Polyhedron 141 (2018) 87–93

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Transition metal coordination networks based on 1,3-bis(1,2,4-triazol-1-yl)benzene and isophthalic acid: Luminescence and magnetic properties

Xiu Juan Shi, Peng Yun Chen, Zhen Ming Yin, Tuo Li, Ming Ze Wu, Li Tian *

Tianjin Key Laboratory of Structure and Performance for Functional Molecule, Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry, Ministry of Education, Tianjin Normal University, Tianjin 300387, PR China

ARTICLE INFO

Article history:
Received 27 September 2017
Accepted 10 November 2017
Available online 24 November 2017

Keywords:
Crystal structure
1,3-Bis(1,2,4-triazol-1-yl)benzene
Isophthalic acid
Luminescent property
Magnetic property

ABSTRACT

Solvothermal reactions of 1,3-bis(1,2,4-triazol-1-yl)benzene (btb), isophthalic acid (H_2ip) with $M(NO_3)_2$ (M = Co^{2+}(**1**), Cu^{2+}(**2**), Cd^{2+}(**3**)) afforded three coordination polymers, $[M(btb)(ip)]_n$ (Co^{2+}(**1**), Cu^{2+}(**2**)) and $[Cd_2(btb)(ip)_2{\cdot}4H_2O]_n{\cdot}4H_2O$ (**3**), respectively. Both compounds **1** and **2** show 2D networks with binuclear paddle-wheel structures, however **3** is confirmed as 1D double-chain ladder. For complex **1**, weak ferromagnetic interactions are detected between Co^{II} ions of Co2 unit without long-range magnetic ordering. Antiferromagnetic interactions are found between the Cu^{II} centers in complex **2**. In addition, complex **3** shows red-shifted luminescence spectra with obviously higher intensity owning to the more rigid arrangement of the π systems.

1. Introduction

Coordination polymers have obtained extensive interest not only because of the structural diversity but also their attractive properties, such as luminescence, chemical sensing, magnetism, catalysis, and gas storage or separation [1–11]. One of the main steps for preparation of polymeric metal complexes with fascinating applications is to select the multidentate bridging ligands or mixed multidentate ligands [12–16]. A lot of N-donor bridging ligands (like containing pyridine, imidazole, pyrazole and triazole rings) have been widely used to construct coordination polymers with fascinating architectures and interesting properties [17–24]. Among the various N-donor bridging ligands, triazole N-donor ligands have been proven to be good candidates for the construction of coordination polymers with versatile topologies and functional properties [25–28]. 1,3-Bis(1,2,4-triazol-1-yl)benzene (abbreviated as btb) is a rigid ligand, which contains two triazole ring and can act as bridging ligand. On the other hand, organic aromatic polyoxometalates play an important role in the formation of coordination polymers with fascinating structures [29–33]. Among them, isophthalic acid (H_2ip), in which the two carboxylate moieties are predisposed at 120°, is a good oxygen donor for building metal–organic networks. In this contribution, we choose btb incorporated with isophthalic acid (H_2ip), as the building blocks, and three new complexes with various topological structure, $[M(btb)(ip)]_n$ (Co^{2+}(**1**), Cu^{2+}(**2**)) and $[Cd_2(btb)(ip)_2{\cdot}4H_2O]_n{\cdot}4H_2O$ (**3**) were fabricated and structurally characterized by X-ray single crystal analyses. In particular, d^{10} metal centers and the conjugated π systems containing aromatic rings favor the development of fluorescent materials.

2. Experimental

2.1. General considerations

The reagents used in the syntheses were of analytical grade, except that the solvent used was dried ($(CH_3)_2SO$ over 4 Å molecular sieve) and distilled prior to use. The elemental analyses (C, H, and N) were carried out on a Perkin–Elmer elemental analyzer. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu Ka radiation. The fluorescent spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer.

2.2. Synthesis of ligand 1,3-bis(1,2,4-triazol-1-yl)benzene (btb)

1,3-Dibromobenzene (0.75 g, 3.2 mmol), triazole (2.18 g, 12.8 mmol), K_2CO_3 (2.96 g, 21.0 mmol), CuI (0.03 g, 0.13 mmol) and 7 drops of N, N'-dimethyl ethane amine were mixed in 15 ml dry DMSO solution and heated at 150 °C for 36 h under a nitrogen atmosphere. The mixture was cooled to room temperature, filtered and the solid was washed with DMSO. The filtrate was distilled under reduced pressure to remove the solvent and the residue

* Corresponding author.
E-mail address: lilytianli@hotmail.com (L. Tian).

https://doi.org/10.1016/j.poly.2017.11.019
0277-5387/

was extracted with CH_2Cl_2 (6 × 30 mL). The organic layer was separated, dried over magnesium sulfate, and evaporated to dryness to give the crude product, which was further separated under column chromatography to give 0.54 g of btb. Yield: 79%; 1H NMR [$CDCl_3$]: 8.61 (s, 2H), 8.09 (s, 2H), 7.67 (dd, 2H), 7.62 (s, 1H); 7.59 (t, 1H) ppm; elemental analysis calcd (%) for $C_{10}H_8N_6$: C 56.59, H 3.80, N 39.61; found C 56.37, H 3.68, N 39.42.

2.3. Synthesis of $[Co(btb)(ip)]_n$ (**1**)

A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (58 mg, 0.2 mmol), btb (21 mg, 0.1 mmol), H_2ip (8 mg, 0.1 mmol), $NaHCO_3$ (8 mg, 0.1 mmol), H_2O (4 mL) and CH_3OH (2 mL) was added into a Parr Teflon-lined stainless steel vessel (15 mL), and then the vessel was sealed and heated to 120 °C, kept for 3 days. After that the autoclave was cooled to room temperature at a rate of 1.2 °C/h^{-1}, a pink crystalline product **1** was filtered off, washed with distilled water and dried in air (yield 58% based on Co). *Anal.* Calc. for $C_{18}H_{12}CoN_6O_4$ (435.27): C, 49.67; H, 2.98; N, 19.31. Found: C, 49.35; H, 3.10; N, 19.10%.

2.4. Synthesis of $[Cu(btb)(ip)]_n$ (**2**)

Blue crystals of **2** were obtained by adopting the same synthetic procedure as **1** only with the use of $Cu(NO_3)_2{\cdot}4H_2O$ instead of $Co(NO_3){\cdot}6H_2O$. Yield: 54% (based on Cu). *Anal.* Calc. for $C_{18}H_{12}CuN_6O_4$ (439.88): C, 49.15; H, 2.75; N, 19.11. Found: C, 49.14; H, 3.02; N, 19.08%.

2.5. Synthesis of $[Cd_2(btb)(ip)_2{\cdot}4H_2O]_n{\cdot}4H_2O$ (**3**)

Colorless crystals of **3** were obtained by adopting the same synthetic procedure as **1** only with the use of $Cd(NO_3)_2{\cdot}4H_2O$ instead of $Co(NO_3){\cdot}6H_2O$. Yield: 48% (based on Cd). *Anal.* Calc. for $C_{26}H_{32}Cd_2N_6O_{16}$ (909.37): C, 34.34; H, 3.55; N, 9.24. Found: C, 34.12; H, 3.62; N, 9.08%.

3. X-ray crystallography

Single-crystal X-ray diffraction measurements of **1**–**3** were carried out with a Bruker Smart CCD diffractometer and a graphite crystal monochromator situated in the incident beam for data collection at 296(2) K. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 programs [34–37]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and refined isotropically. Crystallographic data for **1**–**3** are summarized in Table 1. For **1**–**2**, the squeeze method was applied to solve the void space, and heavily disordered water molecules exist in them.

4. Results and discussion

4.1. Crystal structure of $[Co(btb)(ip)]_n$ (**1**)

Single-crystal X-ray diffraction analyses show that complexes **1**–**2** are isostructural and belong to triclinic $P\bar{1}$ space group with $Z = 2$. In view of their structural similarity, only the structure of **1** will be described herein as a representative example. The structural diagrams of the complex **2** are given in the ESI, Figs. S1 and S2. As shown in Fig. 1, compound **1** possesses a dinuclear paddle-wheel structure with the asymmetric unit containing one crystallographically unique Co^{2+} ion, one btb ligand and one ip ligand. As viewed in Fig. 1a, Co1 is six-coordinated in a highly distorted octahedral coordination sphere that is defined by two nitrogen atoms from two btb ligands occupying the axial positions, while the equatorial positions are finished by four carboxylic oxygen atoms. All the Co–O and Co–N bond lengths fall in the normal range except the Co1–O2 distance is 2.283(5) Å (Table S1), which is a little longer than the normal Co-O bonds. It is noteworthy that two adjacent Co1 ions (Co1 and Co1A (2 − *x*, 2 − *y*, 1 − *z*)) ions formed a dimer by two bridging carboxylic oxygen atoms with a Co1···Co1 distance of 4.205 Å. The dimer arrayed by μ_2-O_{COO}^{-} bridges along *b* direction to give a 1D double-chain

Table 1
Crystallographic data and structure refinement details for **1**–**3**.

	1	**2**	**3**
Formula	$C_{18}H_{12}CoN_6O_4$	$C_{18}H_{12}CuN_6O_4$	$C_{26}H_{32}Cd_2N_6O_{16}$
Mr	435.27	439.88	909.37
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P_2(1)/c$
Unit cell dimensions			
a (Å)	7.6014(6)	7.947(4)	10.3043(13)
b (Å)	10.1582(6)	10.133(5)	13.9700(18)
c (Å)	13.0741(8)	13.004(6)	24.917(3)
α (°)	86.598(5)	86.778(8)	
β (°)	74.655(6)	75.335(10)	107.483(4)
γ (°)	76.477(6)	78.856(9)	
V (Å^3)	946.56(12)	993.9(8)	3421.1(7)
Z	2	2	4
ρ_{calc} (Mg/m^3)	1.527	1.470	1.766
μ (mm^{-1})	0.945	1.135	1.323
F(000)	442	446	1816
θ range(°)	3.625–25.006	2.696–26.499	1.691–26.499
Limiting indices	$-9 \le h \le 8$	$-9 \le h \le 8$	$-10 \le h \le 12$
	$-12 \le k \le 12$	$-12 \le k \le 12$	$-17 \le k \le 17$
	$-15 \le l \le 13$	$-16 \le l \le 10$	$-31 \le l \le 23$
Reflections collected	6180	5119	19772
Goodness-of-fit (GOF) on F^2	0.897	0.924	1.045
R_1/wR_2 [$I > 2\sigma(I)$]	R_1 = 0.0381,	R_1 = 0.0748,	R_1 = 0.0518,
	wR_2 = 0.0611	wR_2 = 0.1493	wR_2 = 0.1215
R_1/wR_2 (all data)	R_1 = 0.0622,	R_1 = 0.1501,	R_1 = 0.0982,
	wR_2 = 0.0644	wR_2 = 0.1684	wR_2 = 0.1419