

Four cadmium coordination polymers based on a flexible bis(triazole) ligand and benzenedicarboxylate isomers



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ABSTRACT

Four cadmium(II) coordination polymers, $[\text{Cd}(\text{bbtz})_{0.5}(\text{1,2-bdc})(\text{H}_2\text{O})]_n$ (**1**), $[\text{Cd}_3(\text{bbtz})_4(\text{1,2-bdc})_2\text{Cl}_2]_n$ (**2**), $\{[\text{Cd}(\text{bbtz})(\text{1,3-bdc})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**3**) and $\{[\text{Cd}(\text{bbtz})_{0.5}(\text{1,4-bdc})(\text{H}_2\text{O})] \cdot \text{CH}_3\text{OH}\}_n$ (**4**), were synthesized (bbtz = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene, 1,2-, 1,3-, 1,4-bdc = 1,2-, 1,3-, 1,4-benzenedicarboxylate). **1** shows a (3,4)-connected 3D network with a point symbol of $(6^3)(6^4 \cdot 8 \cdot 10)$. **2** exhibits a 3-connected 2D network with a point symbol of 8^3 . **3** exhibits a 2D (4,4) network and a 3D hydrogen bonding architecture. **4** consists of a (3,4)-connected 2D network with a point symbol of $(4 \cdot 8^2)(4 \cdot 7^3 \cdot 8^2)$ and a 3D hydrogen bonding architecture. The diverse structures demonstrate that the benzenedicarboxylate isomers play a key role in the assembly of the coordination polymers. The luminescence and thermal stability of the polymers were investigated.

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1. Introduction

The design and synthesis of coordination polymers or metal-organic frameworks (MOFs) is of great interest in modern inorganic chemistry because of their potential applications as functional materials for luminescence, catalysis and gas absorption, and their intriguing variety of topologies [1–10]. The assembly of coordination polymers is mainly affected by a combination of a few factors, including the metal ion, organic ligand and auxiliary ligand, metal-to-ligand ratio, solvent and the reaction temperature [11–16]. The organic ligands are key to get such intriguing topologies and functional materials. The diffusion reaction is an effective method for the construction of coordination polymers with intriguing motifs [17–19]. Aromatic multicarboxylate ligands are frequently used for the construction of coordination polymers. The position isomers 1,2-, 1,3- and 1,4-benzenedicarboxylate are rigid, planar molecules and good bridging ligands for the synthesis of coordination polymers [20–25].

1,2,4-Triazole and its derivatives are very interesting ligands because they combine the coordination geometry of both pyrazole and imidazole, with regard to the arrangement of their three heteroatoms [26]. Flexible bis(triazole) ligands are widely used to construct coordination polymers because flexible ligands can adopt different conformations, according to the geometric needs of the different metal ions [27–34]. 1,4-Bis(1,2,4-triazol-1-ylmethyl)benzene

(bbtz) is a good building block to construct coordination polymers [33,35–37]. $[\text{Cd}_3(\text{bbtz})_6(\text{H}_2\text{O})_6](\text{BF}_4)_6 \cdot 1.75\text{H}_2\text{O}$ shows 2D (4,4) networks and 1D ribbons of rings polycatenated in a 3D array [36]. $[\text{Co}(\text{bbtz})(\text{NO}_2\text{-1,3-bdc})(\text{H}_2\text{O})]_n$ exhibits a 3-fold interpenetrating 4-connected $6^5 \cdot 8$ - CdSO_4 3D network ($\text{NO}_2\text{-1,3-bdc}$ = 5-nitroisophthalate) [33]. With this background information, we sought to investigate the role of three isomeric ligands, 1,2-, 1,3- and 1,4-benzenedicarboxylate (1,2-bdc, 1,3-bdc, 1,4-bdc), and 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz) in the construction of Cd(II) coordination polymers. In the present work, four cadmium(II) coordination polymers, $[\text{Cd}(\text{bbtz})_{0.5}(\text{1,2-bdc})(\text{H}_2\text{O})]_n$ (**1**), $[\text{Cd}_3(\text{bbtz})_4(\text{1,2-bdc})_2\text{Cl}_2]_n$ (**2**), $\{[\text{Cd}(\text{bbtz})(\text{1,3-bdc})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**3**) and $\{[\text{Cd}(\text{bbtz})_{0.5}(\text{1,4-bdc})(\text{H}_2\text{O})] \cdot \text{CH}_3\text{OH}\}_n$ (**4**), were synthesized. The luminescence and thermal stability of these polymers were investigated.

2. Experimental

2.1. Materials and physical measurements

All reagents were of analytical grade and used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyser. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region. The luminescence measurements were carried out in the solid state at room temperature and the spectra were collected with a Perkin-Elmer LS50B spectrofluorimeter. TGA was performed on a Thermal Analyst 2100 TA Instrument

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Table 1
Crystallographic data for **1**, **2**, **3** and **4**.

| | 1 | 2 | 3 | 4 |
|---|---|--|---|---|
| Formula | C ₁₄ H ₁₂ CdN ₃ O ₅ | C ₆₄ H ₅₆ Cd ₃ Cl ₂ N ₂₄ O ₈ | C ₂₀ H ₂₀ CdN ₆ O ₆ | C ₁₅ H ₁₆ CdN ₃ O ₆ |
| Formula weight | 414.67 | 1697.43 | 552.82 | 446.71 |
| T (K) | 223(2) | 220(2) | 223(2) | 220(2) |
| Crystal system | monoclinic | monoclinic | triclinic | monoclinic |
| Space group | P2 ₁ /n | P2 ₁ /n | P1 | P2 ₁ /n |
| a (Å) | 6.1429(9) | 9.5433(3) | 10.224(3) | 9.9625(3) |
| b (Å) | 9.1766(13) | 10.2489(3) | 10.544(3) | 12.6941(3) |
| c (Å) | 25.944(4) | 33.8234(11) | 12.935(3) | 14.4894(4) |
| α (°) | 90 | 90 | 110.887(3) | 90 |
| β (°) | 96.771(3) | 94.492(3) | 93.284(2) | 108.681(3) |
| γ (°) | 90 | 90 | 115.874(3) | 90 |
| V (Å ³) | 1452.3(4) | 3298.06(18) | 1134.0(5) | 1735.86(8) |
| F(000) | 820 | 1700 | 556 | 892 |
| Z | 4 | 2 | 2 | 4 |
| ρ _{calc} (g cm ⁻³) | 1.897 | 1.709 | 1.619 | 1.709 |
| μ (mm ⁻¹) | 1.534 | 1.116 | 1.011 | 1.294 |
| Reflections collected | 7910 | 18742 | 10685 | 9406 |
| Unique reflections | 3290 [R _{int} = 0.0337] | 7060 [R _{int} = 0.0310] | 5126 [R _{int} = 0.0435] | 3714 [R _{int} = 0.0333] |
| Parameter | 222 | 457 | 330 | 234 |
| Goodness-of-fit | 1.066 | 1.015 | 1.062 | 1.008 |
| R ₁ [I > 2σ(I)] | 0.0412 | 0.0402 | 0.0610 | 0.0353 |
| wR ₂ (all data) | 0.0916 | 0.0815 | 0.1449 | 0.0943 |

and SDT 2960 Simultaneous TGA-DTA Instrument under a N₂ atmosphere at a heating rate of 10 °C/min.

2.2. Synthesis of the complexes

2.2.1. Synthesis of [Cd(bbtz)_{0.5}(1,2-bdc)(H₂O)]_n (**1**)

A 5 mL MeOH/H₂O (3:7, v/v) solution was carefully layered over a 5 mL aqueous solution of Cd(NO₃)₂·6H₂O (0.2 mmol) in a test tube. 1,2-H₂bdc (0.2 mmol) in 2 mL water was adjusted to pH 6.5 with a dilute NaOH solution and mixed with bbtz (0.2 mmol) in 2.5 mL MeOH. Then the mixed solution of 1,2-bdc and bbtz was carefully layered over the above solution in a test tube. Colorless crystals **1** were obtained after three weeks. *Anal. Calc.* for C₁₄H₁₂CdN₃O₅ (**1**): C, 40.55; H, 2.92; N, 10.14. Found: C, 40.52; H, 2.88; N, 10.07%. IR (cm⁻¹, KBr): 3422m, 3339m, 1581m, 1554s, 1523s, 1445w, 1416w, 1387s, 1334w, 1278w, 1204w, 1140m, 1086w, 1037w, 1009w, 990w, 871w, 780w, 708m, 671m.

2.2.2. Synthesis of [Cd₃(bbtz)₄(1,2-bdc)₂Cl₂]_n (**2**)

An 8 mL aqueous solution of 1,2-H₂bdc (0.2 mmol) was adjusted to pH 6.5 with a dilute NaOH solution, then bbtz (0.2 mmol) in 5 mL MeOH and CdCl₂ (0.2 mmol) in 8 mL H₂O were slowly added. The mixed solution was stirred for ten minutes and filtered. Colorless crystals **2** were obtained after the filtrate was left to stand for one week. *Anal. Calc.* for C₆₄H₅₆Cd₃Cl₂N₂₄O₈ (**2**): C, 45.29; H, 3.33; N, 19.81. Found: C, 45.26; H, 3.31; N, 19.78%. IR (cm⁻¹, KBr): 1597s, 1539s, 1518m, 1404s, 1372w, 1276w, 1173w, 1135m, 1108w, 988w, 857w, 822w, 761m, 703w, 672m, 644w.

2.2.3. Synthesis of {[Cd(bbtz)(1,3-bdc)(H₂O)]·H₂O}_n (**3**)

The synthetic procedure for **3** is similar to that for **1** except 1,3-H₂bdc (0.2 mmol) was used instead of 1,2-H₂bdc. *Anal. Calc.* for C₂₀H₂₀CdN₆O₆ (**3**): C, 43.45; H, 3.65; N, 15.21. Found: C, 43.38; H, 3.61; N, 15.17%. IR (cm⁻¹, KBr): 3479m, 3155m, 1600s, 1537vs, 1476w, 1439s, 1383s, 1282m, 1177w, 1123s, 1096w, 990w, 857w, 744m, 723s, 670m.

2.2.4. Synthesis of {[Cd(bbtz)_{0.5}(1,4-bdc)(H₂O)]·CH₃OH}_n (**4**)

The synthetic procedure for **4** is similar to that for **1** except 1,4-H₂bdc (0.2 mmol) was used instead of 1,2-H₂bdc. *Anal. Calc.* for C₁₅H₁₆CdN₃O₆ (**4**): C, 40.33; H, 3.61; N, 9.41. Found: C, 40.26; H, 3.57; N, 9.38%. IR (cm⁻¹, KBr): 2987m, 2901m, 1575s, 1558s,

1519m, 1444w, 1376s, 1276m, 1132m, 1076w, 1010w, 985m, 838w, 746m, 670w.

2.3. X-ray crystallography

Suitable single crystals of **1**, **2**, **3** and **4** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Rigaku Saturn CCD diffractometer with graphite monochromated Mo Kα radiation. Intensities were collected by the ω scan technique. The structures were solved by direct methods and refined with the full-matrix least-squares technique (SHELXTL-97) [38]. The parameters of the crystal data collection and refinement of **1**, **2**, **3** and **4** are given in Table 1. Selected bond lengths and bond angles are listed in Table S1 in the Supporting information.

3. Results and discussion

3.1. Structure descriptions

3.1.1. Crystal structure of [Cd(bbtz)_{0.5}(1,2-bdc)(H₂O)]_n (**1**)

Single crystal X-ray analysis reveals that **1** shows a (3,4)-connected 3D network. The asymmetric unit of **1** consists of one Cd(II)

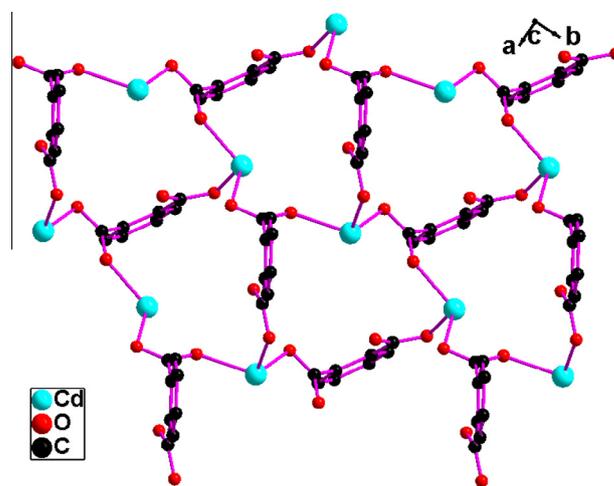


Fig. 1a. The [Cd(1,2-bdc)]_n 2D network in **1**. (Colour online.)

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