A Three-Dimensional Cadmium(II) Coordination Network Based on 1,3-Di-(1,2,4-triazole-4-yl)benzene: Synthesis, Structure, and Luminescence Properties

Shaobin Miao, Zhaohao Li, Chunying Xu, Dongsheng Deng and Baoming Ji *

College of Chemistry and Chemical Engineering, and Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, China; miaoshaobin@126.com (S.M.); lylizh@126.com (Z.L.); xuchunying8@163.com (C.X.); dengdongsheng168@sina.com (D.D.)

* Correspondence: lyhxxjbing@126.com; Tel.: +86-379-6861-8321

Received: 20 October 2019; Accepted: 9 November 2019; Published: 11 November 2019

Abstract: 1,2,4-Triazole and its derivatives have been investigated extensively in the construction of coordination polymers. Using a 1,2,4-triazole ligand 1,3-di-(1,2,4-triazole-4-yl)benzene (dtb), a new three-dimensional coordination polymer, \([\text{Cd}_2(\text{dtb})_2(\text{SO}_4)(\text{H}_2\text{O})]\cdot(\text{1,2-H}_2\text{bdc})\cdot\text{SO}_4\) \(_n\) (1,2-H\(_2\)bdc = 1,2-benzenedicarboxylic acid), was synthesized under solvothermal conditions. Single-crystal X-ray diffraction analysis revealed that there are two crystallographically different Cd(II) ions in 1 with distorted pentagonal bipyramidal \([\text{CdN}_4\text{O}_3]\) geometry and distorted octahedral \([\text{CdN}_4\text{O}_2]\) geometry, respectively. The Cd1 atoms are connected by dtb ligands to generate Cd\(_4\)(dtb)\(_8\) secondary building units (SUBs), and the SUBs are further linked by Cd2 atoms into a three-dimensional network with two different one-dimensional channels of 14.63(2) \(_\times\) 14.63(2) and 7.54(2) \(_\times\) 7.54(2) Å\(^2\) along the c axis. The topological analysis of the framework has also been discussed. In addition, compound 1 exhibits strong fluorescence emission in the solid state at room temperature.

Keywords: 1,3-di-(1,2,4-triazole-4-yl)benzene; coordination polymers; crystal structure; luminescent property

1. Introduction

The self-assembly of coordination polymers (CPs) has attracted considerable research interest due to their fascinating structural topologies and their potential applications in catalysis, gas storage, separation, magnetism, and luminescence [1–6]. In particular, luminescent CPs based on d\(^{10}\) metal ions and conjugated organic ligands that potentially serve as chemical sensors in environmental monitoring applications have made considerable progress in recent years [7–9].

To synthesize targeted CPs, the choice of organic ligands is crucial since the final structures are mainly influenced by the conformation and the coordination ability of the ligands [10]. Aromatic polycarboxylate ligands have been widely accepted as the most effective building blocks in constructing CPs because of their structural rigidity and versatile coordination modes [11–13]. Meanwhile, ligands with nitrogen heterocycle rings are also frequently used as auxiliary linkers to finish the coordination geometries of metal centers in the crystallization process [14–16]. Combining these two kinds of ligands with metal ions tends to provide high-dimensional networks [17–20].

1,2,4-Triazole and its derivatives are efficient N-containing heterocyclic ligands, which can connect with a variety of metal ions to form novel CPs with remarkable structures and properties [21–24]. In recent years, 1,3-di-(1,2,4-triazole-4-yl)benzene (dtb) (Scheme 1) has received our attention in the construction of CPs. As a double triazole rigid ligand, two triazole rings can give several coordination modes, and the resulting CPs always have interesting luminescent properties [25–28]. The present
article is a continuation of our investigation, a novel Cd(II) CPs based on dtb was prepared under solvothermal conditions, namely \([\text{Cd}_2(\text{dtb})_2(\text{SO}_4)(\text{H}_2\text{O})] \cdot \text{(1,2-H}_2\text{bdc}) \cdot \text{SO}_4\text{n}\), (I). Herein, we report the synthesis, crystal structure, and solid-state luminescence of 1.

![Scheme 1. Structure of the 1,3-di-(1,2,4-triazole-4-yl)benzene (dtb) ligand.](image)

2. Materials and Methods

2.1. Reagents and Instruments

Dtb was prepared according to the literature method [25]. All other reagents and solvents were purchased from commercial sources and used without further purification. The IR spectrum was recorded on a Bruker EQUINOX55 spectrophotometer (Bruker, Karlsruhe, Germany) in the 4000–400 cm\(^{-1}\) region using KBr pellets. Powder X-ray diffraction (PXRD) measurement was carried out on a Bruker D8 Advance diffractometer (Bruker, Karlsruhe, Germany) with Cu K\(\alpha\) radiation (\(\lambda = 0.154 18\) nm) at room temperature. The luminescent spectra in the solid states were performed on a Hitachi F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) at room temperature.

2.2. Single-Crystal X-ray Diffraction

The single crystal diffraction data for compound 1 were collected by using a Bruker SMART APEX II CCD area detector at 296 K. The structure was solved by direct methods and refined by full-matrix least-squares methods with the SHELXL program and also refined by the Olex2 program \([29,30]\). Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were added to their calculation positions and refined using the riding model. The SQUEEZE routine in PLATON was used to identify a solvent-accessible volume of 2673 Å\(^3\). A summary of the crystallographic analysis is summarized in Table 1. Selected bond lengths and angles for 1 are listed in Table S1 (Supporting information). CCDC 1921813 contains the supplementary crystallographic data (supplementary materials) for 1. These data can be obtained free of charge via http://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.

| Compound | 1 |
|----------|---|
| Empirical formula | \(\text{C}_{28}\text{H}_{32}\text{N}_{12}\text{O}_{13}\text{S}_{2}\text{Cd}_{2}\) |
| Formula mass | 1025.51 |
| Crystal system | tetragonal |
| space group | \(I-4m2\) |
| \(a/\AA\) | 27.274(5) |
| \(b/\AA\) | 27.274(5) |
| \(c/\AA\) | 12.763(5) |
| \(V/\AA^3\), \(Z\) | 9494(5), 8 |
| \(D_c\) (g cm\(^{-3}\)) | 1.435 |
| \(\mu/mm\) | 1.05 |
| \(F(000)\) | 4064 |
| Reflections collected/unique | 36253/4618 |
| Data/restraints/parameters | 4618/3/272 |
| \(GOF(F^2)\) | 1.072 |
| \(R1/wR2 [I > 2\sigma(I)]\) | 0.0449/0.1458 |
| \(R1/wR2\) (all data) | 0.0470/0.1484 |
2.3. Preparation of Compounds 1

A mixture of dtb (21.2 mg, 0.1 mmol), 1,2-benzenedicarboxylic acid (8.3 mg, 0.05 mmol), CdSO₄·8H₂O (25.6 mg, 0.1 mmol), ethanol (4 mL) and water (8 mL) was stirred for 30 min and then sealed in a 25 mL Teflon-lined stainless steel vessel, which was heated to 90 °C for 72 h, followed by cooling to room temperature at a rate of 10 °C h⁻¹. Colorless block-shaped crystals of 1 were obtained in 52% yield based on cadmium. IR (cm⁻¹): 3107(w), 1605(m), 1544(s), 1361(w), 1295(w), 1107(m), 1060(s), 872(m), 739(m), 684(s). Calcd for: C32.61; H 2.52, N 16.25.

There is no doubt 1,2-H₂bdc did not participate in coordination with Cd(II) ions in the structure, we did several parallel reactions under solvothermal conditions by changing metal salts, solvent, and temperature. For example, we used Cd(CH₃COO)₂·2H₂O or CdCl₂, only distilled water or ethanol as solvent, 80 °C, or 120 °C. It was not possible to get compound 1 by changing any condition. To our surprise, although 1,2-H₂bdc did not participate in coordination with Cd(II) ions in the structure, we could not obtain the framework in the absence of it. There is no doubt 1,2-H₂bdc is present as a template in the construction of the framework.

Single-crystal X-ray diffraction analysis revealed that compound 1 crystallizes in the tetragonal space group I-4m2. The asymmetric unit contains two Cd(II) ions, two dtb ligands, one 1,2-H₂bdc anion, one uncoordinated SO₄²⁻ anion, and one coordinated water molecule. As represented in Figure 1, the Cd1 atom is seven-coordinated by four N atoms from different dtb ligands, two oxygen atoms from two SO₄²⁻ anions, and one oxygen atom from a coordinated water molecule, displaying a distorted pentagonal bipyramidal [CdN₄O₃] geometry. Atoms O1, O1A, N1, N1A, and O3 [symmetry code: (A) –y+3/2, –x+3/2, –z+3/2] are located in the basal plane, with a maximum deviation of 0.026 Å for O1 and O1A, whilst atoms N4 and N4A are at apical positions, with an N4–Cd1–N4A angle of 173.0(3)°. The Cd2 atom is coordinated by four dtb N atoms (N2, N2B, N5, and N5B) and two SO₄²⁻ oxygen atoms (O1 and O1B) [symmetry code: (B) y, x, –z+1]. The bond angles around Cd2 vary between 75.8(2) and 161.9(2)°, furnishing a distorted octahedral geometry. The Cd–O lengths are 2.255(7), 2.317(6), 2.553(6) Å, and the Cd–N lengths are 2.308(6), 2.442(6), 2.299(6), 2.376(6) Å, respectively.

![Figure 1. The coordination environments of the Cd(II) atoms in compound 1. [Symmetry codes: (A) –y+3/2, –x+3/2, –z+3/2; (B) y, x, –z+1; (C) –x+2, y, z; (D) x, –y+1, z.]

In compound 1, the coordinated SO₄²⁻ anions adopt μ₃-bridging mode with three Cd(II) ions (Cd2Cd1Cd2), whereas both of the dtb ligands act as μ₄-η¹: η²: η¹: η¹ mode connecting four metal ions (Cd1Cd2/Cd1Cd2). The dihedral angle between the triazole rings and the benzene ring of one dtb ligand is 30.56(7)°, and the value is 30.20(2)° for another dtb ligand, showing their similar configuration. The coordination mode and the configuration of dtb in 1 are comparable to those observed in other reported dtb-based coordination polymers [28]. Neighboring Cd1 atoms are bridged...
by dtb ligands to give rise to Cd₄(dtb)₈ secondary building units (SUBs), where the Cd···Cd distance is 10.347(2) Å. The Cd₄(dtb)₈ SUBs show an interesting calixarene-like structure, as shown in Figure 2a. These SUBs are interconnected through the coordinate interactions of dtb and Cd2 to generate a three-dimensional framework with the Cd1···Cd2 distance of 3.948(1) Å (Figure 2b). The outstanding structural feature of the 3D framework is that there are two different one-dimensional channels of 14.63 (2) × 14.63 (2) and 7.54(2) × 7.54(2) Å² along the c axis (Figure 2c). The former is filled by uncoordinated SO₄²⁻ anions, and 1,2-H₂bdc molecules reside in the latter (Figure 2d). Coordinated SO₄²⁻ anions and water molecules meet the coordination requirement of center Cd1 and Cd2 atoms, and by which the framework is consolidated. Uncoordinated SO₄²⁻ and 1,2-H₂bdc did not participate in the formation of the framework directly, but as templates, they regulate the construction of the structure. Another porous metal-organic framework from dtb and Cd(II) ions has been reported previously [28]. The structure contains triangular nano-porous channels with edges of 13.622 Å, which is constructed by the Cd₃(dtb)₁₂ trinuclear cluster. From a topological point of view, two Cd(II) atoms linked by one triazole ring can be regarded as 4-connected nodes, and the dtb ligands are reduced to linkers, so the whole framework can be simplified as a 4-connected net with [4₃·8³] topology, as depicted in Figure 2e.

Figure 2. (a) The Cd₄(dtb)₈ secondary building units. (b) The three-dimensional framework of compound 1 along the c axis. (c) The space-filling representations of the 3D structure showing the 1D channels along the c axis. (d) The 3D framework filled by uncoordinated SO₄²⁻ anions and phthalic acid molecules. (e) The 4-connected net with a point symbol of [4₃·8³].
3.2. Powder X-ray Diffraction (PXRD) and Thermal Analysis

The powder X-ray diffraction (PXRD) experiment was carried out to confirm the purity of compound 1. As shown in Figure 3, the major peak positions of the experimental PXRD patterns are almost in agreement with the simulated ones from the single-crystal data, indicating the high phase purity of the bulk sample.

![Figure 3. The simulated and measured powder X-ray diffraction (PXRD) patterns of 1.](image)

The thermal stability of complex 1 was examined by TG analysis in the range of 25–900 °C. The result is given in Figure S1. Compound 1 lost its coordinated water molecule and uncoordinated 1,2-H₂bdc molecule at 290 °C (Obsd. 17.94, Calcd. 17.75%). Then the further losses resulted from the decomposition of 1.

3.3. Luminescent Properties

The solid-state luminescence spectra of 1 and free dtb were recorded at room temperature (Figure 4). Upon excitation at 318 nm, dtb displays an emission maximum at 380 nm, which can be attributed to the π–π* transitions. The maximum emission peak of 1 is located at 409 nm (λex = 326 nm), the emission may originate from intraligand π–π* transitions since a similar peak shape with dtb is found; similar luminescence was also found in other dtb CPs [31]. Compared with the emission spectra of free dtb, the red shift (29 nm) is probably attributed to the coordination of dtb to Cd(II) atoms.

![Figure 4. Solid-state luminescent spectra of compound 1 and dtb at room temperature.](image)

4. Conclusions

In summary, a three-dimensional network [[Cd₂(dtbd)₂(SO₄)(H₂O)]·(1,2-H₂bdc)-SO₄]ₙ has been synthesized. The structure was characterized by IR, PXRD, and single-crystal X-ray crystallography. An interesting calixarene-like Cd₄(dtbd)₈ SUB was found in the structure, and the SUBs were joined to
give a three-dimensional framework with two different one-dimensional channels. The channels are occupied by SO$_4^{2-}$ anions and 1,2-H$_2$bdc molecules, and both act as templates to decide the structure. The CPs exhibits a ligand-based emission, and further research is in progress.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4352/9/11/592/s1. Table S1: Selected bond lengths (Å) and bond angles (°) for 1.

**Author Contributions:** Z.L. and C.X. synthesized the title compound. D.D. and C.X. performed the X-ray structure determination and analyzed the results. S.M. and B.J. wrote the paper.

**Acknowledgments:** This work was supported by the Science and technology research key project of the Education Department of Henan Province (19B150011).

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Li, M.; Li, D.; O’Keeffe, M.; Yaghi, O.M. Topological analysis of metal-organic frameworks with polytopic linkers and/or multiple building units and the minimal transitivity principle. *Chem. Rev.* 2014, 114, 1343–1370. [CrossRef] [PubMed]

2. Huang, Y.B.; Liang, J.; Wang, X.S.; Cao, R. Multifunctional metal-organic framework catalysts: Synergistic catalysis and tandem reactions. *Chem. Soc. Rev.* 2017, 46, 126–157. [CrossRef] [PubMed]

3. Murray, L.J.; Dincă, M.; Long, J.R. Hydrogen storage in metal-organic frameworks. *Chem. Soc. Rev.* 2009, 38, 1294–1314. [CrossRef] [PubMed]

4. Li, J.R.; Sculley, J.; Zhou, H.C. Metal-organic frameworks for separations. *Chem. Rev.* 2012, 112, 869–932. [CrossRef] [PubMed]

5. Jia, Q.X.; Tian, H.; Zhang, J.Y.; Gao, E.Q. Diverse structures and magnetism of cobalt(II) and manganese(II) compounds with mixed azido and carboxylato bridges induced by methylpyridinium carboxylates. *Chem. Eur. J.* 2011, 38, 1330–1352. [CrossRef] [PubMed]

6. Allendorf, M.D.; Bauer, C.A.; Bhakta, R.K.; Houk, R.J.T. Luminescent metal-organic frameworks. *Chem. Rev.* 2009, 14, 2781–2804. [CrossRef] [PubMed]

7. Lu, Z.Z.; Zhang, R.; Li, Y.Z.; Guo, Z.J.; Zheng, H.G. Solvatochromic behavior of a nanotubular metal-organic framework for sensing small molecules. *J. Am. Chem. Soc.* 2011, 133, 4172–4174. [CrossRef] [PubMed]

8. Zhang, M.; Feng, G.; Song, Z.; Zhou, Y.P.; Chao, H.Y.; Yuan, D.; Tan, T.Y.; Guo, Z.; Hu, Z.; Tang, B.Z.; et al. Two-dimensional metal-organic framework with wide channels and responsive turn-on fluorescence for chemical sensing of volatile organic compounds. *J. Am. Chem. Soc.* 2014, 136, 7241–7244. [CrossRef] [PubMed]

9. Ma, D.; Li, B.; Zhou, X.; Zhou, Q.; Liu, K.; Zeng, G.; Li, G.; Shi, Z.; Feng, S. A dual functional MOF as a luminescent sensor for quantitatively detecting the concentration of nitrobenzene and temperature. *Chem. Commun.* 2013, 49, 8964–8966. [CrossRef] [PubMed]

10. Stock, N.; Biswas, S. Synthesis of Metal-organic frameworks (MOFs): Routes to various MOF topologies, morphologies and composites. *Chem. Rev.* 2012, 112, 933–969. [CrossRef] [PubMed]

11. Wang, L.; Yang, M.; Li, G.; Shi, Z.; Feng, S. Highly stable chiral cadmium 1,2,4-benzenetricarboxylate: Synthesis, structure, and NLO and fluorescence properties. *Inorg. Chem.* 2006, 45, 2474–2478. [CrossRef] [PubMed]

12. Sun, D.; Collins, D.J.; Ke, Y.; Zuo, J.L.; Zhou, H.C. Construction of open metal-organic frameworks based on predesigned carboxylate isomers: From achiral to chiral nets. *Chem. Eur. J.* 2006, 12, 3768–3776. [CrossRef] [PubMed]

13. Hu, Y.; Ding, M.; Liu, X.Q.; Sun, L.B.; Jiang, H.L. Rational synthesis of an exceptionally stable Zn(II) metal-organic framework for the highly selective and sensitive detection of picric acid. *Chem. Commun.* 2016, 52, 5734–5737. [CrossRef] [PubMed]

14. Noro, S.; Kitagawa, S.; Akutagawa, T.; Nakamura, T. Coordination polymers constructed from transition metal ions and organic N-containing heterocyclic ligands: Crystal structures and microporper properties. *Prog. Polym. Sci.* 2009, 34, 240–279. [CrossRef]
15. Guo, J.; Sun, D.; Zhang, L.; Yang, Q.; Zhao, X.; Sun, D. Cadmium-organic coordination polymers based on N-donor ligands and small anions: Syntheses, crystal structures, and photoluminescent properties. *Cryst. Growth Des.* 2012, 12, 5649–5654. [CrossRef]

16. Nikolaeva, Y.A.; Balueva, A.S.; Khafizov, A.A.; Strelnik, I.D.; Gerasimova, T.P.; Katsyuba, S.A.; Litvinov, I.A.; Musina, E.I.; Karasik, A.A.; Sinyashin, O.G. The first representatives of tetranuclear gold(I) complexes of PN-containing cyclonaphes. *Dalton Trans.* 2018, 47, 7715–7720. [CrossRef] [PubMed]

17. Hao, J.; Yu, B.; Hecke, K.V.; Cui, G. A series of d10 metal coordination polymers based on a flexible bis(2-methylbenzimidazol) ligand and different carboxylates: Synthesis, structures, photoluminescence and catalytic properties. *CrystEngComm.* 2015, 17, 2279–2293. [CrossRef]

18. Zhou, X.; Liu, D.; Lang, F.F.; Ren, Z.G.; Lang, J.P. Two 2D zinc(II) coordination polymers and their orange IV composites: Preparation, structures, and photocurrent responses. *Cryst. Growth Des.* 2019, 19, 211–218. [CrossRef]

19. Rachuri, Y.; Parmar, B.; Bisht, K.K.; Suresh, E. Mixed ligand two dimensional Cd(II)/Ni(II) metal organic frameworks containing dicarboxylate and tripodal N-donor ligands: Cd(II) MOF is an efficient luminescent sensor for detection of picric acid in aqueous media. *Dalton Trans.* 2016, 45, 7881–7892. [CrossRef] [PubMed]

20. Li, Z.H.; He, S.J.; Xue, L.P.; Wang, X.N.; Zhang, D.D.; Zhao, B.T. Exploring methyl-3-hydroxy-5-carboxy-2-thiophenecarboxylate and varying flexible bis(imidazole)-based synthons as building blocks for the construction of diverse cadmium coordination polymers. *Dye Pigm.* 2018, 149, 498–504. [CrossRef]

21. Aromi, G.; Barrios, L.A.; Roubeau, O.; Gamez, P. Triazoles and tetrazoles: Prime ligands to generate remarkable coordination materials. *Coord. Chem. Rev.* 2011, 255, 485–546. [CrossRef]

22. Yi, L.; Ding, B.; Zhao, B.; Cheng, P.; Liao, D.Z.; Yan, S.P.; Jiang, Z.H. Novel triazole-bridged cadmium coordination polymers varying from zero- to three-dimensionality. *Inorg. Chem.* 2004, 43, 33–43. [CrossRef] [PubMed]

23. Hu, Y.J.; Yang, J.; Liu, Y.Y.; Song, S.; Ma, J.F. Hierarchical symmetry transfer and flexible charge matching in five [M(phen)]2+ directed iodoargentates with 1 to 3D frameworks. *Cryst. Growth Des.* 2015, 15, 3822–3831. [CrossRef]

24. Zhang, S.H.; Wang, J.M.; Zhang, H.Y.; Fan, Y.P.; Xiao, Y. Highly efficient electrochemiluminescence based on 4-amino-1,2,4-triazoles Schiff base two-dimensional Zn/Cd coordination polymers. *Dalton Trans.* 2017, 46, 410–419. [CrossRef] [PubMed]

25. Miao, S.B.; Li, Z.H.; Xu, C.Y.; Ji, B.M. Syntheses, characterization, and luminescence properties of three novel Ag(I) coordination polymers based on polycarboxylic acid ligands and 1,3-di-(1,2,4-triazole-4-yl)benzene. *CrystEngComm.* 2016, 18, 4636–4642. [CrossRef]

26. Miao, S.B.; Li, Z.H.; Xu, C.Y.; Ji, B.M. A new 3-fold interpenetrating 3D Zn(II) metal-organic framework: Synthesis, structure and luminescent property. *Chin. J. Struct. Chem.* 2016, 35, 1960–1966.

27. Miao, S.B.; Xu, C.Y.; Deng, D.S.; Ji, B.M. Synthesis, crystal structure, and properties of a 2D Cu(II) coordination polymer based on Cu3I3 chains linked by 1,3-di-(1,2,4-triazole-4-yl)benzene. *J. Clust. Sci.* 2018, 29, 313–317. [CrossRef]

28. Yang, P.; Wu, X.X.; Huo, J.Z.; Ding, B.; Wang, Y.; Wang, X.G. Hydrothermal synthesis and characterization of a series of luminescent Zn(II) and Cd(II) coordination polymers with the new versatile multidentate ligand 1,3-di-(1,2,4-triazole-4-yl)benzene. *CrystEngComm.* 2013, 15, 8097–8109. [CrossRef]

29. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 2009, 42, 342–346. [CrossRef]

30. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst.* 2015, 71, 3–8.

31. Ding, B.; Yang, P.; Liu, Y.Y.; Wang, Y.; Du, G.X. Hydrothermal syntheses and characterization of a series of luminescent Cd(II) frameworks with pyridine-based and benzene-based bis-triazole ligands. *CrystEngComm.* 2013, 15, 2490–2503. [CrossRef]