DOI: 10.1002/zaac.201100519

Synthesis, Structures, and Properties of two Helical Structures from Rigid Carboxylate Ligand and Flexible N-Bridging Ligands

Xia Li,[a] Wenjie Zhao,[b] Yue Zhang,[a] Yu Zhang,[a] Jinting Tan,[a] Yingli Lu,[a] Xing Feng,[a] and Xuwu Yang*[a]

Keywords: Helical structure; Porous framework; Three-fold interpenetrating architecture; Luminescence; Zinc; Cadmium

Abstract. Two novel coordination polymers based on mixed ligands, $[Zn(dpb)(bdc)(H_2O)]_n$ (**1**) and $[Cd(dpb)(bbdc)(H_2O)(DMF)]_n$ (**2**) [dpb = 1,4-bis(pyridin-3-ylmethoxy)benzene, H_2bdc = 1,4-benzenedicarboxylate, H_2bbdc = 4,4′-dibenzenedicarboxylate], were synthesized under hydrothermal conditions. Compound **1** forms *meso*-helical chain and shows three fold interpenetrating architecture with 4-connected net {66} diamond topology. Compound **2** is a left- and right-handed helical layer, which are interacted by π–π stacking interactions to construct a 3D framework. The luminescent properties of the compounds are discussed.

Introduction

Recently, metal-organic helical coordination polymers have received much attention because of their molecular self-assembly process and potential applications in asymmetric catalysis, non-linear optical materials, and biomimetic chemistry.[1] Until now, many single-, double-, triple-, and even multiple-stranded helices as well as circular and cylindrical helices have been prepared and studied.[2] However, the *meso*-helices and left- and right-handed helices with interpenetrating architecture or porous framework are infrequent.[3] Therefore, the major task for synthesizing such helical structures is to choose appropriate flexible N-bridging ligands and metal cations.[4] Further research is necessary to enrich and develop this field.

In accord with the literatures[5,6] the flexible N-bridging ligands, such as 1,2-bis(2-pyridyloxy)benzene,[5a] 1,3-bis(2-pyridyloxy)benzene,[5a] 1,4-bis(2-pyridylmethoxy)benzene,[5a] 1,4-bis(2-pyridyloxymethyl)-benzene,[5a–c] 1,4-bis(pyridin-3-ylmethoxy)benzene,[6g] 1,4-bis(pyridin-4-ylmethoxy)benzene,[6a,b] 4,4′-bis(pyridin-2-ylmethoxy)biphenyl, and bis[(4-pyridin-2-ylmethoxy)phenyl]methane[5d] were investigated for the construction of metal-organic coordination polymers. Using these flexible N-bridging ligands or their metal-organic coordination polymers with versatile topologies was obtained. These ligands have the following structural characters: (i) the neutral bis(pyridine) ligands exhibit the special ability to coordinate to various central metal atoms in multiform coordination fashions to formulate the compounds. (ii) The pyridine rings can freely twist around the $–O–CH_2–$ group to meet the requirements of the coordination arrangements of metal atoms in the assembly process, which often lead to helical structures, and can easily produce new classes of compounds. (iii) The large aromatic system could provide potential supramolecular recognition sites for π–π stacking interactions that could be used to govern the process of self-assembly.[7]

On the basis of the above considerations, we select 1, 4-bis(pyridin-3-ylmethoxy)benzene (dpb) as main ligand, and introduce 1,4-benzenedicarboxylate and 4,4′-biphenyldimethanoic acid with different spacer angles and lengths as ancillary ligands.[8,11] Two fascinating metal-organic helical coordination polymers, namely, $[Zn(dpb)(bdc)(H_2O)]_n$ (**1**) and $[Cd(dpb)(bbdc)(H_2O)(DMF)]_n$ (**1**) were synthesized under hydrothermal conditions. Compound **1** forms threefold interpenetrating architecture and **2** forms 3D framework by π–π stacking interactions. Both of them represent the rare examples of metal-organic helical coordination polymers with similar flexible N-bridging ligands. In addition, the luminescence properties of two compounds in the solid state have also been investigated.

Results and Discussion

Description of Crystal Structures

$[Zn(dpb)(bdc)(H_2O)]_n$ (1)

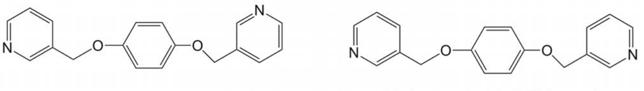
Compound **1** crystallizes in the monoclinic space group *C*2/*c*. The structure unit consists of one Zn^{II}, half of each dpb ligands, half of each deprotonated bdc ligands, and one coordi-

---

* Prof. Dr. X. Yang
Fax: +86-29-88303798
E-Mail: yangxuwu@nwu.edu.cn
[a] College of Chemistry and Materials Science
Agricultural Chemical Technology Institute
Shaanxi Key Laboratory of Physico-Inorganic Chemistry
Key Laboratory of Synthetic and Natural Functional
Molecule Chemistry of Ministry of Education
Northwest University
Xi′an 710069, P R China
[b] Department of Biochemical Engineering
Xian yang Vocational Technical College
Xian yang, 712000, P. R. China

Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201100519** or from the author.

nated water molecule. The Zn^{II} ion is five-coordinate in a distorted square-pyramidal arrangement, defined by one O1 atom from one coordinated water molecules, two oxygen atoms (O2, O2#1) from two half separated H_2bdc ligands, respectively, and two nitrogen atoms (N1, N1#1) from half of each different dpb ligands in the axial direction. The Zn–O bond lengths range from 1.979(2) to 2.024(3) Å, and Zn–N bond length is 2.174(3) Å. The Zn–O and Zn–N distances are quite similar to the normal Zn–O and Zn–N distances.[9,10] Each deprotonated carboxylic group of bdc^{2-} anion adopts monodentate mode to coordinate with adjacent Zn^{II} ions. Both dpb ligands adopt trans-monodentate bridging mode (Scheme 1a) to connect two adjacent Zn^{II} ions by the nitrogen atoms (Figure 1). Three dpb ligands are linked by four adjacent zinc ions to form a "Z" shape with a $Zn^{II}\cdots Zn^{II}\cdots Zn^{II}\cdots Zn^{II}$ torsion angle of 93°. Such "Z" shapes are bridged by dpb to form a extraordinary *meso*-helical chain with Zn···Zn distances of 23.06 Å (Figure 2a). The helical chains are further linked by deprotonated bdc ligands to construct a 3D wavelike structure (Figure 2b). Interestingly, the compound has mutual interpenetration of the independent equivalent frameworks in a normal mode, giving rise to a threefold interpenetrating architecture with 4-connected net {66} diamond topology (Figure 2c).



a) *trans*-monodentate bridging mode b) *cis*-monodentate bridging mode

Scheme 1. Coordination mode of dpb ligand, (a) *trans*-monodentate bridging mode, (b) *cis*-monodentate bridging mode.

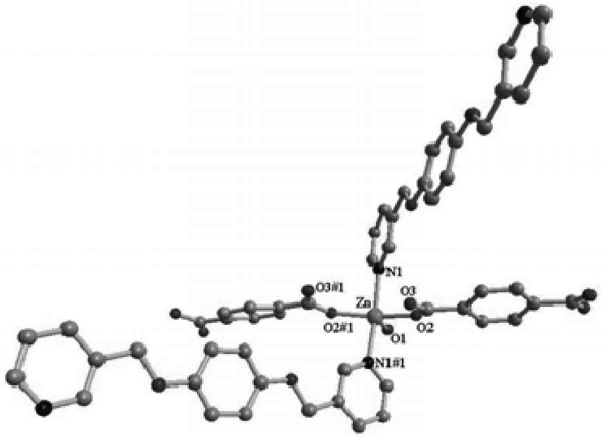


Figure 1. Coordination environment of the Zn^{II} ion in **1** (hydrogen atoms are omitted for clarity).

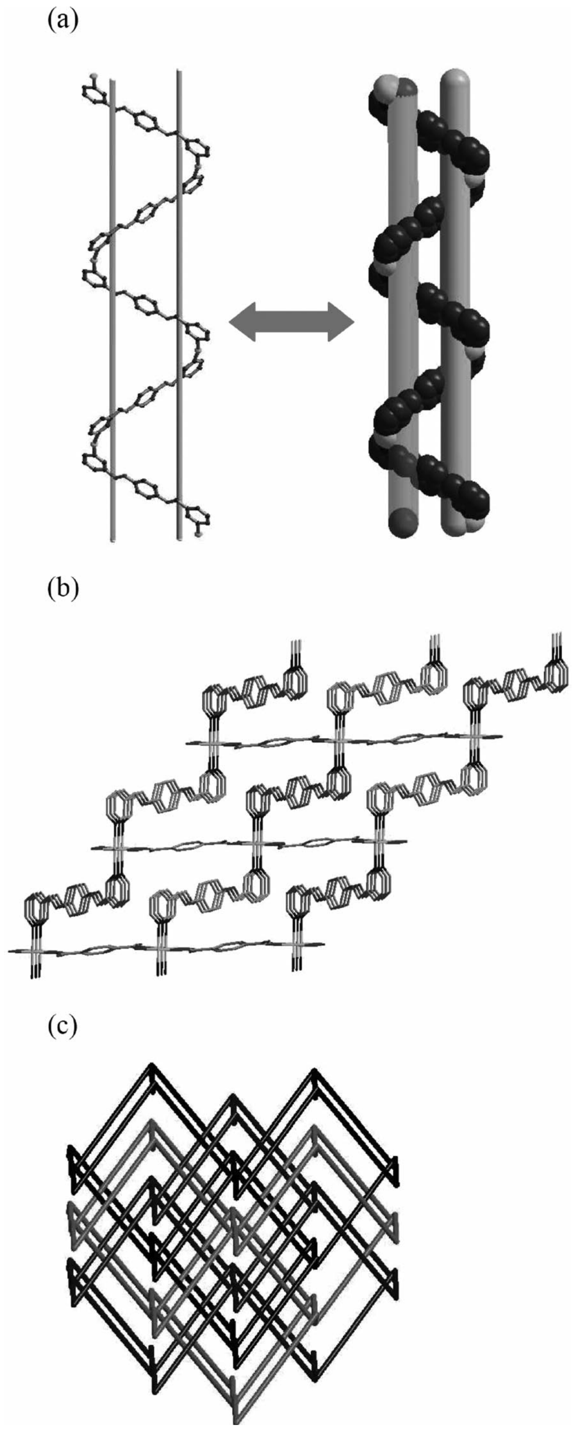


Figure 2. (a) "Z" shapes are bridged by dpb to form a extraordinary *meso*-helical chain. (b) Zn–bdc linear chains are linked by dpb ligands to form a 3D structure along *c* direction. (c)The compound has mutual interpenetration, giving rise to a threefold interpenetrating architecture.

$[Cd(dpb)(bbdc)(H_2O)(DMF)]_n$ *(2)*

Compound **2** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit consists of one Cd^{II}, half of each dpb ligands, half of each deprotonated bbdc ligands, one coordinated water molecule and one guest DMF molecule. The Cd^{II} ion adopts a distorted pentagonal bipyramidal arrangement by coordinating with two nitrogen atoms (N1, N2) from half of each distinct dpb ligands in the apical direction and in axial positions, four oxygen atoms (O1, O2, O3, and O4) from half of each different carboxylic groups, and O8 from one coordination water molecule (Figure 3). The Cd–N bond lengths are in the range of 2.331(7) to 2.347(7) Å, and the Cd–O bond lengths range from 2.390(6) to 2.458(6) Å, which are in the normal range.[10,11] Based on these coordination modes, each dpb ligand adopts *cis*-monodentate bridging mode (Scheme 1b) to connect two adjacent Cd^{II} ions via the nitrogen atoms and each bbdc ligands chelated two Cd^{II} ions via the carboxylate oxygen atoms. Two kinds of different ligands and Cd^{II} ions by appropriate coordination environments alternate one another form an infrequent left-handed right-handed helices (Figure 4a). The dpb–Cd–bbdc angle is 26.967°, four Cd^{II} ions of the single helix form parallelogram (Figure 4b). Interestingly, the pitch of the single helix is different, which dpb–bbdc–dpb is 19.3393 Å and bbdc–dpb–bbdc is 15.5873 Å. Moreover, left-handed right-handed helical 2D layers form a 3D framework by π–π stacking interactions (Figure 4c). In contrast to **1**, the dpb adopts *cis*-monodentate bridging mode owing to the fact that pyridin rings can freely twist around the $–O–CH_2–$ group.

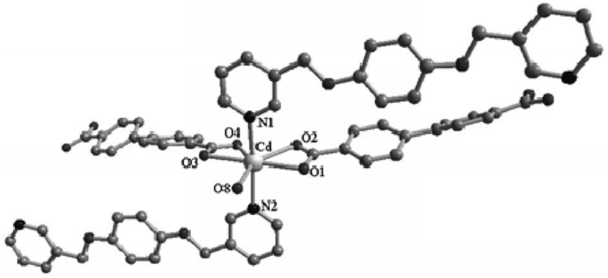


Figure 3. Coordination environment of Cd^{II} ion in **2** (hydrogen atoms and DMF molecules are omitted for clarity).

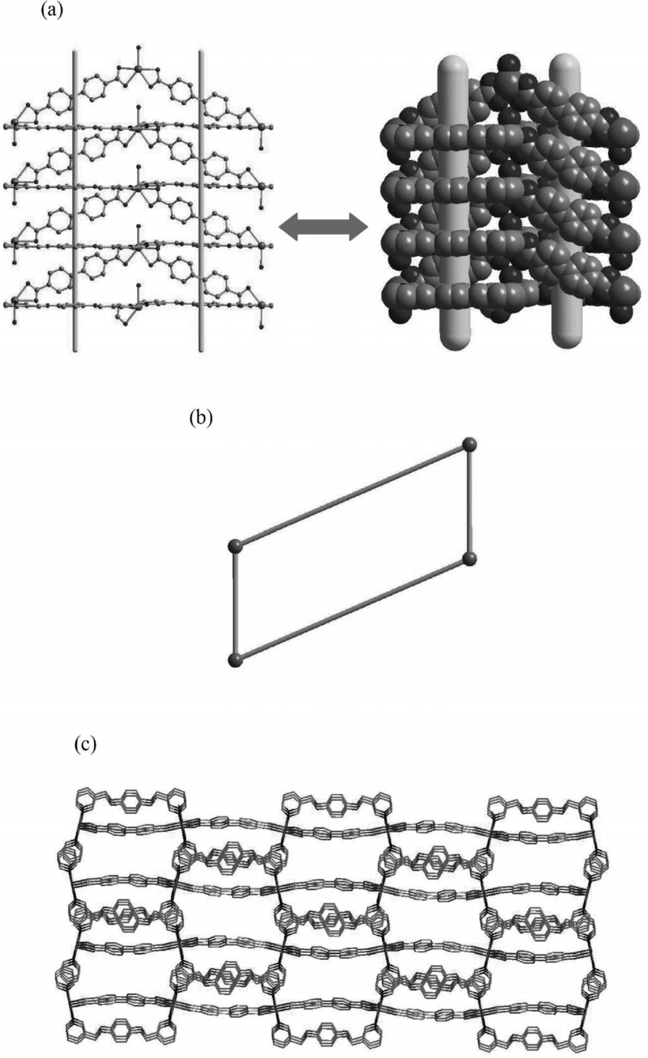


Figure 4. (a) View of the infrequent left-handed right-handed helical build by two different ligands and Cd^{II} ions alternate one another. (b) View the single helix form parallelogram. (c) View of the 3D framework by stacking of 2D layers.

IR Spectroscopy

The IR spectra of compounds **1** and **2** were performed as KBr pellets in the range 4000–400 cm^{-1}. The peaks of 1589 cm^{-1} and 1673 cm^{-1} are assigned to the skeleton vibration of C=N in **1** and **2**, respectively, which display certain shifts in contrast with 1594 cm^{-1} in the ligand (Figure S1, Supporting Information). It is thus assumed that nitrogen atoms in the ligand coordinate to metal atoms. The absorption band of C=O group at 1684 cm^{-1} disappeared in the compounds. The compound **1** shows the characteristic bands of the carboxylate group in the usual region[12] at 1360–1410 cm^{-1} for the symmetric vibration and at 1550–1630 cm^{-1} for the asymmetric, and the $\Delta[\nu_{as}(COO^-) - \nu_s(COO^-)] > 200\ cm^{-1}$ reveals that the carboxylate group is coordinated in a monodentate fashion.[13] And the compound **2** displayed both symmetric and asymmetric stretching vibrations of COO^- at 1388–1472 cm^{-1} and 1520–1578 cm^{-1}, respectively. The $\Delta[\nu_{as}(COO^-) - \nu_s(COO^-)] < 200\ cm^{-1}$ reveals that the carboxylate group is coordinated in a bidentate chelating coordination mode.[14] These proposals are in accordance with the crystal structures.

Luminescent Properties

Taking into account the excellent luminescent properties of d^{10} metal compounds, the luminescence of **1** and **2** were investigated (Figure 5). Additionally, to further comprehend the nature of these emission bands, the fluorescent spectra of dpb, H_2bdc, and H_2bbdc ligands were tested. The intense band in the emission spectra for **1** and **2** are observed at 419.5 nm (λ_{ex} = 280 nm) and 409.7 nm (λ_{ex} = 280 nm), whereas the pure H_2bdc and H_2bbdc ligands exhibit fluorescent emission band at 409.3 nm (λ_{ex} = 280 nm) and 430.5 nm (λ_{ex} = 280 nm), respectively. The emission peak of **1** is red-shifted by about 10.2 nm compared to pure H_2bdc ligand (Figure 5a), but **2** is blue-shifted by about 20.8 nm relative to that of the H_2bbdc ligand (Figure 5b). Since the Zn^{II} and Cd^{II} ions are difficult to be oxidized or reduced.[15] Thus, the significant red or blue shift of the band in contrast to that of ancillary ligand should be attributed to the intraligand (π–π*) fluorescent emission.

Thermogravimetric Analysis and PXRD Patterns

In order to examine the thermal stability of the two compounds, thermal gravimetric (TG) analyses were carried out for **1** and **2** (Figure S2, Supporting Information). The TG curve of **1** exhibits three weight loss stages in the temperature ranges of 160–228 (3.2 %), 228–333 (29.3 %), and 333–590

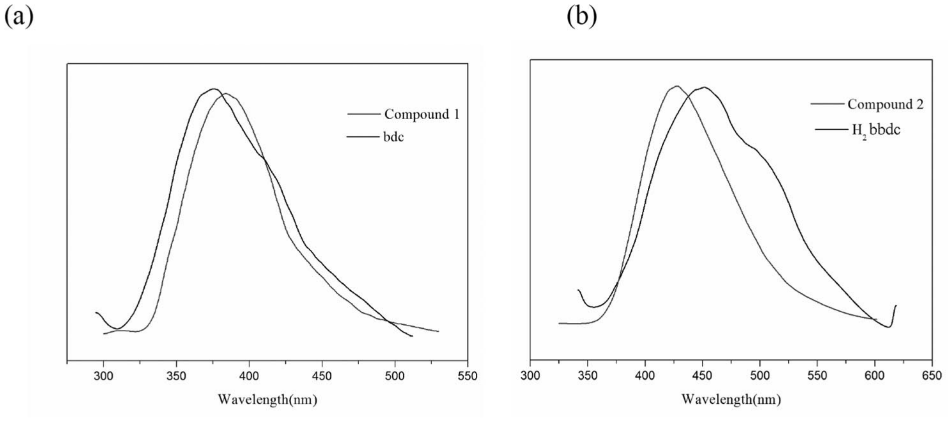


Figure 5. Luminescence spectra of compounds **1** and **2** in the solid state.

(52.72 %), corresponding to the release of water molecules, dpb, and bdc ligands, respectively. The residue is ZnO (15.16 %).

The TG curve of **2** exhibits two weight loss stages in the temperature ranges of 100–190 (12.38 %), 254–641 (72.36 %), corresponding to the release of water and DMF molecules, dpb and bbdc ligands. The residue is CdO (17.31 %). Additionally, to confirm the phase purity of the compounds **1** and **2**, the original samples are both characterized by X-ray powder diffraction (XRPD) at room temperature. The peak positions simulated from the single-crystal X-ray data of **1** and **2** are in good agreement with those observed (Figure S3, Supporting Information).

Conclusions

We have presented a rational synthetic strategy that successfully provides two metal-organic helical coordination polymers by combining long flexible N-bridging ligands and rigid carboxylic group ancillary ligands. The structure of two compounds provides the rare examples of metal-organic helical coordination polymers with similar flexible N-bridging ligands. The solid-state fluorescent analyses show that compounds **1** and **2** exhibit luminescence properties.

Experimental Section

Materials and Physical Measurements: All reagents were obtained commercially and used without further purification. The C, H, and N contents were measured with a Vario EL III elemental analyzer (Germany). The standard deviation for C, H, and N is < 0.1 %. The thermal analysis TG experiment of the complex was performed with a Perkin–Elmer thermogravimetric instrument in a nitrogen atmosphere at a flow rate of 60 $cm^3 \cdot min^{-1}$. The heating rate used was 10 $K \cdot min^{-1}$ from ambient temperature to 1000 K, with a sample weight of about 5 mg. X-ray power diffraction (XRPD) data were recorded with a Rigaku RU200 diffractometer at 60 kV, 300 mA for Cu-K_α radiation (λ = 1.5406 Å), with a scan speed of 2 $K \cdot min^{-1}$ and a step size of 0.02° in 2θ. Fluorescence spectra were measured with a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

Preparation of [Zn(dpb)(bdc)(H_2O)]$_n$ (1): A mixture of Zn(NO_3)$_2 \cdot 6H_2O$ (0.0195 g, 0.08 mmol), H_2bdc (0.0085 g, 0.05 mmol), and dpb (0.013 g, 0.05 mmol) was dissolved in distilled water (8 mL), and sealed into a 25mL Teflon-lined autoclave. The mixture was heated to 180 °C for 4 h and kept under autogenous pressure at 180 °C for 3 days. After cooling to room temperature at a rate 2 $K \cdot h^{-1}$, yellow block-shaped crystals of **1** were filtered out and washed with distilled water. Yield about 45 % based on Zn. Anal. $C_{20}H_{22}N_2O_7Zn$: calcd. C 51.35; H 4.74; N 5.99 %; found: C 51.26; H 4.62; N 5.91 %. **IR** (KBr): $\tilde{\nu}$ = 3729 (s), 3099 (w), 3054 (w), 1589 (m), 1504 (vs), 1427 (s), 1374 (s), 1234(vs), 1120 (m), 1052 (s), 806 (s), 757 (s), 694 (s) cm^{-1}.

Preparation of [Cd(dpb)(bbdc)(H_2O)(DMF)]$_n$ (2):A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.014 g, 0.065 mmol), H_2bbdc (0.0124 g, 0.05 mmol) and dpb (0.013 g, 0.05 mmol) was dissolved in distilled water (5 mL) and DMF (3 mL). The mixture was heated to 150 °C for 4 h and kept under autogenous pressure at 150 °C for 3 days. After cooling to room temperature at a rate 2 $K \cdot h^{-1}$, yellow block-shaped crystals of **2** were filtered out and washed with distilled water. Yield about 50 % based on Cd. Anal. $C_{35}H_{31}N_2O_8Cd$: calcd. C 58.38; H 4.34; N 3.89 %; found: C 58.29; H 4.45; N 3.78 %. **IR** (KBr): $\tilde{\nu}$ = 3415 (vs), 3060 (w), 2917 (w), 1941 (m), 1673 (vs), 1581 (vs), 1523 (vs), 1386 (vs), 1238 (vs), 1199 (m), 1047 (s), 838 (s), 767 (s), 684 (s) cm^{-1}.

X-ray Crystallography: Intensity data were collected with a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at room temperature. The structure was solved by direct methods and refined with full-matrix least-squares on F^2 with the SHELXL-97 program package.[16] All non-hydrogen atoms were located with difference Fourier synthesis, and the hydrogen atoms were generated geometrically. Crystal data collection and refinement parameters for compounds are shown in Table 1, and the selected bond lengths and angles are listed in Table S1 (Supporting Information).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-784391 and CCDC-842458 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): IR spectra, TG curves, Powder X-ray diffraction patterns, and bond lengths and angles of compounds **1** and **2**.

Table 1. Crystallographic data and structure refinement parameters for compounds **1** and **2**.

compounds	1	2
Empirical formula	$C_{26}H_{20}ZnN_2O_7$	$C_{35}H_{31}CdN_3O_8$
Formula weight	537.81	734.03
Temperature /K	296(2)	296(2)
Wavelength /Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1$/c
Unit cell dimensions /Å, °	a = 18.326(3)	a = 6.7730(13)
	b = 5.9882(9)	b = 28.525(5)
	c = 21.995(3)	c = 17.297(3)
	α = 90	α = 90
	β = 101.910(2)	β = 101.967(2)
	γ = 90	γ = 90
Volume /Å^3	2254.8(6)	3120.5(10)
Z	4	4
Calculated density /mg·m^{-3}	1.584	1.562
Absorption coefficient /mm^{-1}	1.142	0.759
F (000)	1104	1496
Crystal size /mm	0.30 × 0.25 × 0.14	0.30 × 0.28 × 0.16
Range for data collection /°	1.98 to 25.09	1.43 to 25.10
Limiting indices	$-21 \leq h \leq 21$	$-8 \leq h \leq 8$
	$-7 \leq k \leq 7$	$-34 \leq k \leq 30$
	$-26 \leq l \leq 18$	$-20 \leq l \leq 13$
Reflections collected/unique	5379 / 1992[R (int) = 0.0244]	15488/5550[R (int) = 0.0563]
Completeness to θ = 25.10	99.5 %	99.5 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3002 / 2 / 256	5522 / 1 / 416
Goodness-of-fit on F^2	1.061	1.161
Final R indices [$I > 2$ sigma (I)]	$R1$ = 0.0358, $wR2$ = 0.0862	$R1$ = 0.0867, $wR2$ = 0.2218
R indices (all data)	$R1$ = 0.0473, $wR2$ = 0.0956	$R1$ = 0.1026, $wR2$ = 0.2
Largest diff. peak, hole /e·Å^{-3}	0.618, –0.307	3.766, –1.293

Acknowledgement

The Author is thankful for “13115“ *S&T Innovation Program of Shaanxi Province* (No. 2008ZDKG-22).

References

[1] a) M. Munakata, L. P. Wu, T. Kuroda-Sowa, *Adv. Inorg. Chem.* **1999**, *46*, 173–303; b) C. R. Woods, M. Benaglia, F. Cozzi, J. S. Siegel, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1830; c) C. Piguet, G. Bernardinelli, *Chem. Rev.* **1997**, *74*, 2005–2062; d) G. W. Orr, L. J. Barbour, J. L. Atwood, *Science* **1999**, *285*, 1049–1052; e) X. H. Bu, M. L. Tong, H. C. Chang, S. Kitagawa, S. R. Batten, *Angew. Chem. Int. Ed.* **2004**, *43*, 192–195; f) J. P. Zhang, Y. Y. Lin, X. C. Huang, X. M. Chen, *Chem. Commun.* **2005**, 1258–1260; g) J. Zhao, L. Mi, J. Hu, H. Hou, Y. Fan, *J. Am. Chem. Soc.* **2008**, *130*, 15222–15223; h) T. B. Lu, X. D. Zheng, *CrystEngComm* **2010**, *12*, 324–336; i) A. Ramaswamy, M. Froeyen, P. Herdewijn, *J. Am. Chem. Soc.* **2010**, *132*, 587–595.

[2] a) S. R. Seidel, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2001**, *123*, 7740–7741; b) N. Malabika, K. Rajesh, S. E. Helen, M. Sasankasekhar, *Cryst. Growth Des.* **2005**, *5*, 1907–1912; c) M. C. Suen, Z. K. Chan, J. D. Chen, J. C. Wang, C. H. Hung, *Polyhedron* **2006**, *25*, 2325–2332; d) S. L. Li, Y. Q. Lan, J. S. Qin, J. F. Ma, J. Liu, J. Yang, *Cryst. Growth Des.* **2009**, *9*, 4142–4146; e) G. Zhang, S. Y. Yao, D. W. Guo, Y. Q. Tian, *Cryst. Growth Des.* **2010**, *10*, 2355–2359.

[3] a) Y. Cui, S. J. Lee, W. Lin, *J. Am. Chem. Soc.* **2003**, *125*, 6014–6015; b) D. R. Xiao, Y. G. Li, E. B. Wang, L. L. Fan, H. Y. An, Z. M. Su, L. Xu, *Inorg. Chem.* **2007**, *46*, 4158–4166; c) Y. Qi, F. Luo, S. R. Batten, Y. X. Che, J. M. Zheng, *Cryst. Growth Des.* **2008**, *8*, 2806–2813; d) J. C. Jin, Y. Y. Wang, P. Liu, R. T. Liu, C. Ren, Q. Z. Shi, *Cryst. Growth Des.* **2010**, *10*, 2029–2032.

[4] a) K. O. Ashiry, Y. H. Zhao, K. Z. Shao, Z. M. Su, Y. M. Fu, X. R. Hao, *Inorg. Chem. Commun.* **2008**, *11*, 1181–1183; b) J. Q. Chen, Y. P. Cai, H. C. Fang, Z. Y. Zhou, X. L. Zhan, G. Zhao, Z. Zhang, *Cryst. Growth Des.* **2009**, *9*, 1605–1613.

[5] a) M. H. Chris, J. S. Peter, *J. Chem. Soc., Dalton Trans.* **1998**, 3927–3933; b) J. S. Gao, Y. Liu, S. Zhang, G. F. Hou, P. F. Yan, *Acta Crystallogr. Sect. E* **2009**, *65*, o2432; c) O. Moonhyun, L. S. Charlotte, A. M. Chad, *Inorg. Chem.* **2005**, *44*, 2649.

[6] a) H. W. Hong, Y. N. Fan, L. P. Zhang, *Inorg. Chem. Commun.* **2001**, *4*, 168–172; b) P. Zou, Y. Liu, S. Zhang, X. Wang, J. S. Gao, *Acta Crystallogr. Sect. E* **2009**, *65*, o2570; c) S. L. Li, H. Y. Bai, J. Yang, *Acta Crystallogr. Sect. E* **2007**, *63*, m2911; d) S. L. Li, J. Liu, J. F. Ma, *Acta Crystallogr. Sect. E* **2007**, *63*, m3050; e) J. S. Gao, Y. Liu, S. Zhang, D. F. Zuo, G. F. Hou, *Acta Crystallogr. Sect. E* **2009**, *65*, o2457; f) P. Zou, Y. Liu, G. F. Hou, J. S. Gao, *Acta Crystallogr. Sect. E* **2011**, *67*, m692; g) Y. Liu, H. F. Zhang, G. F. Hou, J. S. Gao, *Acta Crystallogr. Sect. E* **2011**, *67*, m789.

[7] a) H. Y. Liu, H. Wu, J. F. Ma, Y. Y. Liu, B. Liu, J. Yang, *Cryst. Growth Des.* **2010**, *10*, 4795–4805; b) S. K. Chawla, M. Arora, K. Nattinen, K. Rissanen, J. V. Yakhmi, *Polyhedron* **2004**, *23*, 3007–3019.

[8] a) W. Chen, J. Wang, C. Chen, Q. Yue, H. Yuan, J. Chen, S. Wang, *Inorg. Chem.* **2003**, *42*, 944–946; b) J. Y. Sun, L. H. Weng, Y. M. Zhou, J. X. Chen, Z. X. Chen, Z. C. Liu, D. Y. Zhao, *Angew. Chem. Int. Ed.* **2002**, *41*, 4471–4473; c) Y. C. Liang, M. C. Hong, R. Cao, Y. C. Liang, J. B. Weng, W. P. Su, *Inorg. Chem. Commun.* **2001**, *4*, 599–601; d) J. Tao, X. Yin, R. B. Huang, L. S. Zheng, W. N. Seik, *Inorg. Chem. Commun.* **2002**, *5*, 975–977.

[9] a) M. Arpi, S. Shyamapad, R. C. Chirantan, R. B. Stuart, P. Guillaume, L. Dominique, D. Nathalie, P. S. Jean, C. Nitin, M. Samiran, *Inorg. Chim. Acta* **2005**, *358*, 3855–3864; b) J. P. Zhang, Y. Y. Lin, X. C. Huang, X. M. Chen, *Eur. J. Inorg. Chem.* **2006**, 3407–3412; c) Z. Su, J. Fan, T. A. Okamura, M. S. Chen, S. S.

Chen, W. Y. Sun, U. Norikazu, *Cryst. Growth Des.* **2010**, *10*, 1911–1922.

[10] a) S. L. Zheng, J. H. Yang, X. L. Yu, X. M. Chen, W. T. Wong, *Inorg. Chem.* **2004**, *43*,830–838; b) L. F. Ma, L. Y. Wang, J. L. Hu, Y. Y. Wang, G. P. Yang, *Cryst. Growth Des.* **2009**, *9*, 5334–5342; c) X. L. Chen, B. Zhang, H. M. Hu, F. Fu, X. L. Wu, T. Qin, M. L. Yang, G. L. Xue, J. W. Wang, *Cryst. Growth Des.* **2008**, *8*, 3706–3712.

[11] X. Shi, G. S. Zhu, X. H. Wang, G. H. Li, Q. R. Fang, G. Wu, G. Tian, M. Xue, X. J. Zhao, R. W. Wang, S. L. Qiu, *Cryst. Growth Des.* **2005**, *5*, 207–213.

[12] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, New York, **1958**.

[13] V. Zeleňák, I. Cl′saŕová, P. Llewellyn, *Inorg. Chem. Commun.* **2007**, *10*, 27–32.

[14] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, **1997**.

[15] a) Y. Su, S. Q. Zang, Y. Z. Li, H. Z. Zhu, Q. J. Meng, *Cryst. Growth Des.* **2007**, *7*, 1277–1283; b) L. L. Wen, D. B. Dang, C. Y. Duan, Y. Z. Li, Z. F. Tian, Q. J. Meng, *Inorg. Chem.* **2005**, *44*, 7161–7170.

[16] a) G. M. Sheldrick, *SHELXS-97*, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, **1997**; b) G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, **1997**.

Received: December 01, 2011