

二维镉配位聚合物 $[\text{Cd}(\text{nip})(\text{bix})_{0.5}\text{H}_2\text{O}]_n$ 构筑的 新型(3,5,5)连接的三维氢键超分子体系

胡宗智 赵 君 柯希俊 何秋芬 李 彩 李东升*

(三峡大学机械与材料学院, 功能材料研究所, 宜昌 443002)

摘要: 在水热条件下合成了一个新颖的配位聚合物 $[\text{Cd}(\text{nip})(\text{bix})_{0.5}\text{H}_2\text{O}]_n$ (**1**) (nip =5-硝基间苯二甲酸, bix =1,4-(二亚甲基)咪唑)。单晶 X-射线衍射分析表明, 晶体属三斜晶系, $P\bar{1}$ 空间群, 晶胞参数 $a=0.827\ 1(2)\ \text{nm}$, $b=1.016\ 5(3)\ \text{nm}$, $c=1.147\ 4(3)\ \text{nm}$, $\alpha=70.862(4)^\circ$, $\beta=68.988(4)^\circ$, $\gamma=69.001(4)^\circ$, $V=0.818\ 4(4)\ \text{nm}^3$, $Z=2$, $D_c=1.861\ \text{g}\cdot\text{cm}^{-3}$, $\mu=1.380\ \text{mm}^{-1}$, $F(000)=454$, 最终的 $R_1=0.040\ 0$, $wR_2=0.090\ 1$ 。配合物 **1** 中, nip^{2-} 离子以 μ_3 桥联的方式连接 $\text{Cd}(\text{II})$ 中心形成含有交替 8 元环和 16 元环的一维聚合链, 进而, bix 配体柱撑一维链形成了(3,4)-连接的二维配位网; 最后, 通过 $R_2^2(6)$ 氢键环的作用, 二维网拓展为具有(3,5,5)-连接 $\{3.4.5\}\{3.4^2.5.6^4.7.8\}\{3.4^3.5^2.6^2.7^2\}$ 拓扑结构的三维超分子体系。此外, 本文还研究了配合物 **1** 的热稳定性和荧光性质。

关键词: 镉(II)配合物; 晶体结构; 氢键; 拓扑

中图分类号: O614.24²

文献标识码: A

文章编号: 1001-4861(2011)01-0184-05

A Novel 3D (3,5,5)-Connected H-bonding Architecture Based on 2D Coordination Polymer $[\text{Cd}(\text{nip})(\text{bix})_{0.5}\text{H}_2\text{O}]_n$

HU Zong-Zhi ZHAO Jun KE Xi-Jun HE Qiu-Fen LI Cai LI Dong-Sheng*

(College of Mechanical & Material Engineering, Functional Materials Research Institute,
China Three Gorges University, Yichang, Hubei 443002, China)

Abstract: A novel compound $[\text{Cd}(\text{nip})(\text{bix})_{0.5}\text{H}_2\text{O}]_n$ (**1**) (nip =5-nitroisophthalic acid and bix =1,4-bis(imidazol-1-ylmethyl)-benzene) has been hydrothermally prepared and characterized. Single-crystal X-ray diffraction studies indicate that the compound **1** crystallizes in triclinic, space group $P\bar{1}$ with $a=0.827\ 1(2)\ \text{nm}$, $b=1.016\ 5(3)\ \text{nm}$, $c=1.147\ 4(3)\ \text{nm}$, $\alpha=70.862(4)^\circ$, $\beta=68.988(4)^\circ$, $\gamma=69.001(4)^\circ$, $V=0.818\ 4(4)\ \text{nm}^3$, $Z=2$, $D_c=1.861\ \text{g}\cdot\text{cm}^{-3}$, $\mu=1.380\ \text{mm}^{-1}$, $F(000)=454$, and final $R_1=0.040\ 0$, $wR_2=0.090\ 1$. In **1**, nip^{2-} ions act as μ_3 -linker to bridge Cd^{II} atoms into an infinite 1D chain with alternately 8-member ring and 16-member ring, moreover, the bix ligands pillar these 1D chains into 2D (3,4)-connected coordination network. Eventually, through $R_2^2(6)$ H-bonding rings, these 2D nets are extended to 3D supramolecular framework showing a new (3,5,5)-connected $\{3.4.5\}\{3.4^2.5.6^4.7.8\}\{3.4^3.5^2.6^2.7^2\}$ topology. In addition, the thermal and fluorescence properties associated with the compound **1** were also investigated. CCDC: 778936.

Key words: $\text{Cd}(\text{II})$ complex; crystal structure; H-bonding; topology

Recent years have witnessed an explosion in the self-assembly of metal-organic supramolecular networks with specific shapes/topologies directed by metal-ligand coordination, not only for their intriguing structural

motifs, but also for their potential applications^[1-3]. In the language of supramolecular chemistry, the structure of metal-organic materials is dependent upon how the metal-ligand coordination and intermolecular interac-

收稿日期: 2010-06-07。收修改稿日期: 2010-08-20。

国家自然科学基金(No.21073106, 20773104)、湖北省自然科学基金(No.2008CDB1302)、湖北省教育厅重大基金(No.Z20091301)和青年人才基金(No.Q20101203)资助项目。

*通讯联系人。E-mail: lidongsheng1@126.com, Tel/Fax: 0717-6397516

tions express the recognition information stored in the building blocks, especially the ligand^[4-5]. At this stage, much research has been devoted to the metal-organic supramolecular architectures derived from multidentate O-donor ligands. Among them, aromatic dicarboxylate ligands, such as benzene dicarboxylate and its derivatives, have been extensively employed in the preparation of the metal-organic molecular crystals^[6-8]. On the other hand, polydentate aromatic heterocyclic ligands (polyazoles), especially for imidazoles and triazoles ligands bearing alkyl spacers, are good choice of N-donor ligands, and the flexible nature of spacers allows the ligands to bend and rotate for meeting the steric requirement upon metal binding^[9-10]. The previous studies show that the combination of these polyazoles and aromatic polycarboxylate ligands can result in novel topologies, magnetic and luminescent properties^[11-12]. Along with our work of assembly of various molecular networks based upon polycarboxylate and N-donor ligands^[13-15], in this work, we report a novel 2D (3,4)-connected coordination network with formulas [Cd(nip)(bix)_{0.5}H₂O]_n (**1**) [H₂nip=5-nitroisophthalic acid and bix=1,4-bis(imidazol-1-ylmethyl)-benzene], which are extended via R₂² (6) H-bonding rings to give a 3D supramolecular framework with a new (3,5,5)-connected {3.4.5}{3.4².5.6⁴.7.8}{3.4³.5².6².7²} topology. Also, solid-state properties, such as photoluminescence and thermal stability of **1**, have been discussed.

1 Experimental

1.1 Materials and general methods

All solvents and reagents were of analytical grade and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Infrared spectra (4 000~

650 cm⁻¹) were recorded with a Thermo Nicolet 670 spectrophotometer by OMNI sampler. TG analyses were performed on a Netzsch STA 449C microanalyzer under air atmosphere at a heating rate of 10 °C · min⁻¹. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

1.2 Syntheses of [Cd(nip)(bix)_{0.5}H₂O]_n

Cd(Ac)₂ · 2H₂O (0.1 mmol, 26.65 mg), nip (0.1 mmol, 21.11 mg), bix (0.1 mmol, 32.00 mg), and deionized water (10 mL) were sealed in a Teflon-lined stainless vessel (25 mL), and heated at 160 °C for 120 h under autogenous pressure, then cooled slowly to room temperature. Colorless block crystals were obtained by filtration in 61% yield. Anal. Calcd. for C₁₅H₁₂N₃O₇Cd (%): C, 39.28; H, 1.65; N, 9.16. Found(%): C, 39.25; H, 1.66; N, 9.17. IR/cm⁻¹: 3 321 (br), 1 605 (s), 1 559(s), 1 536 (s), 1 452 (s), 1 382 (s), 1 345 (s), 1 237 (m), 1 110 (m), 1 087 (m), 1 030 (w), 940 (m), 914(m), 847(m), 787 (m), 771(w), 731 (s).

1.3 Crystal structure determination

X-ray diffraction data were collected on a Rigaku Mercury CCD diffractometer equipped with graphite monochromatized Mo K α (λ =0.071 073 nm) by Crystal clear software. Empirical absorption corrections were applied. The structures were solved by direct methods using SHELXS-97 programs^[16]. All of the non-hydrogen atoms were located from the difference Fourier maps, and then refined anisotropically with SHELXL-97 via a full-matrix least-square procedure. The hydrogen atoms were added according to the theoretical model. The crystallographic data of the compound are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

CCDC: 778936.

Table 1 Crystal data and structure refinement for complex 1

Empirical formula	C ₁₅ H ₁₂ CdN ₃ O ₇	α / (°)	70.862(4)
Formula weight	458.68	β / (°)	68.988(4)
Temperature / K	293(2)	γ / (°)	69.001(4)
Crystal system	Triclinic	V / nm ³	0.818 4(4)
Space group	$P\bar{1}$	Z	2
a / nm	0.827 1(2)	D_c / (g · cm ⁻³)	1.861
b / nm	1.016 5(3)	μ / mm ⁻¹	1.38
c / nm	1.147 4(3)	$F(000)$	454

Continued Table 1

Crystal size / mm	0.19×0.16×0.10	Data / restraints / parameters	2 841 / 3 / 239
θ range for data collection / (°)	1.95–25.01	Goodness-of-fit on F^2	1.052
Limiting indices	$-9 \leq h \leq 9, -12 \leq k \leq 10, -13 \leq l \leq 12$	Final R indices ($I > 2\sigma(I)$) ^a	$R_1=0.040\ 0, wR_2=0.090\ 1$
Reflections collected / unique (R_{int})	4 051 / 2 841 (0.039 1)	R indices (all data) ^b	$R_1=0.066\ 3, wR_2=0.116\ 2$
Refinement method	Full-matrix least-squares on F^2	Largest diff. peak and hole / (e·nm ⁻³)	1 327 and -1 609

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [(F_o^2)^2]]^{1/2}.$$

Table 2 Selected bond lengths (nm) and angles (°) for complex 1

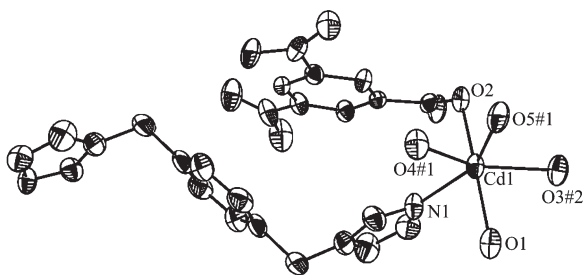
Cd(1)-O(3)#2	0.223 9(4)	Cd(1)-O(2)	0.231 8(5)	Cd(1)-O(1)	0.239 3(5)
Cd(1)-N(1)	0.223 6(5)	Cd(1)-O(5)#1	0.238 6(4)	Cd(1)-O(4)#1	0.240 2(4)
O(3)#2-Cd(1)-N(1)	130.58(18)	O(2)-Cd(1)-O(5)#1	94.55(17)	O(3)#2-Cd(1)-O(4)#1	138.13(15)
O(3)#2-Cd(1)-O(2)	96.64(15)	O(3)#2-Cd(1)-O(1)	83.45(16)	N(1)-Cd(1)-O(4)#1	88.03(16)
N(1)-Cd(1)-O(2)	92.24(18)	N(1)-Cd(1)-O(1)	85.53(19)	O(2)-Cd(1)-O(4)#1	97.26(17)
O(3)#2-Cd(1)-O(5)#1	85.39(15)	O(2)-Cd(1)-O(1)	177.11(16)	O(5)#1-Cd(1)-O(4)#1	54.29(14)
N(1)-Cd(1)-O(5)#1	142.25(16)	O(5)#1-Cd(1)-O(1)	88.34(17)	O(1)-Cd(1)-O(4)#1	84.52(17)

Symmetry codes: #1: 2-x, 1-y, -z; #2: 2-x, -y, -z; #3: 1-x, 1-y, 1-z.

2 Results and discussion

2.1 Crystal structure descriptions

X-ray structural analysis reveals that compound **1** crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit contains one Cd ion, one nip^{2-} anion, one-half bix ligand and one coordinated water molecule. As shown in Fig.1, the Cd centre is coordinated by one nitrogen atom from bix ligand (N1), four carboxylate oxygen atoms from three different nip^{2-} ligands (O2, O3#2, O4#1, O5#1) and one hydroxyl oxygen atom (O1) from aqua ligand, forming a distorted octahedral coordination geometry. The Cd-N distance is 0.223 6(5) nm, while the Cd-O distances are in the range of 0.223 9(4)–0.240 2(4) nm, which are both within the normal ranges^[17–18].



Symmetry codes: #1: 2-x, 1-y, -z; #2: 2-x, -y, -z; Hydrogen atoms are omitted for clarity

Fig.1 ORTEP view of coordination environment of Cd^{II} with thermal ellipsoids at 50% probability

In **1**, each nip^{2-} ligand adopts $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1$ coordination mode to bridge Cd^{II} atoms into an infinite 1D chain, which alternately contains 8-membered rings and 16-membered rings with the Cd···Cd distance of 0.422 7 and 0.769 9 nm, respectively (Fig.2a). Moreover, the bix ligands pillar these 1D chains into 2D coordination network (Fig.2b). Further investigation of the crystal packing of compound **1** suggests that there are one kinds of O–H···O H-bonding ring [$R_2^2(6)$] between adjacent 2D coordination layers, which origin from the coordinated carboxylate groups (O3 and O5) oxygen atoms of different nip^{2-} in the same layer and coordinated water molecules in another layer. The H-bonding cyclic [$R_2^2(6)$: –Cd–O5···H–O1–H···O3–] geometries are as follows O3···H–O1 153.01°, 0.2742 nm (O3···O1), and O1–H···O5 128.40°, 0.2711 nm (O1···O5). Just through H-bonding rings mentioned above, these 2D layers are extended to a 3D supramolecular architecture (Fig.2c).

From a viewpoint of network topology, Cd^{II} ion and nip^{2-} ligand can be defined as 3- and 4-connected nodes, respectively, while bix ligand serves as linker, and thus, the 2D coordination network exhibits a (3,4)-connected V_2O_5 -type topology, and its Schflli symbol is {4².6} {4².6³.8} (Fig.3a). Further, if these hydrogen-bonding interactions are taken into account, water

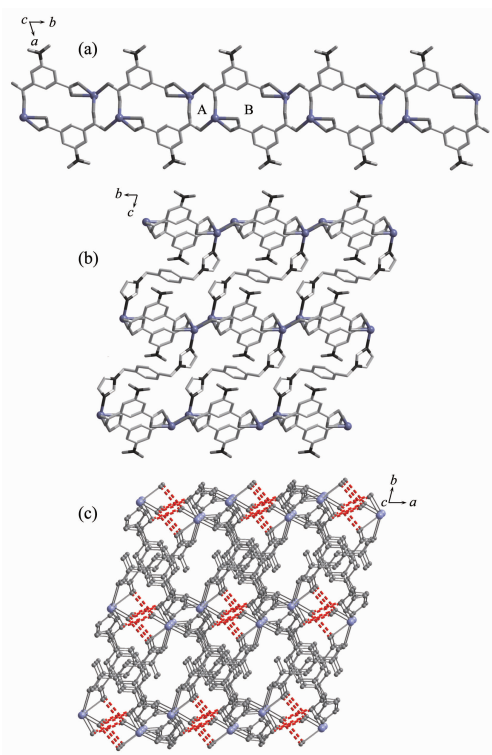


Fig.2 (a) 1D chain structure of complex **1** with alternately contain 8-member (A) ring and 16-member ring (B); (b) 2D layer structure viewed along the *b*-axis; (c) 3D H-bonded supramolecular structure of **1**

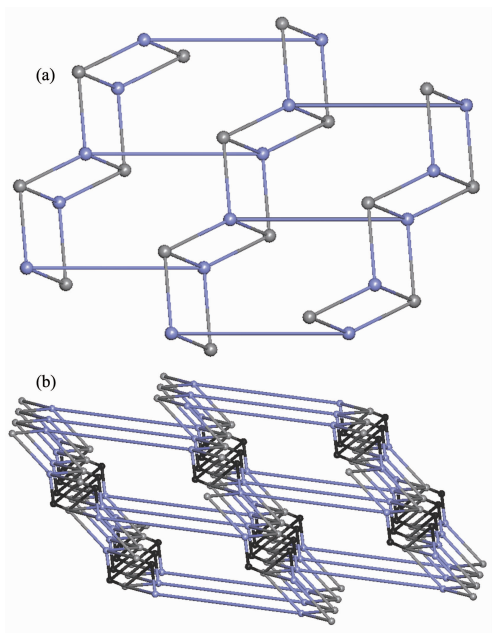


Fig.3 (a) View of (3,4)-connected V_2O_5 topology of **1** (hydrogen bonding is not considered); (b) view of (3,5,5)-connected topology (hydrogen bonding is considered, sky-blue for Pb^{II} , gray for H_2pimdc^- and block for water ligand)

molecules can be regarded as 3-connected nodes with vertex symbols of (3.4.5), while Cd^{II} and nip^{2-} ligand act as 5-connected nodes with vertex symbol of (3.4.4.5.6.6.6.6.7.8₅) and (3.4.4.4.5.5.6.6.2.7.7₃), respectively. In this case, the overall 3D network is trinodal (3,5,5)-connected net, and its Schlfli symbol is {3.4.5} {3.4².5.6⁴.7.8} {3.4³.5².6².7²} analyzed by Topos program^[19], as shown in Fig.3b. As far as we know, although mixed-connected or high connected supramolecular networks have been demonstrated^[20-21], the unique topological net with mixed-connected node is rarely discussed in supramolecular framework based on 2D coordination networks up to now^[22]. The net in **1** represents a new mixed connected topology supramolecular structure.

2.2 Thermogravimetric analyses

The TG curves of complex **1** exhibits two weight-loss steps. The first minor weight-loss of 3.96% ranging from 140 to 180 °C, which can be attributed to the removal of the coordinated water molecule (calcd. 3.92%). The second weight-loss of 69.24% in the temperature range of 350~460 °C can be ascribed to the loss of all organic ligands. The whole weight losses of 73.20% are in good agreement with the calculated values 72.00%.

2.3 Photoluminescent properties

The photoluminescent spectra of **1** has been measured at room temperature, as shown in Fig.4, the compound **1** exhibits two intense emission peaks at 425 and 470 nm ($\lambda_{\text{ex}}=300$ nm). In comparison with the N-donor ligand, the first emission peak (425 nm) may arise from $\pi^* \rightarrow \pi$ transitions of the bix ligands because

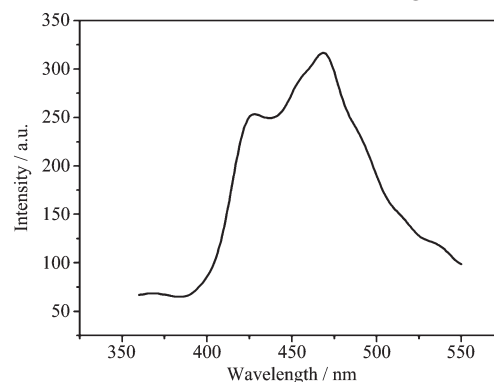


Fig.4 Solid-state photoluminescent spectra of **1** at room temperature

a similar peak also appears for the free bix ligand^[23-24], the second emission peak (470 nm) may be due to the ligand-to-metal charge-transfer (LMCT) band^[25].

References:

- [1] Krische M J. *Angew. Chem., Int. Ed.*, **2007**, **46**:8342-8345
- [2] Spokoyny A M, Kim D, Sumrein A, et al. *Chem. Soc. Rev.*, **2009**, **38**:1218-1227
- [3] Hoebein F J M, Jonkheijm P, Meijer E W, et al. *Chem. Rev.*, **2005**, **105**:1491-1502
- [4] Xu G C, Ding Y J, Okamura T A, et al. *CrystEngComm*, **2008**, **10**:1052-1062
- [5] Beatty A M. *Coord. Chem. Rev.*, **2003**, **246**:131-143
- [6] Su Z, Xu J, Fan J, et al. *Cryst. Growth Des.*, **2009**, **9**:2801-2811
- [7] Rowsell J L C, Spencer E C, Eckert J, et al. *Science*, **2005**, **309**:1350-1354
- [8] Williams C A, Blake A J, Hubberstey P, et al. *Chem. Commun.*, **2005**:5435-5437
- [9] Yang J, Ma J F, Batten S R, et al. *Chem. Commun.*, **2008**:2233-2235
- [10] Habib H A, Sanchiz J, Janiak C. *Inorg. Chim. Acta*, **2009**, **362**:2452-2460
- [11] Chen P K, Batten S R, Qi Y, et al. *Cryst. Growth Des.*, **2009**, **9**:2756-2762
- [12] Lan Y Q, Li L S, Qin J S, et al. *Inorg. Chem.*, **2008**, **47**:10600-10614
- [13] Zhang M L, Li D S, Wang J J, et al. *Dalton Trans.*, **2009**:5355-5364
- [14] Fu F, Li D S, Wu Y P, et al. *CrystEngComm*, **2010**, **12**:1227-1237
- [15] Gao X M, Li D S, Wang J J, et al. *CrystEngComm*, **2008**, **10**:479-482
- [16] Sheldrick G M. *SHELX-97, Program for Crystal Structure Determinations*, University of Göttingen, Germany, **1997**.
- [17] CHEN Hong(陈宏), XU Heng(徐衡), LIU Guang-Xiang(刘光祥), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2009**, **25**(8):1508-1512
- [18] Ma Y, Han Z B, He Y K, et al. *J. Coord. Chem.*, **2008**, **63**:563-570
- [19] Blatov V A, Shevchenko A P, Serezhkin V N. *J. Appl. Cryst.*, **2000**, **33**:1193
- [20] Fu F, Li D S, Yang X G, et al. *Synth. React. Inorg. M.*, **2009**, **39**:373-378
- [21] Baburin I A, Blatov V A, Carlucci L. *CrystEngComm*, **2008**, **10**:1822-1838
- [22] Baburin I A, Blatov V A, Carlucci L, et al. *Cryst. Growth Des.*, **2008**, **8**:519-539
- [23] Zheng S L, Zhang J P, Chen X M, et al. *Chem. Eur. J.*, **2003**, **9**:3888-3906
- [24] Guo Z, Cao R, Li X, et al. *Eur. J. Inorg. Chem.*, **2007**, **5**:742-748
- [25] Luo J H, Hong M C, Wang R H, et al. *Eur. J. Inorg. Chem.*, **2003**, **14**:2705-2710