

Note

Synthesis and Crystal Structure of a Novel Hydrogen-Bonded Three-Dimensional Polymer [Zn(1,4-benzenedicarboxylate)(pyridine)·H₂O]_n

WANG, Rui-Hu(王瑞虎) HONG, Mao-Chun*(洪茂椿) WENG, Jia-Bao(翁家宝)
CAO, Rong*(曹荣) LUO, Jun-Hua(罗军华)

State Key Laboratory of Structural Chemistry, Fujian Institute of the Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

A zinc(II) complex [Zn(bdc)(py)·H₂O]_n (bdc = 1,4-benzenedicarboxylate, py = pyridine) has been prepared and characterized. Single crystal X-ray diffraction analysis reveals that the complex crystallizes in the monoclinic space group *P*2₁/*n* with *a* = 0.84823(3), *b* = 0.91440(3), *c* = 1.65141(2) nm, β = 91.243(2)°, *V* = 1.28057(6) nm³, *Z* = 4. The coordination geometry at each Zn(II) center is a distorted tetrahedron. Two independent bdc ligands in a herringbone pattern link alternatively four-coordinated Zn(II) centers into a one-dimensional polymeric chain. Hydrogen bonds among coordinated water molecules and uncoordinated oxygen atoms of two independent bdc ligands from different polymeric chains extend one-dimensional polymeric chains into a three-dimensional structure.

Keywords crystal structure, 1,4-benzenedicarboxylate, zinc(II) polymer, hydrogen bonding

Introduction

Design and syntheses of novel supramolecular complexes with unusual and tailorable structures are fundamental steps in discovery and fabrication of various technologically useful functional supramolecular devices.¹⁻³ Recently, considerable efforts have been devoted to crystal engineering of supramolecular architectures sustained by coordination covalent bonding, hydrogen bonding or some molecular interactions and their combination owing to their fascinating structural diversity and potential appli-

cation in design of porous materials with novel inclusion or reactivity properties and in supramolecular devices such as sensor and indicator.⁴⁻¹³ Many promising supramolecular architectures in crystal engineering have been designed and constructed from mono- or poly-nuclear complexes,⁵⁻¹⁰ low-dimensional coordination polymers¹⁰⁻¹⁴ through using hydrogen bonds as a tool.

The 1,4-benzenedicarboxylate (bdc) ligand has been extensively studied in the field of molecular magnetism and microporous materials due to bdc exhibiting a variety of chelating or bridging abilities.¹⁵⁻²⁶ Assembly with suitable metal ions has produced a series of coordination polymers, such as one-dimensional chain coordination polymers,^{15,16} two- or three-dimensional coordination polymers in the shape of layers and networks.¹⁷⁻²³ In Zn-bdc complexes, several porous polymers which could absorb and disabsorb small gas molecules have been reported by Yaghi.¹⁹⁻²² We have also obtained a porous zeotype polymer {[Zn₄(OH)₂(bdc)₃(dmsO)₄]·2H₂O}_n built from [Zn₄(OH)₂]⁶⁺ rhombic cluster units and bdc ligands.²³ These are constructed by means of covalent bonds. Considering that materials held together by weak interactions such as hydrogen bonding and π-π stacking interactions have more advantages in synthetic modification and manipulation, host-guest application, molecular recognition, separation and catalysis,^{24,26} some hydrogen-

* E-mail: hmc@ms.fjirsm.ac.cn; Fax: 86-591-3714946

Received March 4, 2002; revised May 13, 2002; accepted May 12, 2002.

Project supported by the National Natural Science Foundation of China (No. 29825103), the Natural Science Foundation (No. 8982003) of Fujian Province and Chinese Academy of Sciences.

bonded one-dimensional and two-dimensional zinc (II)-bdc polymers have been designed and synthesized so far.^{25,26} Herein, a hydrogen-bonded three-dimensional zinc(II) polymer $[\text{Zn}(\text{bdc})(\text{py}) \cdot \text{H}_2\text{O}]_n$, constructed from one-dimensional polymer chain building blocks through inter-chain hydrogen bonding interactions is reported.

Experimental

Materials and measurements

1,4-benzenedicarboxylic acid was purchased from Fluka, and other reagents were purchased from Shanghai reagent Co. . All reagents were of reagent grade and used without further purification. IR spectrum as KBr disk was recorded on a Magna 750 FT-IR spectrophotometer. C, H and N elemental analyses were determined on an Elementar Vario ELIII elemental analyzer.

Synthesis of $[\text{Zn}(\text{bdc})(\text{py}) \cdot \text{H}_2\text{O}]_n$

A mixture of 1,4-benzenedicarboxylic acid (0.08 g, 0.5 mmol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 g, 0.5 mmol), 4,4'-diaminodiphenylmethane (0.10 g, 0.5 mmol) and pyridine (1 mL) in H_2O (16 mL) was placed in a Parr Teflon-lined stainless steel vessel and heated at 160 °C for 72 h, then cooled to room temperature during 5 h. Colorless crystals were obtained and collected by filtration

and washed with water (yield 65%, based on bdc). IR (KBr) ν : 3080 (br. s), 1610 (s), 1585 (vs), 1551 (s), 1504 (vs), 1487 (s), 1450 (vs), 1400 (vs), 1379 (vs), 1309 (m), 1215 (m), 1151 (w), 1095 (vw), 1066 (m), 1047 (m), 1020 (m), 976 (vw), 889 (vw), 879 (vw), 849 (m), 837 (m), 808 (w), 762 (m), 750 (s), 739 (s), 706 (s), 642 (m), 588 (m), 565 (m), 509 (w), 496 (v), 442 (vw), 424 (w) cm^{-1} . Anal. calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_5\text{Zn}$: C 48.16, H 3.37, N 4.29; found C 48.28, H 3.21, N 4.33.

X-Ray crystallography

Intensity data were measured on a Siemens Smart CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.071073$ nm) at 298 K. Empirical absorption corrections were applied by using the SADABS program. The structure was solved by direct methods and all calculations were performed using the SHELXL PC program. The positions of H atoms were generated geometrically (C—H bond lengths were fixed at 0.096 nm), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The structure was refined by full-matrix least-squares minimization of $\sum (F_o^2 - F_c^2)$ with anisotropic thermal parameters for all atoms except the H atoms. The crystal data and structure determination summary are given in Table 1, atomic coordinates and equivalent isotropic displacement parameters are given in Table 2 and the selected bond lengths and angles are listed in Table 3.

Table 1 Crystallographic data for $[\text{Zn}(\text{bdc})(\text{py}) \cdot \text{H}_2\text{O}]_n$

Formula	$\text{C}_{13}\text{H}_{11}\text{NO}_5\text{Zn}$	μ (mm^{-1})	1.936
M_r	326.60	$F(000)$	664
Crystal size (mm)	$0.54 \times 0.22 \times 0.08$	T (K)	293(2)
Crystal system	monoclinic	λ (Mo K α) (nm)	0.071073
Space group	$P2_1/n$	Reflections collected	4591
a (nm)	0.84823(3)	Unique reflections	2255
b (nm)	0.91440(3)	Observed reflections	1569
		[$F > 4.0\sigma(F)$]	
c (nm)	1.65141(2)	Parameters	181
β (°)	91.243(2)°	Goodness-of-fit on F^2	1.063
Z	4	R_1	0.0755
V (nm^3)	1.28057(6)	R_w	0.2192
ρ_{calcd} (g/cm^3)	1.694	$\Delta\rho_{\text{min}}$ and $\Delta\rho_{\text{max}}$ (e/nm^3)	1816 and -852

Table 2 Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($\text{nm}^2 \times 10^{-5}$) for $[\text{Zn}(\text{bdc})(\text{py}) \cdot \text{H}_2\text{O}]_n$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Zn(1)	3059(1)	4722(1)	3721(1)	30(1)
N(1)	5303(7)	4140(8)	3434(4)	34(2)
O(1)	1909(7)	3485(6)	4493(4)	39(1)
O(2)	2210(7)	2012(6)	3453(3)	38(1)
O(3)	3376(7)	6482(6)	4381(3)	38(1)
O(4)	3811(8)	7714(6)	3255(3)	48(2)
O(5)	1929(7)	5035(6)	2669(4)	37(1)
C(11)	1707(9)	2256(8)	4134(5)	28(2)
C(12)	819(9)	1096(8)	4587(4)	28(2)
C(13)	411(11)	-210(10)	4206(5)	39(2)
C(14)	-392(10)	-1294(9)	4593(5)	39(2)
C(15)	4579(11)	10096(9)	5804(5)	34(2)
C(16)	4027(9)	8945(9)	5330(5)	32(2)
C(17)	4420(9)	8853(8)	4523(5)	30(2)
C(18)	3815(9)	7618(8)	4009(5)	33(2)
C(21)	6548(10)	4694(10)	3860(6)	40(2)
C(22)	8072(11)	4288(12)	3679(6)	48(2)
C(23)	8307(11)	3324(12)	3068(6)	53(3)
C(24)	7060(12)	2762(12)	2647(6)	54(3)
C(25)	5572(11)	3175(11)	2840(5)	43(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected bond lengths and angles for $[\text{Zn}(\text{bdc})(\text{py}) \cdot \text{H}_2\text{O}]_n$

Bond lengths (nm)		Bond angles ($^\circ$)	
Zn(1)—O(3)	0.1958(5)	O(3)—Zn(1)—O(1)	100.1(2)
Zn(1)—O(1)	0.1977(5)	O(3)—Zn(1)—O(5)	115.2(2)
Zn(1)—O(5)	0.1987(6)	O(1)—Zn(1)—O(5)	114.3(2)
Zn(1)—N(1)	0.2042(6)	O(3)—Zn(1)—N(1)	103.1(3)
O(1)—C(11)	0.1280(10)	O(1)—Zn(1)—N(1)	118.4(3)
O(2)—C(11)	0.1231(9)	O(5)—Zn(1)—N(1)	105.6(3)
O(3)—C(18)	0.1267(9)	O(4)—C(18)—O(3)	123.2(8)
O(4)—C(18)	0.1248(10)	O(2)—C(11)—O(1)	122.4(7)

Results and discussion

The IR spectrum of the complex displays strong characteristic peaks of the dicarboxylate groups in the usual region at 1610 and 1551 cm^{-1} for the antisymmetric stretching frequency and 1400 and 1379 cm^{-1} for the symmetric stretching frequency. The separations (Δ) between $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ are 210 and 172 cm^{-1} ,

respectively. The Δ value of 210 cm^{-1} is much larger than 170 cm^{-1} in K_2bdc ²⁷ and consistent with the monodentate or bis-monodentate coordination mode of bdc.²⁸ However, the Δ value of 172 cm^{-1} from two slightly broad absorption bands suggests the existence of the semi-chelating bdc ligand.^{26,29}

Single crystal X-ray diffraction analysis reveals that the complex is made up of one-dimensional polymeric chains formed through two independent bdc ligands alternatively linking four-coordinated Zn(II) centers in a herringbone pattern. As shown in Fig. 1, each Zn(II) is in a distorted tetrahedral geometry and is coordinated by two carboxylate oxygen atoms from two independent bdc ligands, nitrogen atom of a pyridine and a water molecule. The dihedral angle of phenyl rings in two independent bdc ligands attached to Zn(II) center is 9.5°, exhibiting that they are approximately coplanar. The bond distances of Zn(1)—O(1) and Zn(1)—O(3) are 0.1977(5) and 0.1958(5) nm, respectively, which are close to those in $[\text{Zn}_2(\mu\text{-tu})(\text{tu})_2(\mu\text{-bdc})_2] \cdot 4\text{H}_2\text{O}$ (tu = thiourea).²⁵ However, the Zn(1)⋯O(2) distance of 0.2615 nm suggests a noticeable interaction between Zn(II) and the uncoordinated oxygen of one bis-monodentate bdc ligand, which may be described as a semi-chelating coordination mode,^{26,29} but Zn(1)⋯O(4) distance of 0.2917 nm suggests a non-bonded interaction between Zn(II) and the uncoordinated oxygen of the other bis-monodentate bdc ligand. Thus, the entirely bis-monodentate and semi-chelating bdc ligands link alternatively four-coordinated Zn(II) centers into a one-dimensional chain coordination polymer. To our knowledge, this is the first complex consisting of four-coordinated metal centers and two independent bdc ligands with entirely bis-monodentate and semi-chelating modes. The dihedral angle between carboxylate and phenyl ring in semi-chelating bdc ligand is 7.1° which is smaller than corresponding 20.9° in the entirely bis-monodentate ligand. The dihedral angles among pyridine ring and phenyl rings in the semi-chelating and entirely bis-monodentate bdc ligands are 116.6° and 122.2°, respectively.

It is worthy to note that water molecules act as hydrogen bonding donors and form hydrogen bonds with uncoordinated carboxylate oxygen atoms of two independent bdc ligands in different polymeric chains [O(5)—O(4)ⁱ 0.2680(8), O(5)—O(2)ⁱⁱ 0.2702(8) nm; symmetry code: (i) $-x + 1/2, y - 1/2, -z + 1/2$; (ii) $-x + 1/2, y + 1/2, -z + 1/2$]. As shown in Fig. 2, hydrogen

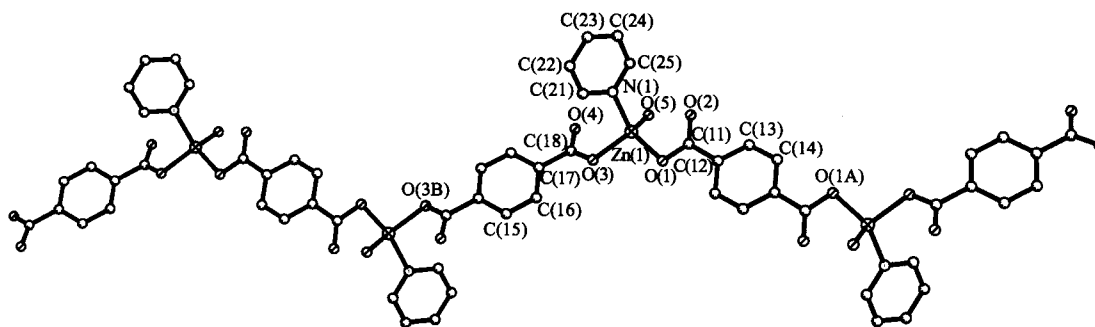


Fig. 1 View of one-dimensional chain in $[\text{Zn}(\text{bdc})(\text{py})\cdot\text{H}_2\text{O}]_n$ with atomic numberings.

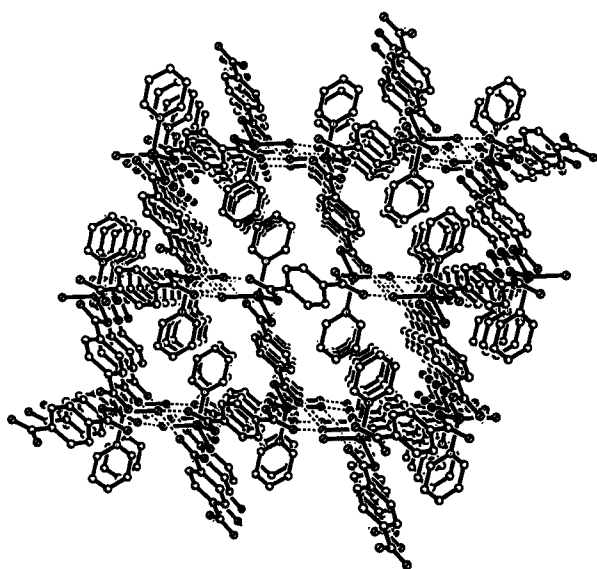


Fig. 2 View of the hydrogen-bonded three-dimensional structure in $[\text{Zn}(\text{bdc})(\text{py})\cdot\text{H}_2\text{O}]_n$ along b -axis.

bonding interactions extend the one-dimensional polymeric chains into a three-dimensional structure with pyridine ligands as space-filler.

Conclusion

Hydrothermal reaction of 1,4-dibenzene dicarboxylic acid, pyridine, 4,4'-diaminodiphenylmethane with $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ has produced a hydrogen-bonded three-dimensional complex constructed from one-dimensional polymeric chains, consisting of two independent bdc ligands and four-coordinated Zn(II) centers, via hydrogen bonding interactions. This work exhibits that the combination of coordination covalent bonds and hydrogen bonds is an important tool to construct promising supramolecular architectures by using one-dimensional polymeric chains

as building blocks.

References

- Hagman, P. J.; Hagman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.
- Makarevic, J.; Jokic, M.; Peric, B.; Tomisic, V.; Kojic-Prodic, B.; Zinic, M. *Chem. Eur. J.* **2001**, *7*, 3328.
- Zhang, H.; Wang, X.; Zhu, H.; Xiao, W.; Zhang, K.; Teo, B. K. *Inorg. Chem.* **1999**, *38*, 886.
- Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629.
- Pan, L.; Ching, N.; Huang, X.; Li, J. *Chem. Eur. J.* **2001**, *7*, 4431.
- Lai, S. F.; Cheng, C. Y.; Lin, K. J. *Chem. Commun.* **2001**, 1082.
- Kuehl, C. J.; Tabellion, F. M.; Arif, A. M.; Stang, P. J. *Organometallics* **2001**, *20*, 1956.
- Ma, B. Q.; Gao, S.; Sun, H. L.; Xu, G. X. *J. Chem. Soc., Dalton Trans.* **2001**, 130.
- Cai, J.; Chen, C. H.; Feng, X. L.; Liao, C. Z.; Chen, X. M. *J. Chem. Soc., Dalton Trans.* **2001**, 2370.
- Burrows, A. D.; Harrington, R. W.; Mahon, M. F.; Price, C. E. *J. Chem. Soc., Dalton Trans.* **2000**, 3845.
- You, X. Z. *Mater. Sci. Eng., C* **1999**, *10*, 59.
- Dong, Y. B.; Smith, M. D.; Layland, R. C.; Loye, H. C. J. *J. Chem. Soc., Dalton Trans.* **2000**, 775.
- Prior, T. J.; Rosseinsky, M. J. *Chem. Commun.* **2001**, 1222.
- Goher, M. A. S.; Mautner, F. A. *J. Coord. Chem.* **2001**, *53*, 79.
- Bakalbassis, E. G.; Bozopoulos, A. P.; Mrozinski, J.; Rentzeperis, P. J.; Tsiapis, C. A. *Inorg. Chem.* **1988**, *27*, 529.
- Deakin, L. D.; Arif, A. M.; Miller, J. S. *Inorg. Chem.* **1999**, *38*, 5072.
- Fun, H. K.; Raj, S. S. S.; Xiong, R. G.; Zuo, J. L.; Yu, Z.; You, X. Z. *J. Chem. Soc., Dalton Trans.*

- 1999, 1915.
- 18 Huang, Z. L.; Drillon, M.; Masciocchi, N.; Sironi, A.; Zhao, J. T.; Rabu, P.; Panissod, P. *Chem. Mater.* **2000**, *12*, 2805.
- 19 Li, H.; Eddaoudi, M.; O'keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.
- 20 Eddaoudi, M.; Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 1391.
- 21 Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8571.
- 22 Li, H.; Davis, C. E.; Groy, T. L.; Kelly, D. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 2186.
- 23 Wang, R. H.; Mao, C. H.; Liang, Y. C.; Cao, R. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2001**, *E57*, 277.
- 24 Aakeröy, C. B.; Beatty, A. M.; Leinen, D. S.; Lorimer, K. R. *Chem. Commun.* **1999**, 935.
- 25 Burrows, A. D.; Menzer, S.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 4237.
- 26 Guilera, G.; Steed, J. W. *Chem. Commun.* **1999**, 1563.
- 27 Bakalbassis, E. G.; Mrozinski, J.; Tsipis, C. A. *Inorg. Chem.* **1986**, *25*, 3684.
- 28 Zhang, H. X.; Kang, B. S.; Xu, A. W.; Chen, Z. N.; Zhou, Z. Y.; Chan, A. S. C.; Yu, K. B.; Ren, C. J. *J. Chem. Soc., Dalton Trans.* **2001**, 2559.
- 29 Addison, C. C.; Logan, N.; Wallwork, S. C.; Garner, C. D. *Quart. Rev. Chem. Soc.* **1971**, *25*, 289.

(E0203042 PAN, B. F.; DONG, H. Z.)