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The diversity of five metal–organic complexes based on an unsymmetrical biphenyl tetracarboxylate: Synthesis, structures, magnetism and luminescence

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ABSTRACT

Careful investigation of the effects of metal ions and pH value resulted in five multi-dimensional metal–organic complexes, $[Co_5(\mu_3\text{-}OH)_2(\alpha\text{-bptc})_2(H_2O)_6]_n$ (**1**), $\{(H_3O)_2[Co_4(\mu_3\text{-}O)(\alpha\text{-bptc})_2(H_2O)]\cdot 4H_2O\}_n$ (**2**), $\{K_2[Zn_4(\mu_3\text{-}OH)_2(\alpha\text{-bptc})_2(H_2O)_3]\}_n$ (**3**), $[Zn_4(\alpha\text{-bptc})_2(H_2O)_3]_n$ (**4**), and $\{[Cd_4(\alpha\text{-bptc})_2(H_2O)_7]\cdot 2H_2O\}_n$ (**5**) (α-H_4bptc = 2,3,3′,4′-biphenyl tetracarboxylic acid). The complexes consisted of different highly connected secondary building units (SBUs) assembled *via* hydrothermal *in situ* routes. The pH value as well as the kinds of metal ions influenced the coordination modes of α-H_4bptc and also introduced the hydroxyl ligand at high pH value, resulting in the diversity of SBUs and dimensionality. Variable temperature magnetic measurements indicated the antiferromagnetic behavior in the Co_5 core in **1**, and the intra-chain ferrimagnetic behavior in complex **2**. Moreover, the luminescent properties of the complexes **3**–**5** indicated the existence of intra-ligand charge transfer.

1. Introduction

In recent years, the rational design and construction of coordination polymers (CPs) composed of metal nodes and bridging linkers have attracted considerable attention due to their unique structures and potential applications in gas absorption and separation [1], luminescence [2], catalysis [3], sensors [4], delivery [5], and so on. Among various synthetic strategies, utilizing the diversity of polynuclear secondary building units (SBUs) is one of the most efficient ways to construct CPs rationally [6]. Suitable selection of SBUs not only has a significant impact on the topology and stability of CPs, but also provides functional properties that may contribute to the whole framework [7]. However, it is still a challenge to rationally synthesize CPs bearing desired SBUs, because even a minor change in reaction conditions will lead to completely different SBUs, such as coordination geometries of the central metals, configurations, and nature of the organic ligands [8], as well as some external factors, such as solvent, temperature, pH value, template effect, etc. [9].

The most important factor is the selection of organic ligands. Compared to common organic ligands, multifunctional carboxylic acid ligands which display multiple coordination sites could connect more than one metal to form prospective SBUs and sequentially expand the dimension of CPs [10]. Numerous structurally diverse polycarboxylate-based CPs have been constructed and their properties have been researched systematically, such as the CPs based on 1,4-benzenedicarboxylic acid, [11] benzene-1,3,5-tricarboxylic acid, [12] 3,4′,5-biphenyltricarboxylic acid, [13] 3,3′,5,5′-biphenyltetracarboxylic acid [14], 3,3′,4,4′-biphenyltetracarboxylic acid [15] and so on. The specific forms of polycarboxylate ligands are highly dependent on the reaction conditions, which are affected by the degree of protonation of the carboxylic group and therefore their coordination mode [16]. Although a large number of polycarboxylate-based CPs have been synthesized, systematic investigations of physical or chemical stimuli effects on the structures of these CPs are rare [17]. Thus, much effort must be invested in further investigating the self-assembly processes.

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We have been working on CPs constructed by aromatic polycarboxylate ligands [18]. In our previous work, we have shown the pH [19] and template effects [20] on the structures of a series of polycarboxylate-based coordination polymers prepared by the solvothermal method. In this work, we employed an unsymmetrical tetracarboxylate ligand 2,3,3′,4′-biphenyl tetracarboxylic acid (α-H_4bptc) as the organic linker, which has the following unique structural features: a) the coordination sites are more concentrated which can be beneficial to construct polynuclear SBUs. b) the two phenyl rings are severely twisted across the C–C single bond, and the skew coordination orientations of the carboxylate groups provide the potential formation of a helix. [21a] Up to now, the complexes based on α-H_4bptc ligands are less explored. [21–23]

In this paper, five new CPs $[Co_5(\mu_3\text{-}OH)_2(\alpha\text{-}bptc)_2(H_2O)_6]_n$ (**1**), $\{(H_3O)_2[Co_4(\mu_3\text{-}O)(\alpha\text{-}bptc)_2(H_2O)]\cdot 4H_2O\}_n$ (**2**), $\{K_2[Zn_4(\mu_3\text{-}OH)_2(\alpha\text{-}bptc)_2(H_2O)_3]\}_n$ (**3**), $[Zn_4(\alpha\text{-}bptc)_2(H_2O)_3]_n$ (**4**), and $\{[Cd_4(\alpha\text{-}bptc)_2(H_2O)_7]\cdot 2H_2O\}_n$ (**5**) synthesized under hydrothermal conditions are investigated. Details of the synthesis and characterization of these complexes are described. Furthermore, the thermal stability, luminescent properties and magnetic properties of the complexes are systematically studied.

2. Experimental

All reagents and solvents were of standard commercial grade and directly used without further purification. Infrared (IR) spectra were obtained on a BRUKER TENSOR27 spectrometer with KBr disks. Samples for elemental analysis experiments were dried under vacuum, and the analyses were performed with a CHN-O-Rapid instrument. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Magnetic susceptibility data were obtained with SQUID magnetometer (Quantum MPMS) in the temperature range 2.0–300 K by using an applied field of 1000 *Oe*. Thermal analyses (TA) were performed on a Dupont thermal analyzer under N_2 atmosphere with a heating rate of 20 K/min. Luminescence analyses were performed on a Varian Cary Eclipse luminescence spectrometer.

2.1. Synthesis of $[Co_5(\mu_3\text{-}OH)_2(\alpha\text{-}bptc)_2(H_2O)_6]_n$ (1)

A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.3 mmol, 0.0873 g), 2,2′-di(pyridin-2-yl)-[4,5′-biisoindoline]-1,1′,3,3′-tetraone (abbreviated as L1) (0.1 mmol, 0.0448 g), distilled water (6 mL) and KOH (0.7 mL, 0.5 mol/L) was placed in a Teflon lined vessel (17 mL) with constant stirring (pH = 7.0 after stirring for 30 min). The mixture was then sealed in a stainless steel container and heated under autogenous pressure at 433 K for 3 days. After cooling to room temperature, purple-red sheet-like crystals were obtained. Yield: 34% based on L1. Elemental analysis (EA) (%): calcd for $C_{32}H_{26}Co_5O_{24}$ (**1**): C 35.29; H 2.41. Found: C 35.51; H 2.31. IR (KBr, υ/cm^{-1}): 3404(s), 3130(m), 1589(vs), 1572(vs), 1543(s), 1475(vs), 1452(vs), 1425(m), 1402(s), 1373(m), 1218(s), 814(m), 783(m), 752(m), 466(m).

2.2. Synthesis of $\{(H_3O)_2[Co_4(\mu_3\text{-}O)(\alpha\text{-}bptc)_2(H_2O)]\cdot 4H_2O\}_n$ (2)

A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.2 mmol, 0.0582 g), L1 (0.1 mmol, 0.0448 g), distilled water (8 mL) and KOH (0.5 mL, 0.2 mol/L) was placed in a Teflon lined vessel (23 mL) with constant stirring (pH = 5.0 after stirring for 30 min). The mixture was then sealed in a stainless steel container and heated under autogenous pressure at 433 K for 3 days. After cooling to room temperature, pink rod-like crystals were obtained. Yield: 35% based on L1. EA (%): calcd for $C_{16}H_{14}Co_2O_{12}$ (**2**): C 37.23; H 2.73. Found: C 37.61; H 2.62. IR (KBr, υ/cm^{-1}): 3462(m), 3362(m), 3184(m), 1630(s), 1593(vs), 1553(vs), 1452(m), 1383(s), 1165(w), 821(w), 777(w), 748(w), 702(w), 685(w), 482(w).

2.3. Synthesis of $\{K_2[Zn_4(\mu_3\text{-}OH)_2(\alpha\text{-}bptc)_2(H_2O)_3]\}_n$ (3)

A mixture of $Zn(NO_3)_2\cdot 4H_2O$ (0.3 mmol, 0.0891 g), L1 (0.1 mmol, 0.0448 g), distilled water (6 mL) and KOH (1.0 mL, 0.5 mol/L) was placed in a Teflon lined vessel (17 mL) with constant stirring (pH = 7.5 after stirring for 30 min). The mixture was then sealed in a stainless steel container and heated under autogenous pressure at 433 K for 3 days. After cooling to room temperature, colorless rod-like crystals were obtained. Yield: 48% based on L1. EA (%): calcd for $C_{32}H_{20}K_2Zn_4O_{21}$ (**3**): C 35.58; H 1.87. Found: C 35.89; H 1.97. IR (KBr, υ/cm^{-1}): 3503(s), 3336(m), 3034(m), 1633(s), 1575(vs), 1495(w), 1460(m), 1438(m), 1380(s), 1336(m), 1164(v), 935(v), 836(w), 778(m), 692(m), 507(vs), 453(vs).

2.4. Synthesis of $[Zn_4(\alpha\text{-}bptc)_2(H_2O)_3]_n$ (4)

Complex **4** was prepared by the same procedure as that for **3** except for the consumption of KOH (0.5 mL, 0.5 mol/L, pH = 6.5 after stirring for 30 min). After cooling to room temperature, colorless bulk crystals were obtained. Yield: 42% based on L1. EA (%): calcd for $C_{32}H_{18}Zn_4O_{19}$ (**4**): C 39.70; H 1.46. Found: C 39.97; H 1.52. IR (KBr, υ/cm^{-1}): 3495(m), 3362(s), 1599(s), 1564(s), 1503(m), 1427(s), 1386(s), 1323(s), 1168(m), 1144(m), 937(w), 863(m), 839(m), 772(s), 705(m), 682(m), 505(m).

2.5. Synthesis of $\{[Cd_4(\alpha\text{-}bptc)_2(H_2O)_7]\cdot 2H_2O\}_n$ (5)

A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.1 mmol, 0.0309 g), L1 (0.1 mmol, 0.0448 g), distilled water (4 mL) and KOH (0.2 mL, 0.5 mol/L) was placed in a Teflon lined vessel (17 mL) with constant stirring (pH = 7.0 after stirring for 30 min). The mixture was then sealed in a stainless steel container and heated under autogenous pressure at 433 K for 3 days. After cooling to room temperature, colorless bulk crystals were obtained. Yield: 45% based on L1. EA (%): calcd for $C_{32}H_{30}Cd_4O_{25}$ (**5**): C 30.40; H 2.39. Found: C 30.56; H 2.35. IR (KBr, υ/cm^{-1}): 3383(m), 3101(w), 2924(w), 1599(s), 1545(s), 1420(s), 1387(s), 1223(m), 1074(m), 824(m).

2.6. X-ray crystallography

Single-crystal X-ray diffraction data for complexes **1**, **2** and **5** were collected at 100 (2) K in the Beijing Synchrotron Radiation Facility (BSRF) beamline 3W1A, which was equipped with a MARCCD-165 detector (λ = 0.7200 Å) with the storage ring working at 2.5 GeV. Data were collected by the MARCCD diffractometer and processed using HKL 2000. [24] Single-crystal X-ray diffraction patterns for **3** and **4** were measured on a Bruker Smart Apex II diffractometer with a CCD area detector and Mo-*Kα* radiation (λ = 0.71073 Å) at room temperature. Multi-scan program SADABS was used for absorption correction. [25] The structures were solved by direct methods and refined by the full-matrix least squares on F^2 using the SHELXS-2014. [26] All the non-H atoms were refined anisotropically. Hydrogen atoms attached to C atoms were placed geometrically and refined using a riding model approximation, with C–H = 0.93–0.96 Å. Hydrogen atoms in water and hydroxyls were located from difference Fourier maps and refined using their global *U*iso value with O–H = 0.82 Å. The topological analyses were performed on the TOPOS program [27]. For complex **2**, the PLATON/SQUEEZE [28] program was used to remove the contributions of all disordered solvent molecules and anions. The full details of the solvent and anions removed are included in the PLATON/SQUEEZE details section of the CIF. There is a total potential solvent accessible void of 1031.4 $Å^3$ with 27.2% of per unit cell volume. EA and TGA (Fig. S7) results matched with the formula $C_{16}H_{14}Co_2O_{12}$, corresponding to $\{(H_3O)_2[Co_4(\mu_3\text{-}O)(\alpha\text{-}bptc)_2(H_2O)]\cdot 4H_2O\}_n$.

A summary of the crystallographic data as well as the data collection and refinement parameters for compounds **1**–**5** are provided