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Supramolecular Isomerism in Cadmium Hydroxide Phases. Temperature-Dependent Synthesis and Structure of Photoluminescent Coordination Polymers of α - and β -Cd₂(OH)₂(2,4-pyda)

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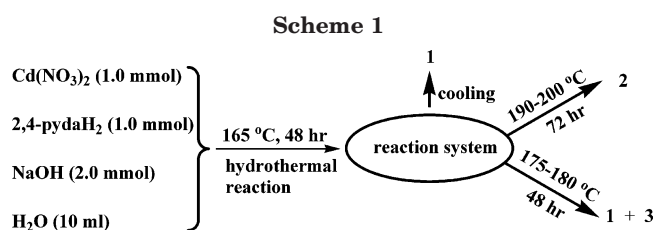
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ABSTRACT: Two isomeric inorganic–organic hybrid materials formulated as [Cd₂(OH)₂(2,4-pyda)] (2,4-pyda = 2,4-pyridinedicarboxylate) have been hydrothermally synthesized via transformation of one-dimensional coordination chains formulated as [Cd(H₂O)₂(2,4-pyda)] into three-dimensional coordination polymers at different temperatures and characterized by crystallography.

The construction of coordination polymers based on metal centers and multifunctional bridging ligands are of great current interest owing to their potential applications such as magnetism, electric conductivity, molecular adsorption, and heterogeneous catalysis.^{1,2} The hydrothermal method has been of advantage to prepare low-solubility crystalline organic–inorganic hybrid materials.³ However, it is still a challenge to obtain the desired products because the final products are greatly affected by a variety of hydrothermal parameters such as reaction time, temperature, pH value, and molar ratio of reactants. Much work is required to extend the knowledge of the hydrothermal process and establish proper synthetic strategies leading to the desired species. On the other hand, supramolecular isomerism, the existence of more than one superstructure for a given set of components, is of particular importance because the superstructure plays an essential role in determining the properties of crystalline solids.^{4,5} We are investigating the synthesis of metal hydroxide-based coordination polymers by the hydrothermal method. Recently, we presented the hydrothermal transformation of a two-dimensional (2D) bilayered coordination polymer into a novel three-dimensional (3D) coordination polymer with one-dimensional (1D) Co₃(OH)₂ chains by the controlled hydrothermal reactions.⁶ Herein we report two novel 3D organic–inorganic hybrid materials with isomeric metal hydroxide phases, which were rearranged from a precursor of 2D coordination layers of [Cd(μ_2 -H₂O)(H₂O)(2,4-pyda)] (**1**) under hydrothermal conditions at different temperatures, namely, α -Cd₂(μ_3 -OH)₂(2,4-pyda) (**2**) and β -Cd₂(μ_3 -OH)₂(2,4-pyda) (**3**) (2,4-pyda = 2,4-pyridinedicarboxylate).

Reaction (see Supporting Information) of Cd(NO₃)₂·4H₂O, 2,4-pydaH₂, NaOH, and water (10 mL) in the molar ratio of 1:1:2:555 at 165 °C for 48 h yielded colorless needle crystals of **1** (75%) in a single phase. Interestingly, a second phase product of colorless rhombic crystals of **2** (45%) was obtained when the same reaction was carried out at 165 °C for 48 h and then at 190–200 °C for a further 72 h. Parts of the aqua ligands in **1** were obviously deprotonated into hydroxide groups at higher temperature, which is a key to the formation of Cd₂(OH)₂ layers in **2**, consistent



with our previously observed case⁶ and the following structural features. The yield of **2** grows as the reaction temperature increases, which is also consistent with the dependence of the deprotonated degree of water molecules on temperature. Curiously, when the same reaction as **1** was carried out at 165 °C for 48 h and then at 175–180 °C for a further 48 h, a third byproduct of colorless rhombic crystals of **3** was manually isolated (less 2%). However, the yield of **3** does not grow as the reaction time is lengthened, and if the reaction time at 175–180 °C is over 72 h, XRPD analysis reveals the final product phase is **2**, suggesting that **3** is a metastable phase in the hydrothermal reaction system (Scheme 1).

X-ray structural analysis⁷ reveals that the precursor **1** crystallizes in an orthorhombic space group *Pbca*, and there are one crystallographically independent cadmium atom, one 2,4-pyda, and two aqua ligands (Figure 1). The Cd atom, in a distorted octahedral geometry, coordinated by three aqua ligands (Cd–O(water) = 2.103(2)–2.201(4) Å), two carboxylato O atoms (Cd–O = 2.152(4) and 2.179(4) Å), and one N atom (Cd–N = 2.297(2) Å) from two 2,4-pyda ligands. The cis and trans O(N)–Cd–O angles are in the range of 73.2(1)–116.6(2)° and 155.3(1)–170.02(3)°, respectively. The Cd atoms are bridged by the 2,4-pyda ligands into 1D coordination chains along the *b*-axis. Adjacent Cd(2,4-pyda) chains are further linked into 2D coordination rectangular layers via μ_2 -H₂O bridges with a Cd–O_{2w}–Cd bond angle of 134.8(1)°. The whole structure of **1** is a 3D net extended by interlayer hydrogen bonds between the aqua and the carboxylates (Figure S1, Supporting Information).

2 and **3** are supramolecular isomeric and crystallize in the same monoclinic *P2₁/c*. There are two crystallographically independent cadmium atoms, one 2,4-pyda and two hydroxy groups.

In **2**, the Cd1 atom adopts a slightly distorted triangular bipyrimid geometry (Figure 2a), coordinated by three

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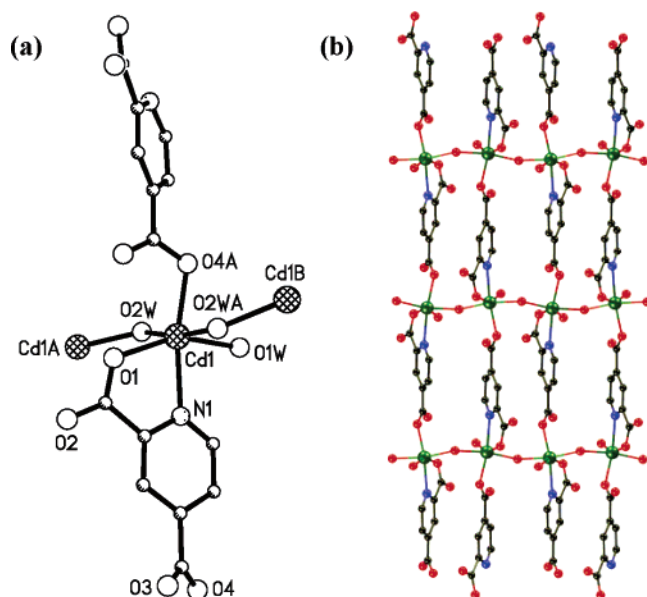


Figure 1. Perspective views of the coordination environments of the Cd atoms (a) and the 2D coordination layer (b) in **1**.

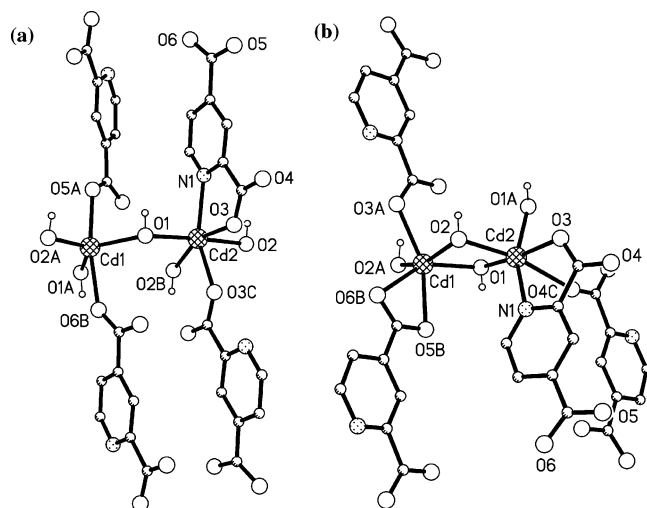


Figure 2. Perspective views of the coordination environments of the Cd atoms in **2** (a) and **3** (b).

hydroxy groups ($\text{Cd1-O} = 2.171(2)–2.242(2) \text{ \AA}$; $\text{O-Cd1-O} = 106.38(8)–126.31(8)^\circ$) at the basal positions and two carboxylate O atoms from two 2,4-pyda ligands ($\text{Cd1-O} = 2.261(2)$ and $2.359(3)$, $\text{O5-Cd1-O6} = 168.89(9)^\circ$) at the apical positions. The Cd2 atom adopts a distorted-octahedral geometry, being surrounded by one pyridyl N atom and two carboxylate O atoms from two 2,4-pyda ligands and three hydroxy O atoms ($\text{Cd2-O} = 2.248(2)–2.343(2)$ and $\text{Cd2-N} = 2.355(3) \text{ \AA}$). Each Cd1 atom is connected to six other Cd atoms (two Cd1 and four Cd2 atoms) via hydroxy groups, while each Cd2 atom is connected to five other Cd atoms (four Cd1 and one Cd2 atoms) via hydroxy groups, leading to the formation of 2D cadmium-hydroxide layers with $[\text{Cd}(\text{OH})_2]_2$, $[\text{Cd}(\text{OH})_3]$, and $[\text{Cd}(\text{OH})_4]$ circular units (Figure 3a), which are quite different from those in other coordination polymers incorporating $\text{Cd}_3(\text{OH})_2$ layers with $[\text{Cd}(\text{OH})_6]$ circular unit or $\text{Fe}_2(\text{OH})_2$ layers with $[\text{Fe}(\text{OH})_2]$ and $[\text{Fe}(\text{OH})_4]$ circular units.⁸ The intralayer Cd...Cd distances are $3.455(1)–4.007(1) \text{ \AA}$, and the Cd–OH–Cd angles are in the range of $98.76(7)–129.88(9)^\circ$. Adjacent layers are connected by 2,4-pyda pillars along the *a*-axis to generate 3D organic–inorganic hybrid materials

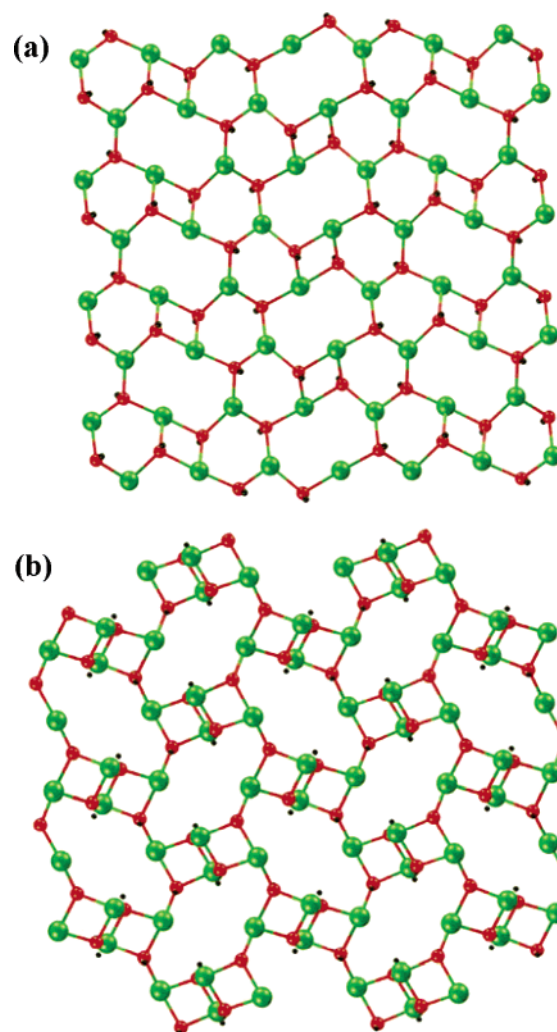


Figure 3. Perspective views of the isomeric $\text{Cd}_2(\text{OH})_2$ layers in **2** (a) and **3** (b).

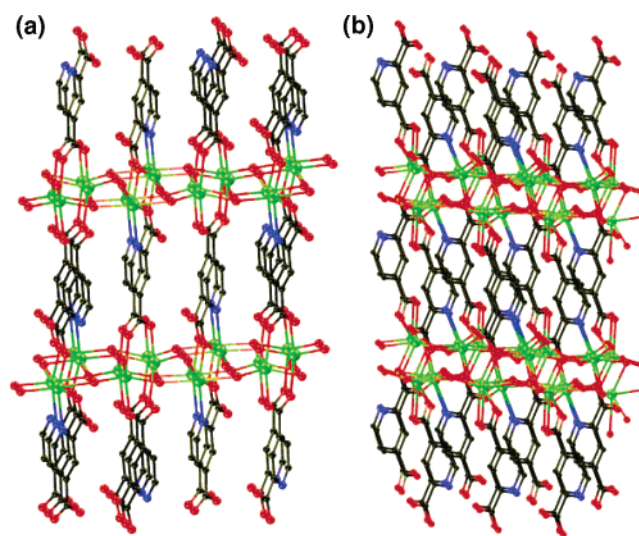


Figure 4. Two views, slightly offset from down the *b*-axis, of the network connectivity in the structures of **2** (a) and **3** (b).

(Figure 4a) in which each 2,4-pyda bridges four Cd atoms (Scheme S1, Supporting Information).

While in **3**, the Cd1 atom is in a greatly distorted octahedral geometry, coordinated by three carboxylate O atoms from two 2,4-pyda ligands and three hydroxy groups

(Figure 2b). The Cd1–O bond lengths are in the range of 2.225(3)–2.402(3) Å. The cis and trans O–Cd1–O angles are in the range of 54.9(1)–117.1(1) and 144.2(1)–157.0(1)°, respectively. The coordination environment of Cd2 is similar to that of **2**, being chelated by N1 and O3 atoms from one 2,4-pyda ligand (Cd2–O and Cd2–N = 2.325(3) and 2.307(4) Å). The remaining four coordination sites are occupied by four O atoms from another 2,4-pyda ligand and three hydroxy groups (Cd2–O = 2.238(3)–2.464(4) Å). The cis and trans O–Cd2–O(N) angles are in the range of 71.2(1)–117.1(1) and 159.9(1)–170.7(1)°, respectively. Each Cd1 atom is connected to five other Cd atoms (two Cd1 and three Cd2 atoms) via hydroxy groups, while each Cd2 atom is connected to four other Cd atoms (three Cd1 and one Cd2 atoms) via hydroxy groups. These connections result in the formation of 2D cadmium-hydroxide layers with [Cd(OH)₂] and [Cd(OH)₆] circular units parallel to the *bc* plane (Figure 3b). It should be noted that such metal-hydroxide layer is unprecedented compared with the documented species⁸ and also quite different from that in **2**. The intralayer Cd···Cd distances are 3.439(1)–4.043(1) Å and the Cd–OH–Cd angles are in the range of 96.7(1)–128.8(1)°. Each 2,4-pyda acts in a different μ_4 -bridging mode from that in **2** (Scheme S1, Supporting Information); adjacent layers are pillared by these 2,4-pyda ligands to generate a 3D organic–inorganic hybrid network along the *a*-axis (Figure 4b).

Most phenomena regarding supramolecular isomerism in coordination networks reported so far show crystal structures that contain solvent or guest molecules to satisfy crystal packing, which result from different stoichiometry of the included solvent.⁹ Only a few examples of coordination networks have been reported of supramolecular isomerism with a fixed stoichiometry for all components.^{4,5} For example, reaction-temperature-dependent supramolecular isomerism of coordination networks based on the organo-metallic building block [Cu₂(μ -BQ)(μ -OAc)₂] (BQ = *p*-benzoquinone) was very recently reported.^{5a} Therefore, we isolate for the first time isomeric metal hydroxide phases employing a hydrothermal technique, which has not been determined previously.

In the solid state, **2** and **3** exhibit intense photoluminescence upon photoexcitation at 325 nm. The emissions of **2** (λ_{max} = 425 nm) and **3** (λ_{max} = 420 nm) may be assigned as ligand-to-metal charge transfer (LMCT); a similar emission band at about 430 nm has also been observed previously for other Zn(II) or Cd(II) cluster-based coordination polymers with aromatic carboxylate ligands.¹⁰ Moreover, thermogravimetric analysis (TGA) performed on the polycrystalline samples of **2** and **3** indicates that they are thermally stable up to 340–350 °C. They may be good candidates for blue-light emitting materials due to their highly thermal stability and insolubility in common solvents.

In summary, we have isolated the first example of isomeric metal hydroxide phases mediated simply by changing the hydrothermal reaction temperature. This result is expected to provide new important information for understanding supramolecular isomerism of coordination networks.

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Supporting Information Available: X-ray crystallographic file in CIF format, synthesis of **1–3**, crystal packing diagram for **1** (Figure S1), the simulated and experimental powder diffraction patterns for **2** and **3** (Figure S2), and the coordination modes of the 2,4-pyda ligand in **2** and **3** (Scheme S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) X-ray single-crystal diffraction data collections were collected on a Rigaku/MSC Mercury CCD diffractometer for **1** and **3** and on a Bruker Smart Apex CCD diffractometer for **2** with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Crystal data for **1**: orthorhombic, space group *Pbca*, *a* = 12.137(7) Å, *b* = 7.742(5) Å, *c* = 18.618(9) Å, *V* = 1749.5(18) Å³, *Z* = 8, ρ_{calcd} = 2.381 g cm⁻³, (Mo K α) = 25.06 cm⁻¹. *R*₁ = 0.0391, *wR*₂ = 0.0939 (for all data). Crystal data for **2**: monoclinic, space group *P2₁/c*, *a* = 10.4291(9) Å, *b* = 6.0983(5) Å, *c* = 15.2762(13) Å, β = 106.992(2)°, *V* = 929.15(14) Å³, *Z* = 4, ρ_{calcd} = 3.030 g cm⁻³, (Mo K α) = 45.88 cm⁻¹. *R*₁ = 0.0220, *wR*₂ = 0.0508 (for all data). Crystal data for **3**: monoclinic, space group *P2₁/c*, *a* = 10.523(6) Å, *b* = 11.065(8) Å, *c* = 8.061(4) Å, β = 94.643(12)°, *V* = 935.5(10) Å³, *Z* = 4, ρ_{calcd} = 3.010 g cm⁻³, (Mo K α) = 45.57 cm⁻¹. *R*₁ = 0.0211, *wR*₂ = 0.0725 (for all data).
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