of Na₂pydca. Compound **1** shows a maximum emission at 467 nm, while compound **2** exhibits a strong emission band at 513 nm. The emissions of those two compounds might be attributable to the π_{tz} -5s ligand-to-metal charge transfer transition [13]. Interestingly, the emission band of compound **2** is red-shifted 46 nm, together with apparently enhanced emission intensity compared with that of compound **1**. The increased rigidity of compound **2** can effectively reduce



Fig. 6. The emission spectra of compound 1, compound 2 and Na₂pydca in solid state at room temperature.

the non-radiation decay and enhance the luminescence intensity. Furthermore, the coordination of pydca^{2–} with Cd(II) as a five-dentate ligand may reduce the energy gap between the HOMO and LUMO levels of compound **2**, and as a result cause apparently red-shifted emission. The above result demonstrated that luminescent property of compounds can be strongly affected by metal-ligand chelating mode and the crystal structure.

In conclusion, two novel Cd(II) coordination compounds have been successfully synthesized by the in-situ reaction of (pydcy) with Cd(NO₃)₂·6H₂O under the similar reaction condition but different solvent media. The single crystal X-ray structural analysis reveals that the cyanogen moieties of the ligand were hydrolyzed to carboxylic acids at this process and the resultant coordination frameworks are profoundly influenced by the solvent media. Compound **1** forms a new dimeric structure by using H₂O as a solvent, while compound **2** is a 3D 3-connected novel network with Schläfli symbol of {8³} when the solvent used was H₂O/pyridine/ EtOH (1:2:2, v/v). TGA and XRPD indicated that the guest water molecules in **2** can be easily removed to result in a porous network with hexagon channels.

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Appendix A. Supplementary data

CCDC 794475 and 794476 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.09.029.

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