



Hydrothermal syntheses and anion-induced structural transformation of three Cadmium phosphonates



Han Hu, Fupeng Zhai, Xiaofeng Liu, Yun Ling, Zhenxia Chen*, Yaming Zhou

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, PR China

ARTICLE INFO

Keywords:

Metal phosphonate
Structure
Anion-induced transformation

ABSTRACT

Three cadmium phosphonate coordinated polymers, namely as $[\text{Cd}_5(\text{ptz})_3(\text{SO}_4)_2(5\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$ (**Cdptz-1**), $[\text{Cd}_3(\text{ptz})_2(\text{Cl})_2(4\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (**Cdptz-2**) and $[\text{Cd}_4(\text{ptz})_2(\text{SO}_4)(\text{Cl})(\text{OH})\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$ (**Cdptz-3**) have been hydrothermally synthesized using 4-(1,2,4-triazol-4-yl)phenylphosphonic acid (H_2ptz) as ligand. Single crystal X-ray analyses revealed **Cdptz-2** as layered structure and **Cdptz-1,3** as pillar-layered structures with Cl^- or SO_4^{2-} as bridging anions. Due to the weak bonding between metal and anions, **Cdptz-1** and **2** can reversibly convert into each other by simple immersing in the corresponding solution at room temperature. While the transformations between **Cdptz-1,2** and **Cdptz-3** can only happen under hydrothermal condition. The causes for the transformation involve the metal-ligand bond breaking/formation, replacement of anions and enhancement/decrement of the network dimensionality.

1. Introduction

Metal phosphonates frameworks (MPFs) have received great interests due to the applications on gas sorption [1–3], catalysis [4–6], fluorescence [7–9], proton conductivity [10–12] and ion exchange [13]. Compared with other conventional metal-organic frameworks (MOFs), such as metal carboxylate [14,15] and metal imidazolate [16,17], they show multiple coordination modes and high thermal and chemical stabilities [18–20]. Syntheses of MOFs can be influenced by many synthetic factors such as temperature [21,22], solvent [23], pH values [24] and the impact of anions [25,26]. The choice of anions, which can serve as bridging linkers as building block to adjust the coordination geometry [27,28] or serve as anionic templates that occupy void spaces [29], will have great effects on the structures. The uses of coordinative anions, such as Cl^- and SO_4^{2-} , also benefit for the research about single-crystal-to-single-crystal (SCSC) transformation due to their exchangeable properties [30,31]. Although there have been several researches on anion induced crystal transformation among Cd-based MOFs [32,33], such structural transformation is relatively rare in the phosphonate MOFs. It would provide great help for us to understand the chemical bonding, the crystal growth mechanism and the stability about phosphonate chemistry. Herein, three Cd phosphonates were hydrothermally synthesized through regulating anionic species. The structural transformations were investigated under the anion control; showing **Cdptz-1** and **Cdptz-2** can mutual transform at room

temperature and convert into **Cdptz-3** under hydrothermal conditions. We also studied the thermal behaviors and fluorescence properties of these three compounds.

2. Experiments

2.1. Materials and general methods

All reagents were purchased from commercial sources and used without further purification. FT-IR spectra (KBr pellets) were recorded on a Nicolet 470 FT-IR spectrometer in the range 4000–400 cm^{-1} . C, H and N elemental analyses were determined on the Elementar Vario EL III. The bulk crystal phase was confirmed by powder X-ray diffraction collected on a Bruker D8 powder diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Variable temperature powder X-ray diffraction (VT-PXRD) of the bulk crystals were also collected on a Bruker D8 powder diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Thermal analyses were carried out on a TGA/SDTA 851 thermoanalyzer in the temperature range of 25–800 $^\circ\text{C}$ under N_2 flow at a heating rate of 10 $^\circ\text{C min}^{-1}$. The luminescence analyses were performed on a Hitachi F-4500 spectrofluorometer in the solid state at room temperature.

2.2. Single-crystal X-ray crystallographic study

Crystal structures determination of **Cdptz-1 ~ 3** were performed

* Corresponding author.

E-mail address: zhxchen@fudan.edu.cn (Z. Chen).

Table 1
Crystallographic data of **Cdptz-1-3**.

Code	Cdptz-1	Cdptz-2	Cdptz-3
formula	C ₂₄ H ₄₀ N ₉ Cd ₅ O ₂₈ P ₃ S ₂	C ₁₆ H ₂₄ N ₆ Cd ₃ O ₁₂ P ₂ Cl ₂	C ₁₆ H ₁₇ N ₆ Cd ₄ O ₁₃ P ₂ SCl
formula weight	1621.68	962.45	1080.41
crystal system	Orthorhombic	Triclinic	Monoclinic
space group	<i>Pnma</i>	<i>P-1</i>	<i>P2₁c</i>
a (Å)	23.712(8)	7.7388(10)	6.883(2)
b (Å)	19.929(7)	9.3438(12)	24.234(8)
c (Å)	9.450(4)	9.9987(13)	15.962(5)
α (deg.)	90	91.086(2)	90
β (deg.)	90	102.024(2)	97.404(4)
γ (deg.)	90	109.678(2)	90
V (Å ³)	4466(3)	662.72(15)	2640.1(15)
Z	4	1	4
ρ _{Cacl} (g/cm ³)	2.412	2.412	2.718
μ (mm ⁻¹)	2.650	2.780	3.558
F(000)	3152	466	2056
Collected/Unique	17682 / 4055	4040 / 2340	12748 / 4600
R _{int}	0.1047	0.0206	0.0708
GOF on F ²	1.229	0.999	0.996
R1(I > 2σ (I))	0.0824	0.0328	0.0474
wR ₂ (all data)	0.1915	0.1742	0.2133
Δρ _{max} , Δρ _{min} (e/Å ³)	2.909, -1.767	1.619, -1.584	1.582, -1.084

on a Bruker Smart APEX diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA at 293 K. A hemisphere of intensity data were collected at room temperature with a scan width of 0.60° in ω. Empirical absorption correction was based on SADABS program. The structures were solved by direct methods and refined using full-matrix least-squares treatment (SHELXTL) with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms were theoretically added. CCDC-1579792 (**1**), 1579790 (**2**), 1579791 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. The detailed crystallographic data are shown in Table 1. Selected bond lengths and angles are listed in Tables S1-S3.

2.3. Synthesis of [Cd₅(ptz)₃(SO₄)₂(5H₂O)]·6H₂O (**Cdptz-1**)

A mixture of CdSO₄·8/3H₂O (0.128 g, 0.5 mmol), H₂ptz (0.068 g, 0.3 mmol), trimethylamine (0.125 g, 1.2 mmol) and deionized water (10 mL) was stirred at room temperature for 1 h and transferred into a 15 mL Teflon-lined stainless steel autoclave. The mixture was then heated at 180 °C for 24 h, followed by cooling down to room temperature. As a result, 0.072 g colourless crystals were obtained after filtration, washing and drying. Yield: 44% (based on H₂ptz). Elemental analysis calculated for Cd₅C₂₄H₄₀N₉O₂₈P₃S₂ (1621.72): C, 17.77%; H, 2.49%; N, 7.77%. Found: C, 17.69%; H, 2.57%; N, 7.82%. IR (KBr, cm⁻¹) 3547 (w), 3417(b), 3133 (w), 3104 (w), 1603 (m), 1537 (s), 1419 (w), 1325 (w), 1293 (w), 1266 (w), 1235 (w), 1177 (m), 1120 (w), 1089 (w), 1046 (w), 992(m), 971 (m), 942 (m), 895(w), 828 (m), 747 (m), 649 (w), 616 (s), 556 (m), 454 (w).

2.4. Synthesis of [Cd₃(ptz)₂(Cl)₂(4H₂O)]·2H₂O (**Cdptz-2**)

A mixture of CdCl₂·5/2H₂O (0.069 g, 0.3 mmol), H₂ptz (0.046 g, 0.2 mmol), trimethylamine (0.101 g, 1 mmol) and deionized water (10 mL) was stirred at room temperature for 1 h and transferred in a 15 mL Teflon-lined stainless steel autoclave. The mixture was then heated at 180 °C for 24 h, followed by cooling down to room temperature. As a result, 0.032 g colourless crystals with yield of 32% (based on H₂ptz) were obtained after filtration. Elemental analysis calculated for Cd₃C₁₆H₂₄N₆O₁₂P₂Cl₂ (962.48): C, 19.97%; H, 2.51%; N, 8.73%. Found: C, 19.89%; H, 2.58%; N, 8.82%. IR (KBr, cm⁻¹) 3549 (w), 3412 (b), 3115 (w),

1609(m), 1547 (s), 1416 (w), 1330 (w), 1295 (w), 1255 (m), 1222 (w), 1135 (m), 1086 (s), 1036 (s), 991(w), 958 (s), 834 (w), 748 (m), 649 (w), 592 (m), 558 (w), 454 (w).

2.5. Synthesis of [Cd₄(ptz)₂(SO₄)(Cl)(OH)H₂O]·H₂O (**Cdptz-3**)

A mixture of CdSO₄·8/3H₂O (0.103 g, 0.4 mmol), H₂ptz (0.046 g, 0.2 mmol), trimethylamine (0.101 g, 1 mmol), KCl (0.008 g, 0.1 mmol) and deionized water (10 mL) was stirred at room temperature for 1 h and transferred in a 15 mL Teflon-lined stainless steel autoclave. The mixture was then heated at 180 °C for 24 h, followed by cooling down to room temperature. 0.062 mg colourless flake crystals were obtained after filtration with yield of 57%, based on H₂ptz. Elemental analysis calculated for Cd₄C₁₆H₁₇N₆O₁₃P₂SCl (1080.45): C, 17.79%; H, 1.59%; N, 7.78%. Found: C, 17.72%; H, 1.65%; N, 7.83%. IR (KBr, cm⁻¹) 3547 (w), 3418 (b), 3340 (w), 3106 (w), 1603 (m), 1537 (s), 1419 (w), 1326 (w), 1294(w), 1264 (w), 1235 (w), 1176 (m), 1120 (w), 1089 (w), 1046 (w), 971 (m), 895 (w), 829 (m), 747 (m), 650 (w), 614 (s), 557 (m), 453 (w).

2.6. Reversible transformations between **Cdptz-1** and **2**

Powder of **Cdptz-1** (100 mg) was soaked in the solution of 0.1 M HCl and triethylamine was used to regulate pH value to 7. The mixture was stirred for 12 h at room temperature. The product after filtration was conformed as **Cdptz-2** by powder X-Ray diffraction (PXRD) pattern. Powder of **Cdptz-2** (100 mg) was soaked in mixture of 0.1 M H₂SO₄ and trimethylamine and the pH value of this solution is 7. The mixture was stirred for 12 h at room temperature. The product after filtration was conformed as **Cdptz-1** by PXRD pattern.

2.7. Transformations from **Cdptz-1**~**2** to **3**

Powder of **Cdptz-1** (100 mg) and **Cdptz-2** (100 mg) was soaked in the solution of 0.1 M HCl and H₂SO₄ respectively, and then the solution was regulated by trimethylamine until pH value is 7. The mixture was then sealed in a 15 mL Teflon-lined stainless steel autoclave, heated at 180 °C for 24 h and cooled down slowly to room temperature. Both product after filtration were conformed as **Cdptz-3** by PXRD pattern.

Download English Version:

<https://daneshyari.com/en/article/7757755>

Download Persian Version:

<https://daneshyari.com/article/7757755>

[Daneshyari.com](https://daneshyari.com)