

Fluorescent and magnetic properties of three complexes based on 4,4'-(1H-1,2,4-triazol-1-yl)methylene-bis(benzonic acid)

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ABSTRACT

Three new complexes, namely, $\{[\text{Cd}(\text{TZMB})(1,3\text{-bimb})]\cdot(\text{H}_2\text{O})_2\}_n$ (**1**), $\{[\text{Mn}_2(\text{TZMB})_2(1,4\text{-bib})_{0.5}(\text{H}_2\text{O})_2]\cdot(\text{H}_2\text{O})_2(\text{DMA})\}_n$ (**2**), $\{[\text{Co}_2(\text{TZMB})_2(1,4\text{-bib})]\cdot(\text{H}_2\text{O})_{1.5}\}_n$ (**3**), have been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction analysis, elemental analysis (EA), IR spectra (IR), powder X-ray diffraction (PXRD) and thermogravimetric (TG) analysis. Single X-ray diffraction analysis reveals that complex **1** is a 5-connected net 2D network with the point symbol of $(4^8\cdot6^2)$, complex **2** is a 3,3,3,5,9-connected net 3D framework with the point symbol of $\{3\cdot4\cdot5\}\{3\cdot4^3\cdot5^3\cdot6^2\cdot7\}\{3\cdot4^5\cdot5^4\cdot6^{11}\cdot7^{11}\cdot8^3\cdot9\}\{4\cdot5\cdot6\}\{4^2\cdot6\}$ and complex **3** is a 3,4-connected 3D framework. The topological type of **3** is **dmc** (topos&RCSR.ttd) with the point symbol of $(4\cdot8^2)(4\cdot8^5)$. Furthermore, luminescent properties of **1** and the magnetic properties of complexes **2** and **3** were also investigated.

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1. Introduction

With the development of economy, environmental issues have turned into the hot topics and been drawn lots of attention. Various kinds of toxic pollutants including metal ions and nitrobenzene derivatives pose a serious threat to human health. The traditional methods to detect contaminants are not always convenient and available because of high cost and frequent careful calibrations for instruments. So it is necessary that developing chemical sensors for fast detecting harmful chemicals. Up to now, a lot of luminescent coordination polymers (LCPs), which are considered to be a sort of materials for recognizing toxic substances, have been reported [1,2]. The magnetic properties of CPs, which can be fine-tuned by modifying their chemical composition through varying metal ions and the linkers, have been drawn considerable interest [3,4]. Therefore, it is extremely urgent to synthesize CPs with desired structures and properties.

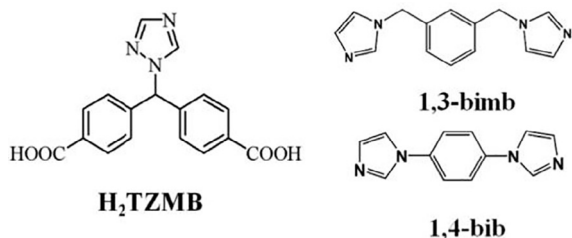
In the past decades, functional CPs have been a booming development, due to their potential applications in the field of gas storage, adsorption and separation, catalysis, drug delivery, luminescence and magnetism [5–8]. But it is difficult and a great challenge to construct CPs with target properties, which affected by various factors such as the coordination mode of the ligand,

the metal ions, temperature, pH value and the solvent system [9,10]. Among them the organic ligands play a vital role in determining final structures and the properties of CPs. To the best of our knowledge, versatile aromatic carboxyl ligands that could assume different kinds of bridging or chelating modes have been extensively employed in the construction of CPs with novel structural motifs and interesting properties [11,12]. In the meantime, the triazole group could exhibit versatile coordination modes and result in variable functional materials by the appropriate connection modes with metal ions. So the utilization of a ligand that fuses two functional groups into one linker in the self-assembly process of CPs is promising by the consideration of the superiority of aromatic carboxyl and triazole ligands [13].

Herein, a rigid ligand possessing two carboxylic groups in symmetrical positions and a N-donor triazole group, namely, 4,4'-(1H-1,2,4-triazol-1-yl)methylene-bis(benzonic acid) (H_2TZMB), was chosen as the main linker. Thus, with the help of auxiliary 1,3-bimb and 1,4-bib, three CPs, namely, $\{[\text{Cd}(\text{TZMB})(1,3\text{-bimb})]\cdot(\text{H}_2\text{O})_2\}_n$ (**1**), $\{[\text{Mn}_2(\text{TZMB})_2(1,4\text{-bib})_{0.5}(\text{H}_2\text{O})_2]\cdot(\text{H}_2\text{O})_2(\text{DMA})\}_n$ (**2**) and $\{[\text{Co}_2(\text{TZMB})_2(1,4\text{-bib})]\cdot(\text{H}_2\text{O})_{1.5}\}_n$ (**3**), have been synthesized by hydrothermal methods and characterized by single-crystal X-ray diffraction analysis, elemental analysis, IR spectrum analysis, thermogravimetric analysis, topological analysis and powder X-ray diffraction. Besides, the luminescent properties of **1** and the magnetic properties of **2** and **3** were also investigated in detail (Scheme 1).

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Scheme 1. Selected organic ligands in the self-assembly of the titled CPs.

2. Experimental

2.1. Materials and physical measurements

H₂TZMB ligand, 1,3-bimb, 1,4-bib and other materials were obtained from commercial sources and used as received without further purification. Powder X-ray diffraction patterns were determined on a Rigaku D/Max-2500 PC diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$, $2\theta = 5\text{--}50^\circ$) at room temperature. IR spectra were characterized by a FTIR-8400s spectrometer in the wavenumber range of 4000–400 cm^{-1} . TG curves were recorded on a METTLER TGA analyzer from room temperature to 800 $^\circ\text{C}$ (10 $^\circ\text{C}\cdot\text{min}^{-1}$) over the N₂ atmosphere. The elemental analyses (C, N, and H) were measured on a Vario MACRO cube elemental analyzer. Luminescence measurements were collected on a F-2700 fluorescence spectrophotometer and the magnetic properties of complexes **2** and **3** were tested by using a superconducting quantum interference device (SQUID) magnetometer from Quantum Design, Inc.

2.2. Syntheses of complexes

2.2.1. $\{[\text{Cd}(\text{TZMB})(1,3\text{-bimb})] \cdot (\text{H}_2\text{O})_2\}_n$ (**1**)

A mixture of H₂TZMB (0.024 mmol, 7.8 mg), 1,3-bimb (0.024 mmol, 5.8 mg), Cd(NO₃)₂·6H₂O (0.036 mmol, 11.1 mg), NaOH aqueous solution (0.1 mL, 0.25 mol·L⁻¹) and 3 mL H₂O was sealed in a Teflon-lined stainless steel vessel (25 mL), heated at 150 $^\circ\text{C}$ for 50 h and cooled to room temperature at a cooling rate of 10 $^\circ\text{C}\cdot\text{h}^{-1}$. The colorless block crystals of **1** were obtained with a yield of 60% (based on H₂TZMB). *Anal. Calc.* (%) for C₃₁H₂₉N₇O₆Cd: C, 52.54; H, 4.09; N, 13.84. Found (%): C, 52.02; H, 4.24; N, 13.71. IR (KBr pellet, cm^{-1}): 3461 (m), 3128 (m), 1650 (w), 1593 (s), 1554 (s), 1388 (s), 1083 (s), 837 (s), 742 (s).

2.2.2. $\{[\text{Mn}_2(\text{TZMB})_2(1,4\text{-bib})_{0.5}(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_2(\text{DMA})\}_n$ (**2**)

The synthetic procedure of complex **2** is similar to **1** except that H₂TZMB (0.024 mmol, 7.8 mg), 1,4-bib (0.024 mmol, 5.0 mg) and MnCl₂·4H₂O (0.024 mmol, 4.73 mg) were dissolved in mixed DMA/EtOH/H₂O (3 mL, v:v:v = 1:1:1), added a bit of NaOH aqueous solution (0.05 mL, 0.25 mol·L⁻¹) and heated at 100 $^\circ\text{C}$. The colorless block crystals of **2** were obtained with a yield of 58% (based on H₂TZMB). *Anal. Calc.* (%) for C₄₄H₄₄N₉O₁₃Mn₂: C, 51.92; H, 4.32; N, 12.39. Found (%): C, 51.34; H, 4.51; N, 12.89. IR (KBr pellet, cm^{-1}): 3460 (w), 3145 (w), 1652 (m), 1614 (s), 1558 (vs), 1417 (vs), 1272 (w), 1124 (w), 995 (w), 838 (w), 779 (w), 649 (w).

2.2.3. $\{[\text{Co}_2(\text{TZMB})_2(1,4\text{-bib})_{0.5}(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_2\}_n$ (**3**)

The H₂TZMB (0.008 mmol, 2.6 mg), 1,4-bib (0.008 mmol, 1.6 mg), CoCl₂·6H₂O (0.012 mmol, 2.85 mg), NH₃ aqueous solution (0.05 mL, 0.25 mol·L⁻¹) and 1 mL H₂O were mixed in a pressure-resistant glass tube, heated at 120 $^\circ\text{C}$ for 50 h and cooled to room temperature at 15 $^\circ\text{C}\cdot\text{h}^{-1}$. The colorless block crystals of **4** were obtained with a yield of 62% (based on H₂TZMB). *Anal. Calc.* (%)

for C₄₆H₃₂Co₂N₁₀O₈: C, 55.32; H, 3.50; N, 14.03. Found (%): C, 55.24; H, 3.61; N, 13.89. IR (KBr pellet, cm^{-1}): 3444 (w), 3097 (w), 1603 (s), 1557 (vs), 1414 (vs), 1138 (m), 778 (m), 654 (m).

2.3. Single crystal X-ray diffraction studies

Crystals with appropriate dimensions of complexes **1–3** were determined on a Bruker Apex II CCD diffractometer. Data were collected at 298 K by using a graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied using the multiscan technique and the structures were solved and refined by using the SHELXL program [14,15]. All of non-hydrogen atoms were located with successive difference Fourier syntheses and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters. The approximate positions of hydrogen atoms for H₂O were obtained from a difference Fourier map, restrained to ideal configuration of water molecule, and fixed in the final stages of refinements. For **1–3**, there are some disordered solvent molecules accessible void volumes that can be removed by PLATON/SQUEEZE. The crystallographic data of complexes **1–3** are presented in Table S1. Selected bond lengths and angles are listed in Table S2. Topologies of complexes **1–3** were analyzed using the TOPOS soft package [16].

3. Results and discussion

3.1. IR spectral studies of the complexes

To confirm the functional groups in complexes **1–3**, their IR spectra were characterized (Fig. S1). The IR absorption bands: 3461 cm^{-1} for **1**, 3460 cm^{-1} for **2**, and 3444 cm^{-1} for **3** might be attributed to the characteristic peaks of O–H stretching vibrations of water molecules. The vibration bands of 1400–1600 cm^{-1} and 1340–1454 cm^{-1} belong to the asymmetric and symmetric skeletal vibrations of the aromatic rings, respectively. There are no strong absorption bands from 1650 cm^{-1} to 1710 cm^{-1} reveal that the H₂TZMB is completely deprotonated in complexes **1–3**.

3.2. Descriptions of crystal structures

3.2.1. Crystal structure of $\{[\text{Cd}(\text{TZMB})(1,3\text{-bimb})] \cdot (\text{H}_2\text{O})_2\}_n$ (**1**)

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the monoclinic system with space group $P2_1/n$, which possesses a 2D framework with a mononuclear structure. The asymmetrical unit contains one crystallographic independent Cd(II) ion, one TZMB²⁻, one 1,3-bimb and two free water molecules. As shown in Fig. 1, the central Cd1 is six coordinated by three oxygen atoms from two TZMB²⁻ [Cd1–O1 = 2.237(3) Å , Cd1–O3¹ = 2.344(2) Å , Cd1–O4¹ = 2.577(3) Å], one nitrogen atom from the triazole ring of a TZMB²⁻ [Cd1–N3^{II} = 2.437(4) Å] and two nitrogen atoms from two 1,3-bimb ligands [Cd1–N4 = 2.253(3) Å , Cd1–N7^{III} = 2.294(4) Å], which presents a distorted octahedral geometry. The H₂TZMB ligands in **1** are fully deprotonated and the carboxyl groups of TZMB²⁻ adopt two coordination modes: η^1 (monodentate mode) and η^2 (chelating mode) (Scheme S1. Mode I), respectively. The TZMB²⁻ links Cd(II) ions to give a 1D chain Fig. 2a. Simultaneously, Cd(II) ions connect with 1,3-bimb ligands to generate 1D wavy chain Fig. 2b. Two kinds of 1D chain interlace one another to form a 2D network by connecting with adjacent Cd(II) ions Fig. 3a. By topological analysis, Cd(II) ions can be acted as 5-connected nodes and the TZMB²⁻/1,3-bimb can be defined as lines, then the structure of complex **1** can be simplified as a 5-connected net with the point symbol of (4⁸.6²) Fig. 3b.

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