



Alkali/alkaline earth metal and solvents-regulated construction of novel heterometallic coordination polymers based on a semirigid ligand and tetranuclear metal clusters



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ABSTRACT

Five novel three-dimensional (3D) heterometallic coordination polymers, [ZnCa(dcppa)(DMF)₂]_n (**1**), [ZnCa(dcppa)(DMA)₂]_n (**2**), [ZnBa(dcppa)(DMF)₂]_n (**3**), [ZnBa(dcppa)(DMA)₂]_n (**4**), and [ZnNa(dcppa)(DMF)]_n·n(Me₂NH₂)·n(H₂O)₂ (**5**) (Me₂NH₂⁺ = dimethylammonium cation; DMA = N,N-dimethylacetamide; DMF = N,N-dimethylformamide; H₄dcppa = 3-(3',5'-dicarboxylphenoxy) phthalic acid), have been hydrothermally synthesized and structurally characterized with the aid of single-crystal X-ray diffraction. Complexes **1–5** are heterometallic Zn/M (M = Ca, Ba, Na) coordination polymers constructed from a semirigid H₄dcppa ligand and tetranuclear metal clusters. Topological analyses show that **1/3/4** and **2/5** exhibit complicated 3D framework that could be simplified into binodal (3,6)-connected **rtf** nets and binodal (3,6)-connected **flu** nets, respectively. Unlike **1–4**, **5** features a unique 3D anionic framework with Me₂NH₂⁺ cations occupying the voids. From the viewpoint of crystal structure diversity and comparison, our results further prove that the coordination modes of metal ions and ligands play indispensable roles in the construction of the final crystal structure. Moreover, the thermal stability and solid-state luminescence properties of **1–5** have also been investigated at room temperature.

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1. Introduction

In recent years, the design and self-assembly synthesis of coordination polymers (CPs) or metal-organic frameworks (MOFs) have attracted great interest due to their fascinating architectures and various functional properties such as luminescence, gas storage, ion-exchange, heterogeneous catalysis, and porous materials [1–13]. These CPs or MOFs can be rapidly and efficiently synthesized from relatively simple subunits, where the kind of metal ions, geometry, and number of coordination sites provided by organic ligands are all significant parameters for directing the self-assembly processes [4]. The rational design and reasonable use of the characteristic ligand is very important in the construction of desired CPs or MOFs [4]. It is well known that polycarboxylate groups are excellent building blocks for the construction of CPs or MOFs because they may induce core aggregation and link these discrete clusters into an extended framework by virtue of its bridging ability [14–19]. Compared with rigid aromatic ligands, semi-

rigid polycarboxylate ligands enable the formation of uncommon frameworks or even novel topologies and interesting properties because of their flexibility and conformational diversity [20–26].

With the above consideration, a new semirigid polycarboxylate ligand, 3-(3',5'-dicarboxylphenoxy) phthalic acid (H₄dcppa) has been selected to construct novel CPs. The H₄dcppa ligand possesses the following features: (1) two rigid benzene rings of H₄dcppa ligand are connected by a rotatable –O– group, which allows the ligand with subtle conformational adaptation; (2) eight potential coordination sites of H₄dcppa ligand, which can provide more varied coordinating patterns in the construction of fascinating coordination frameworks, especially with high dimensionalities. However, the organic frameworks constructed from the H₄dcppa ligand, especially its assembly with two different metal atoms, have not been reported. Therefore, there is still a great challenge to synthesize heterometallic H₄dcppa complexes, and further research is necessary to enrich and develop this field. In order to synthesize novel heterometallic H₄dcppa complexes, the reactions of H₄dcppa ligand and d¹⁰ metal with alkali/alkaline earth metal were carried out under solvothermal conditions. In this paper, five novel heterometallic coordination polymers, [ZnCa(L)(DMF)₂]_n (**1**),

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[ZnCa(L)(DMA)₂]_n (**2**), [ZnBa(L)(DMF)₂]_n (**3**), [ZnBa(L)(DMA)₂]_n (**4**), [ZnNa(L)(DMF)]_n·n(Me₂NH₂)·n(H₂O)₂ (**5**) (Me₂NH₂⁺ = dimethylammonium cation; DMA = N,N-dimethylacetamide; DMF = N,N-dimethylformamide) have been synthesized. The synthesis, crystal structures, thermal stabilities and luminescent properties of these complexes have been studied extensively.

2. Experimental

2.1. Materials and methods

The metal salts, organic ligand and solvents for synthesis and analysis were of analytical grade and obtained from commercial sources without further purification. All complexes were synthesized in 23 ml polytetrafluoroethylene glass containers under autogenous pressure. Elemental analyses of carbon, hydrogen and nitrogen were performed on an EA1110 CHNS-O CE elemental analyzer. FT-IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT-IR spectrometer in the range of 400–4000 cm⁻¹. Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) with a scan speed of 5°/min. TG data were collected at a heating rate of 10 °C/min on a NETSCHZ STA-449C thermal analyzer in the temperature range 20–800 °C under nitrogen atmosphere. The luminescence spectra were measured at 293 K with an Edinburgh FLS920 TCSPC luminescence spectrophotometer.

2.2. Syntheses of complexes

2.2.1. [ZnCa(dcppa)(DMF)₂]_n (**1**)

The starting materials of Zn(NO₃)₂·6H₂O (0.030 g, 0.10 mmol), Ca(NO₃)₂·4H₂O (0.024 g, 0.10 mmol) and 3-(3',5'-dicarboxylphenoxy) phthalic acid (H₄dcppa) (0.035 g, 0.10 mmol) were added in 23 ml polytetrafluoroethylene glass container. 2 ml DMF and 1 ml H₂O were then added. The resulting mixture was stirred for 10 min at room temperature, and then the mixture was sealed and kept at 110 °C for three days, and then cooled naturally to the room temperature. Colorless rod crystals suitable for single-crystal X-ray diffraction were obtained by filtration, washed several times with DMF/H₂O (v/v = 2/1), and then dried in air at ambient temperature. Yield: 67% (based on H₄dcppa). *Anal.* Calc. for C₂₂H₂₀CaN₂O₁₁Zn (593.87): C, 44.49; H, 3.39; N, 4.72. Found: C, 44.47; H, 3.36; N, 4.75%. IR (KBr pellet, cm⁻¹): 3435 (m), 2421 (w), 1598 (s), 1487 (s), 1342 (s), 1297 (s), 1203 (m), 1135 (w), 996 (w), 920 (s), 878 (s), 814 (m), 782 (w), 716 (w), 675 (w).

2.2.2. [ZnCa(dcppa)(DMA)₂]_n (**2**)

The reaction was carried out in a procedure similar to that for **1** except that 2 ml DMF and 1 ml H₂O were replaced by 1 ml DMA and 2 ml H₂O. Colorless rod crystals suitable for single-crystal X-ray diffraction were obtained by filtration, washed several times with DMA/H₂O (v/v = 1/2), and then dried in air at ambient temperature. Yield: 65% (based on H₄dcppa). *Anal.* Calc. for C₄₈H₄₁Ca₂N₄O₂₂Zn₂ (1236.7855): C, 46.62; H, 3.34; N, 4.53. Found: C, 46.61; H, 3.36; N, 4.51%. IR (KBr pellet, cm⁻¹): 3442 (m), 2430 (w), 1600 (s), 1490 (s), 1344 (s), 1302 (s), 1208 (m), 1148 (w), 999 (w), 923 (s), 888 (s), 819 (m), 787 (w), 721 (w), 675 (w).

2.2.3. [ZnBa(dcppa)(DMF)₂]_n (**3**)

The reaction was carried out in a procedure similar to that for **1** except that Ca(NO₃)₂·4H₂O (0.024 g, 0.10 mmol) was replaced by Ba(NO₃)₂ (0.026 g, 0.10 mmol). Colorless prism crystals suitable for single-crystal X-ray diffraction were obtained by filtration, washed several times with DMF/H₂O (v/v = 2/1), and then dried in air at ambient temperature. Yield: 71% (based on H₄dcppa). *Anal.*

Calc. for C₄₃H₃₆Ba₂N₄O₂₂Zn₂ (1366.20): C, 37.80; H, 2.66; N, 4.10. Found: C, 37.79; H, 2.68; N, 4.12%. IR (KBr pellet, cm⁻¹): 3455 (m), 2432 (w), 1605 (s), 1497 (s), 1352 (s), 1304 (s), 1213 (m), 1145 (m), 1005 (w), 928 (s), 891 (s), 825 (m), 794 (w), 722 (w), 680 (w).

2.2.4. [ZnBa(dcppa)(DMA)₂]_n (**4**)

The reaction was carried out in a procedure similar to that for **2** except that Ca(NO₃)₂·4H₂O (0.024 g, 0.10 mmol) was replaced by Ba(NO₃)₂ (0.026 g, 0.10 mmol). Colorless prism crystals suitable for single-crystal X-ray diffraction were obtained by filtration, washed several times with DMA/H₂O (v/v = 1/2), and then dried in air at ambient temperature. Yield: 68% (based on H₄dcppa). *Anal.* Calc. for C₂₄H₂₄BaN₂O₁₁Zn (719.16): C, 40.08; H, 3.36; N, 3.90. Found: C, 40.09; H, 3.35; N, 3.89%. IR (KBr pellet, cm⁻¹): 3457 (m), 2434 (w), 1608 (s), 1499(s), 1356 (s), 1308 (s), 1215 (m), 1148 (m), 1007 (w), 929 (s), 893 (s), 834 (m), 800 (w), 725 (w), 682 (w).

2.2.5. [ZnNa(dcppa)(DMF)]_n·n(Me₂NH₂)·n(H₂O)₂ (**5**)

The reaction was carried out in a procedure similar to that for **1** except that Ca(NO₃)₂·4H₂O (0.024 g, 0.10 mmol) was replaced by NaNO₃ (0.010 g, 0.10 mmol). Colorless block crystals suitable for single-crystal X-ray diffraction were obtained by filtration, washed several times with DMF/H₂O (v/v = 2/1), and then dried in air at ambient temperature. Yield: 60% (based on H₄dcppa). *Anal.* Calc. for C₄₂H₅₀N₄Na₂O₂₃Zn₂ (1155.624): C, 43.65; H, 4.36; N, 4.85. Found: C, 43.63; H, 4.34; N, 4.88%. IR (KBr pellet, cm⁻¹): 3430 (m), 2417 (w), 1596 (s), 1484 (s), 1340 (s), 1292 (s), 1201 (m), 1134 (w), 990 (w), 914 (s), 875 (s), 812 (m), 781 (w), 710 (w), 674 (w).

2.3. X-ray crystallography

After carefully collected under an optical microscope, suitable single crystals of **1–5** were glued to thin glass fibers. The X-ray intensity data for **1–5** were collected on a computer-controlled Oxford Xcalibur E diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at T = 293(2) K. All absorption corrections were applied using the SADABS program [27]. The structures were solved by the direct method and refined by full-matrix least-squares methods on F² by using the SHELX-97 program package [28]. All non-hydrogen atoms were refined anisotropically except some badly disordered atoms and some solvent molecules. The hydrogen atoms bound to carbon were generated by geometrical calculations and their positions and thermal parameters were fixed during the structure refinement. The details of crystallographic parameters, data collection and refinements for the complexes are listed in Table 1. Moreover, selected bond lengths and angles with their estimated standard deviations are listed in Table S1 (Supporting information).

3. Result and discussion

3.1. Synthesis

Solvothermal method was employed to synthesize the goal complexes in this work rather than conventional solution method. Solvothermal reactions, which can enhance the solubility of the organic ligand and the reaction pressure, were generally carried out in Teflon bombs under autogenous pressure. The one-pot mixture was heated to an appropriate temperature and held for 60–72 h and then cooled to the room temperature. Complexes **1–5** reported here were obtained in high yield from the simple combination of H₄dcppa ligand, d¹⁰ metal and alkali/alkaline earth metal

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