



Two novel metal–organic coordination polymers based on diphosphonate and oxalate: Synthesis, structures and properties



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ABSTRACT

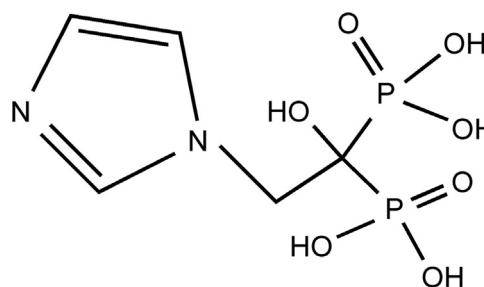
Two 2-(1-imidazole)-1-hydroxyl-1,1'-ethylidenediphosphonate and oxalic acid bridged coordination polymers $(\text{H}_2\text{en})[\text{Co}_3(\text{H}_2\text{zdn})_2(\text{ox})(\text{H}_2\text{O})_2]$ (**1**) and $\text{Cd}_2(\text{H}_2\text{zdn})(\text{ox})_{0.5}(\text{H}_2\text{O})$ (**2**) (2-(1-imidazole)-1-hydroxyl-1,1'-ethylidenediphosphonic acid = H_5zdn ; oxalic acid = H_2ox) were synthesized under hydrothermal conditions and characterized by the infrared (IR), thermogravimetric analyses (TGA), elemental analyses (EA) and X-ray diffraction (XRD). Compound **1** is bridged by phosphonate anions to 1D chain, and further linked by oxalate anions to 2D layer. Compound **2** is bridged by O–P–O units of H_5zdn to the layer, and then pillared by oxalate anions to generate 3D frameworks. Compound **1** shows anti-ferromagnetic behaviors analyzed with the temperature-dependent zero-field ac magnetic susceptibilities, while compound **2** exhibits an influence on the luminescent property.

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1. Introduction

Metal organic coordination polymers have been developed extremely rapidly over the past decade due to their intriguing network topologies and promising applications in many aspects such as catalysis, luminescence, gas storage, selective adsorption and magnetic devices [1,2]. In order to construct unusual coordination polymers with high connectivity, desired structural motifs and expected properties, the utilization of diverse bridging ligands have proved to be a feasible method. As compared with the fruitful reports of such materials based on carboxylic acids [3], the assembly of bisphosphonic acids coordination networks have attracted an upsurge of interest in recent years. As multidentate ligands, bisphosphonates (BPs) with three oxygen atoms of phosphonate groups can facily chelate transition metal ions to form diverse structure characteristic. Also, such bisphosphonates ligands have multiple protonated groups which can be fully or partially deprotonated and its various bridging abilities and strong coordination tendency with transition metals to form different topological networks. Therefore, considerable efforts have been focused on metal phosphonates with their novel architectures as well as the potential applications [4]. As the third-generation bisphosphonate, the zoledronic acid is the most representative material in those bisphosphonate ligands, and the most important is that the structure of zoledronic acid contains nitrogen atoms, which can contribute to coordinate with the

metal atoms. To date, a number of metal diphosphonates based on zoledronate has been prepared, especially cobalt and copper salts [5]. However, to the best of our knowledge, the complexes which were assembled together by zoledronate and the other negative ions have not been reported. It should to be noted that the choice of negative ions are generally carboxylic ions, sulfonic ions, or oxalate anions, because such anions can act as pillars to construct coordination polymers. Therefore, such synthetic method has been found to be an effective approach to build fascinating structures [6,7]. In present work, we employed zoledronic acid (Scheme 1) as the basic unit and another auxiliary anion oxalic acid (H_2ox) with metal salts to extend the framework, successfully obtained two coordination polymers $(\text{H}_2\text{en})[\text{Co}_3(\text{H}_2\text{zdn})_2(\text{ox})(\text{H}_2\text{O})_2]$ (**1**) and $\text{Cd}_2(\text{H}_2\text{zdn})(\text{ox})_{0.5}(\text{H}_2\text{O})$ (**2**).



Scheme 1. The structure of the zoledronic acid (H_5zdn).

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2. Experimental section

2.1. Materials

All chemicals of reagent grade were commercially available and used without further purification.

2.2. Physical methods

Powder X-ray diffraction measurements were carried out with a Bruker D8 Focus X-ray diffractometer to check the phase purity. The C, N and H microanalyses were performed with a Perkin Elmer 2400II elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. Thermogravimetric measurement was performed under a flow of nitrogen gas from room temperature to 1000 °C at a heating rate of 10 °C/min using a Seiko Exstar 6000 TG/DTA 6300 apparatus. Single crystal X-ray diffraction data were collected by a Rigaku R-Axis Rapid X-ray diffractometer. Photo-luminescence properties were investigated in solid state at room temperature with an F-7000 FL spectrophotometer. Magnetic susceptibility datas for **1** were determined with a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made for the sample holder and the compound estimated from Pascal's constants [8].

2.3. Synthesis of $(\text{H}_2\text{en})[\text{Co}_3(\text{H}_2\text{zdn})_2(\text{ox})(\text{H}_2\text{O})_2]$ (**1**)

A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.249 g, 1 mmol), $\text{H}_5\text{zdn} \cdot \text{H}_2\text{O}$ (0.290 g, 1 mmol) and $\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$ (0.126 g, 1 mmol) in 8 mL of H_2O , adjusted to a pH of 5 with ethylenediamine, was stirred for about 0.5 h at room temperature, sealed in a 23 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 3 days under autogenous pressure. After the mixture was cooled slowly to room temperature, red block crystals were filtered off and dried at room temperature. Yield 78% (based on Co). Anal. calc. for $\text{C}_{14}\text{H}_{28}\text{Co}_3\text{N}_6\text{O}_{20}\text{P}_4$: C, 18.66; H, 3.13; N, 9.33. Found: C, 18.62; H, 3.10; N, 9.29. IR (KBr, cm^{-1}): 3303(w), 3173(m), 3104(m), 3011(m), 2943(w), 2620(m), 2545(w), 2483(w), 1656(s), 2627(s), 1551(m), 1464(w), 1302(m), 1302(m), 1183(s), 956(m), 892(m), 829(m), 799(m), 724(w), 681(w), 638(w), 613(m), 529(s), 519(s), 470(m), 439(w).

2.4. Synthesis of $\text{Cd}_2(\text{H}_2\text{zdn})(\text{ox})_{0.5}(\text{H}_2\text{O})$ (**2**)

A mixture of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (0.384 g, 0.5 mmol), $\text{H}_5\text{zdn} \cdot \text{H}_2\text{O}$ (0.058 g, 0.2 mmol) and $\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$ (0.126 g, 1 mmol) in 8 mL of H_2O , adjusted to a pH of 6 with ethylenediamine, was stirred for about 0.5 h at room temperature, sealed in a 23 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 3 days under autogenous pressure. After the mixture was cooled slowly to room temperature, colorless block crystals were filtered off and dried at room temperature. Yield 85% (based on Cd). Anal. calc. for $\text{C}_6\text{H}_9\text{Cd}_2\text{N}_2\text{O}_{10}\text{P}_2$: C, 13.01; H, 1.27; N, 5.06. Found: C, 12.97; H, 1.23; N, 5.01. IR (KBr, cm^{-1}): 3440(v), 3156(m), 3125(m), 3002(m), 2959(w), 2817(m), 2601(w), 1627(s), 1571(m), 1442(w), 1318(m), 1158(s), 974(m), 832(m), 795(m), 671(w), 647(w), 585(s), 523(s), 480(m), 437(w).

2.5. X-ray crystallography

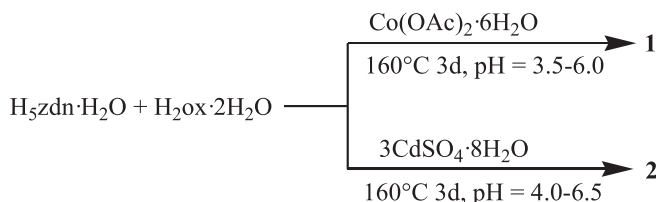
Suitable single crystals were selected under a polarizing microscope and fixed with epoxy cement on respective fine glass fibers which were then mounted on a Rigaku R-Axis Rapid diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($=0.71073 \text{ \AA}$) for cell determination and subsequent data collection. The reflection intensities in the suitable θ ranges were collected at 293 K using the scan technique. The employed single crystals exhibit no detectable decay

during the data collection. The data were corrected for L_p and absorption effects. The SHELXS-97 and SHELXL-97 program [9,10] are used for structure solution and refinement. All structures were solved by direct methods and all non-hydrogen atoms to be located in the subsequent difference Fourier syntheses. After several cycles of refinement, all hydrogen atoms associated with carbon atoms are geometrically generated, and the rest of the hydrogen atoms are located in the successive difference Fourier syntheses. Finally, all non-hydrogen atoms are refined with anisotropic displacement parameters by the full-matrix least-squares technique and hydrogen atoms with isotropic displacement parameters set to 1.2 times of the values for the associated heavier atoms. Detailed information about the crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are given in Tables 2 and 3.

3. Results and discussion

3.1. Syntheses

Compounds **1** and **2** were prepared by hydrothermal method with $\text{H}_5\text{zdn} \cdot \text{H}_2\text{O}$, oxalic acid and the corresponding metal salts at 160 °C for 3 days. It was found that the value of pH with mixture, metal/ligand molar ratio, and the metal source play key roles about the formation of the final products. Compound **1** can be prepared as pure phase at 160 °C, pH of 3.5–6.0, and with the $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}/\text{H}_5\text{zdn} \cdot \text{H}_2\text{O}/\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$ molar ratio of 1:1: (0.8–1.2). Compound **2** can be obtained at 160 °C with the pH in the range of 4.0–6.5 and the molar ratio $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}/\text{H}_5\text{zdn} \cdot \text{H}_2\text{O}/\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}=5:2: (2.0-10.0)$. Along with the increase of the amount of oxalic acid, the yield increases to 85% without precipitation, thus the best mole ratio is $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}/\text{H}_5\text{zdn} \cdot \text{H}_2\text{O}/\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}=5:2:10$. Moreover, if we use $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ as the starting material in preparing **1**, or $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in preparing **2**, large amounts of the floccules-like materials would be obtained. The corresponding reaction can be formulated as follows:



Upon exposure to air, crystals of **1** and **2** retain their crystallinity and luster for a longer time, suggesting them to be air-stable. Product purities were checked by PXRD, and the experimental and simulated PXRD patterns are shown in Fig. S1 Supplementary material. The peak positions in the experimental and simulated patterns are in agreement, indicating good phase purity.

3.2. Description of the crystal Structures.

3.2.1. Crystal structure of $(\text{H}_2\text{en})[\text{Co}_3(\text{H}_2\text{zdn})_2(\text{ox})(\text{H}_2\text{O})_2]$ **1**

Compound **1** crystallizes in triclinic space group $P\bar{1}$. The asymmetric unit contains one and a half Co(II) atoms (namely Co1 and Co2), one $\text{H}_2\text{zdn}^{3-}$ anion, half of an oxalate anion, one coordinated water molecule and half a protonated ethanediamine (Fig. 1). The crystallographically distinct cobalt anions are centered at the Wyck-off 1e and 2i sites, respectively, and exhibit six coordination behaviors. The $\text{H}_2\text{zdn}^{3-}$ ion can be described as a hexadentate bridging mode, which chelates with two different Co centers (Co1, Co2) via four phosphonate oxygen atoms (O1, O2, O4 and O5) and one hydroxyl oxygen atom (O7), and bridges another Co2 atom through the phosphonate oxygen atom (O3). The P–O distances are

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