Utilization of mixed ligands to construct two new coordination polymers: Syntheses, structures and properties

Yansong Wang, Zhimin Zhou *

Institute of Natural Resources and Environment, College of Environment and Planning, Henan University, Kaifeng, Henan 475004, PR China

ABSTRACT

The use of triazine and aromatic carboxylic acid as mixed chelating ligands in preparing two coordination polymers is described. Two new transition-metal coordination polymers, namely, $[Co_2(bpdc)_4(phdat)_2]$ (**1**) and $[Zn(bpdc)]_n$ (**2**) ($H_2bpdc=2,4$-biphenyldicarboxylic acid, phdat=2,4-diamine-6-phenyl-1,3,5-triazine), have been hydrothermally synthesized and structurally characterized by IR, elemental analyses, X-ray single-crystal diffraction and TGA. Compound **1** is a 0D structure and extends to a 3D network by two different N–H···O and N–H···N hydrogen bonds. Compound **2** exhibits a 2D network with $4^4.6^2$ topological net, which contains two kinds of single helical chains. The interactions within each Co(II)–Co(II) pair of compound **1** are antiferromagnetic ($g=2.19$, $J=-22$ K, $zj'=-0.00351$ K). Furthermore, the photoluminescence property of **2** was also investigated in the solid state at room temperature.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Metal–organic coordination polymers have attracted great attention during the last two decades, not only due to their versatile intriguing architectures and remarkable chemical properties [1–12], but also for their various potential applications ranging from catalysis, magnetism, material science, luminescence to gas adsorption and separation [13–27]. It must be realized that the detailed mechanism of formation of coordination polymers is far from being understood and often described as a self-assembly progress, which is highly sensitive to various factors, such as the metal/ligand nature [28–29], solvent system [30–31], pH value of the solution [32], counterions [33], reaction temperature [34], and concentration and ratio of reagents [35]. From the view point of synthesis, the utilization of appropriate mixed-ligands is proved to be an effective way to synthesize the novel transition metal coordination polymers.

The preliminary work shows the 2,4-diamine-6-phenyl-1,3,5-triazine (phdat) is a potentially versatile amino-containing N-heterocycle ligand which presents a diverse number of potential coordination and bridging modes, along with multiple accessible hydrogen bonding interaction due to the presence of the amino groups [36–39]. In addition, the aromatic phenyl rings of phdat provide weak $\pi\cdots\pi$ stacking interactions. On the other hand, the multidentate carboxylates are important auxiliary organic ligands and can be applied as effective tectons for building diverse coordination networks with desired structural features owing to their diverse coordination modes and orientations [23,40–44]. However, among the various fascinating architectures of coordination complexes, only a small number of phdat-based analogs have been isolated [45–47], and, to our knowledge, the coordination polymer constructed from 2,4′-biphenyldicarboxylic acid/phdat-mixed ligands (Scheme 1) has not been reported to date.

Herein, we present the syntheses and characterizations of two new coordination polymers, $[Co_2(bpdc)_4(phdat)_2]$ (**1**) and $[Zn(bpdc)]_n$ (**2**), from the mixed ligands containing 2,4′-biphenyldicarboxylic acid (H_2bpdc) and phdat. Furthermore, the magnetic property of **1** as well as the luminescent property of **2** is also studied.

2. Experimental

2.1. Materials and general techniques

2,4-diamine-6-phenyl-1,3,5-triazine (phdat), 2,4′-biphenyldicarboxylic acid (H_2bpdc), cobalt chloride hexahydrate and zinc chloride were used as purchased without further purification. Infrared (IR) spectra were recorded on an AVATAR360 FT-IR spectrophotometer using KBr pellets in the range of 4000–400 cm^{-1}. The following abbreviations were used to assign the peak intensities: s=strong, m=medium, and w=weak. C, H and N
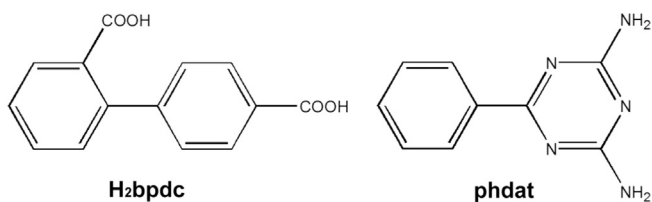
Scheme 1. Molecular structures of the H₂bpdc and phdat ligands..

elemental analyses were performed via Vario EL III Etro Elemental Analyzer. Thermogravimetric analyses (TGA) were performed under N_2 atmosphere with a heating rate of $10\,^{\circ}\text{C min}^{-1}$ using TGA/SDTA851e. Powder X-ray measurements were performed using a Philips X'-PertPro diffractometer with Cu $K\alpha$ radiation. Magnetic measurement was carried out on a Quantum Design MPMS-XL SQUID magnetometer. The fluorescent data were collected on an EDINBURGH fluorescence spectrophotometer FLS980.

2.2. Synthesis of [Co₂(bpdc)₄(phdat)₂] (1)

A mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol, 0.238 g), H₂bpdc (0.50 mmol, 0.121 g) and phdat (0.40 mmol, 0.075 g) and H_2O (5 mL) was placed in a 25 mL Teflon-lined reactor and heated to 150 °C for 72 h. The solution was cooled down to room temperature over 6–7 h. Green crystals were isolated from the mother liquid, washed with deionised water and dried in air. Yield: 0.264 g, 0.18 mmol (36% based on bpdc²⁻). Anal. Calcd: $C_{74}H_{50}N_{10}O_{16}Co_2$ (%): C, 61.16; H, 3.47. Found: C, 62.07; H, 3.63. IR (cm^{-1}): 3426(m), 3325(w), 3170(w), 2924(s), 2854(s), 1623(m), 1532(m), 1399(s), 1284(m), 1093(w), 856(m), 817(m), 757(s), 702(w), 671(w).

2.3. Synthesis of [Zn(bpdc)]ₙ (2)

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in compound **1** was replaced with ZnCl_2, heated to 180 °C for 72 h, then cooled to room temperature. Colorless crystals were isolated from the mother liquid, washed with deionised water and dried in air. Yield: 0.064 g, 0.21 mmol (42% based on bpdc²⁻). Anal. Calcd: $C_{14}H_8O_4Zn$ (%): C, 55.02; H, 2.64. Found: C, 55.68; H, 2.89. IR (cm^{-1}): 3429(m), 3058(w), 1578(m), 1542(s), 1411(s), 1143(w), 1101(w), 889(m), 858(m), 783(m), 763(s), 705(m), 682(m).

2.4. X-ray crystallographic analyses

X-ray single crystal data were collected at 296(2) K (for **1**–**2**) on a Bruker Apex-II CCD area detector diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Data reduction and absorption correction were made with empirical methods. The structures were solved by direct methods using SHELXS-97 [48] and refined by full-matrix least-squares techniques using SHELXL-97 [49]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Carbon-bound hydrogen atoms were included in idealized positions and refined using a riding model. Selected details of the data collection and structural refinement of compounds **1** and **2** can be found in Table 1 and selected bond lengths (Å) and bond angles (°) in Tables S1–S2 (Supporting information). CCDC-1050999 (**1**) and CCDC-1051000 (**2**) can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Table 1
Crystal data and structure refinements for **1**–**2**.

	1	**2**
Empirical formula	$C_{74}H_{50}N_{10}O_{16}Co_2$	$C_{14}H_8O_4Zn$
Formula weight	1453.11	305.62
Crystal system	Triclinic	Orthorhombic
Space group	$P-1$	$Pbca$
a (Å)	11.7078(16)	12.7080(5)
b (Å)	12.3962(16)	7.1786(3)
c (Å)	12.9998(18)	25.3307(10)
α (deg)	67.853(2)	90
β (deg)	67.940(2)	90
γ (deg)	79.041(2)	90
V (Å³)	1617.0(4)	2310.81(16)
Z	1	4
D_c (g cm⁻³)	1.492	1.757
μ (mm⁻¹)	0.595	2.131
F_{000}	746	1232
Crystal size (mm³)	$0.41 \times 0.20 \times 0.16$	$0.51 \times 0.26 \times 0.20$
Theta range for data collection (deg)	1.776–28.153	4.54–56.652
Reflns collected/unique	10366/7402	13684 / 2874
R_{int}	0.0200	0.0249
goodness-of-fit on F^2	1.005	1.061
$^a R_1$, $^b wR_2$ $[I > 2\sigma(I)]$	0.0426, 0.1003	0.0271, 0.0658
R indices (all data)	0.0630, 0.1126	0.0350, 0.0692

1: $a = 0.0525$, $b = 0.4931$; **2**: $a = 0.0315$, $b = 1.2705$.

^{a} $R_1 = \sum \lVert F_o \rvert - \lvert F_c \rVert / \sum \lvert F_o \rvert$.
^{b} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussions

3.1. Syntheses

The use of flexible bridging ligands in the formation of coordination polymers and discrete assemblies has the potential to produce a degree of uncertainty in the connectivity of products resulting from self-assembly reactions [50–51]. Here, the self-assembly of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with 2,4-diamine-6-phenyl-1,3,5-triazine (phdat), 2,4′-biphenyldicarboxylic acid (H₂bpdc) in water under hydrothermal conditions led to the formation of **1** and **2** (Scheme 2). Notably, phdat is essential for the formation of **2**, although it does not appear in the structure. Such observation has also been made by Li et al. [52]. It is inferred that the –NH₂ groups of triazine and the carboxyl groups of H₂bpdc form a buffer solution, which can adjust the pH value in a small scope, providing a suitable condition for the crystals.

3.2. Crystal structures of compound 1

Single-crystal X-ray diffraction analysis reveals that the compound **1** crystallizes in the triclinic system P-1 space group. The asymmetric unit of **1** consists of two Co(II) ions, four bpdc²⁻ ligands and two phdat ligands. As shown in Fig. 1a, each of the two Co atoms is coordinated by one N_{triazine} atom from phdat ligand and four O atoms from four carboxyl groups, leading to a distorted square-pyramid geometry with the bond angles spanning from 85.98(7) to 103.67(7)° (Fig. S1). The Co–N distance is 2.1101(18) Å, and Co–O distances fall in the range 2.0257(17)–2.0583(16) Å, which are comparable to the reported compound [Co(btzbp)]ₙ (btzbp = 6,6′-dicyano-2,2′-bipyridine) [53]. In compound **1**, the binuclear cobalt units are linked by four $syn,syn-\mu_2-\eta^1:\eta^1:\eta^0:\eta^0$ carboxyl groups with Co···Co distance of 2.90 Å.

It can be clearly seen that the phenyl and triazinyl rings of phadat ligand are not located in the same plane, and the corresponding interplanar angle is 52.1°, while the dihedral angle between two aromatic phenyl rings of bpdc ligands is in the range of 26.1–89.0°. Furthermore, the intramolecular N–H···O hydrogen bonds [N4···O6 = 3.040(3), N5···O5 = 3.038(3), and N5···O7 = 2.976(3) Å] partially attribute to the stability of this discrete molecule (Fig. 1b). The adjacent units of **1** are