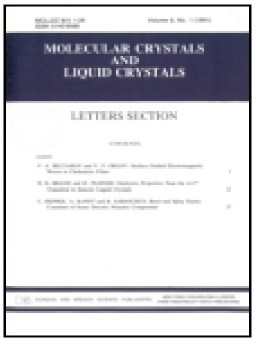

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A two-dimensional Zn(II) coordination polymer with a three-dimensional supramolecular architecture comprising 5-dimethylamino-isophthalic acid and 1,3-bis(4-pyridyl)propane

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ABSTRACT

A new zinc coordination polymer, $[Zn(L)(bpp)\cdot H_2O]_n$, was synthesized using 5-dimethylamino-isophthalic acid (H_2L) and 1,3-bis(4-pyridyl)propane (bpp) as organic linkers. In the complex, adjacent Zn^{2+} ions are linked by L^{2-} anions to form a one-dimensional (1D) $[ZnL]_n$ chain. Then bpp ligands expand the 1D chains into a corrugated two-dimensional (2D) layer network by linking neighboring Zn^{2+} ions. These adjacent layers are further stacked together by direct C—H$\cdots\pi$ supramolecular interactions, generating a three-dimensional (3D) supramolecular structure. From the viewpoint of topology, the 2D network can be rationalized to a uninodal four-connected non-interpenetrated sql/Shubnikov tetragonal plane net with $\{4^4.6^2\}$ topology. Moreover, the solid state properties such as thermogravimetric analysis and luminescence were also investigated.

KEYWORDS
Crystal structure; zinc coordination polymer; 1,3-bis(4-pyridyl)propane; 5-dimethylamino-isophthalate

Introduction

Research on the design and synthesis of coordination polymers (CPs) based on the selection of organic moieties and metal ions has received enormous attention in view of their novel structures and potential applications in many areas such as gas storage, molecular magnetism, nonlinear optical devices, catalysis, luminescence, and so on [1–5]. It is well known that many factors have great influence on structural control in self-assembled CPs, such as the choice of organic ligands, the coordination trend of metal ions, the metal/ligand ratio, anions, etc. Among the reported studies, polycarboxylate ligands such as benzenepolycarboxylates, pyridinecarboxylates, and imidazolecarboxylates have been employed as bridging ligands to construct diverse CPs, since they can exhibit a variety of coordination modes while coordinating to metal ions [6–8]. Recently, 5-tert-butyl isophthalic acid containing large steric hindrance has been employed as bridging ligand for constructing multidimensional CPs [9–11]. For example, Pan et al. reacted $Zn(NO_3)_2\cdot 6H_2O$ with 5-tert-butyl isophthalic acid and generated a highly stable guest-free microporous metal organic framework with unique gas separation capability [12]. Sun et al. recently has successfully applied 5-tert-butyl isophthalic acid

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and trans-1-(2-pyridyl)-2-(4-pyridyl) ethylene to construct four distinct CPs [13]. The presence of the electron-donating (-C(CH_3)$_3$) non-coordinating groups in isophthalic acid ligand changes its electronic and steric properties, which can generate CPs different from isophthalic acid ligand in the self-assembling of CPs.

Inspired by the above-mentioned work, bent 5-dimethylamino-isophthalic acid (H_2L) is introduced to construct CPs. From a structural point of view, H_2L is an efficient multidentate bridging ligand mainly because of their multiple carboxylate oxygen coordination sites, steric hindrance, and electronic properties on one hand. One the other hand, deprotonated H_2L may act as anions when coordinating to metal ions, and thus achieve charge balance without other anions as Cl^- or NO_3^- involved in the structure. Both of these features may increase the opportunity for novel structures and interesting properties to some extent. In this contribution, we report the synthesis and crystal structure of a new compound derived from H_2L and 1,3-bis(4-pyridyl)propane (bpp) mixed ligands.

Experimental

Materials and physical measurements

H_2L was prepared according to the literature method [14]. $Zn(NO_3)_2{\cdot}6H_2O$ and bpp were purchased from Fluka, and used as received. The reaction was performed in a 15 mL Pyrex glass tube under autogenous pressure. Elemental analyses for C, H, and N were carried out on a Flash 2000 elemental analyzer. The IR spectra were recorded as KBr pellets on a Nicolet Avatar-360 spectrometer in the range of 4000 to 400 cm^{-1}. Thermogravimetric analyses (TGA) were carried out on a SDTQ600 thermogravimetric analyzer. A platinum pan was used for heating the sample with a heating rate of 10°C min^{-1} under an N_2 atmosphere. Fluorescence measurements were recorded with a Hitachi F4500 fluorescence spectrophotometer.

Synthesis of the compound $[Zn(L)(bpp){\cdot}H_2O]_n$ (1)

A mixture of H_2L (20.9 mg, 0.1 mmol), bpp (19.8 mg, 0.1 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (29.8 mg, 0.1 mmol), 0.10 M NaOH (0.25 mL), and 5 mL deionized water was sealed in a 15 mL Pyrex glass tube and heated at 60°C for 5 days under autogenous pressure, followed by cooling to room temperature at a rate of 5°C hr^{-1}. Yellow block crystals of **1** were collected (yield: 23% based on Zn). Elemental analysis calcd (%) for $C_{23}H_{25}N_3O_5Zn$: C, 56.46; H, 5.11; N, 8.59. Found: C, 56.45; H, 5.18; N, 8.53. IR data (KBr, cm^{-1}): 3069(w), 3069(w), 2948(w), 2821(w), 1632(s), 1618(m), 1601(m), 1582(s), 1496(m), 1417(s), 1452(s), 1322(s), 1288(s), 1266(w), 1184(m), 1127(m), 1072(m), 1027(m), 934(s), 809(m), 703(m), 683(m), 666(s).

Crystallographic data collection and refinement

The structure of **1** was determined by the single-crystal X-ray diffraction technique. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with Mo-Ka radiation ($\lambda = 0.71073$ Å) at 293 K using phiand ω scan mode. Data reduction and absorption correction were made with SADABS software [15]. The structure was solved by direct methods and refined by full-matrix least-squares techniques using SHELXL-97 [16]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on water molecules were located from difference Fourier maps and were refined using riding model.

Table 1. Crystallographic data.

Empirical formula	$C_{23}H_{25}N_3O_5Zn$
Formula weight	488.83
Crystal system	Monoclinic
Space group	*P*2(1)/*c*
Unit cell dimensions	$a = 8.606(4)$ (Å), $b = 15.835(7)$ (Å), $c = 17.418(7)$ (Å), $\beta = 100.504(5)$ °
Volume (Å^3), Z	2334.0(17), 4
Calculated density (kg/m^3)	1.391
μ(mm^{-1})	1.090
Reflections collected/unique	13225/4328
F(000)	1016
R (int)	0.0416
GOF on F^2	1.022
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0438$, $wR_2 = 0.1022$
Final *R* indices (all data)	$R_1 = 0.0705$, $wR_2 = 0.1154$

Table 2. Selected bond lengths (Å) and bond angles (°) for **1** (symmetry code for **1**: #1 $x, -y + 0.5, z + 0.5$; #2 $2 - x, y - 0.5, 1.5 - z$).

Zn(1)–O(1)	1.943 (2)	Zn(1)–O(4)#1	1.971 (2)	Zn(1)–N(1)	2.054 (3)
Zn(1 –N(2)#2	2.046 (3)				
O(1)–Zn(1)–O(4)#1	109.66 (11)	O(1)–Zn(1)–N(2)#2	104.24 (11)	O(4)#1–Zn(1) –N(2)#2	120.74 (11)
O(1) –Zn(1) –N(1)	97.25 (11)	O(4)#1–Zn(1) –N(1)	117.23 (11)	N(2)#2–Zn(1) –N(1)	104.53 (11)

Other hydrogen atoms were placed at the calculation positions. A summary of the crystallographic data, selected bond lengths, and of **1** is listed in Tables 1 and 2, respectively.

Results and discussion

Complex **1** is a two-dimensional (2D) wavelike coordination polymer. Single crystal X-ray structural analysis exhibits that **1** crystallizes in the monoclinic system with a space group of *P*2(1)/*c*. As shown in Fig. 1, the asymmetric unit has one crystallographically independent Zn^{2+} ion, one L^{2-} anion, one bpp ligand, as well as one lattice water molecule. The Zn^{2+} ions are four-coordinated surrounded by two O atoms from two L^{2-} anions and two N atoms from two bpp ligands to form a distorted tetrahedron geometry. The maximum and minimum bond angles for Zn1 are 97.25(11) and 120.74(11)°, respectively, with an average value of 108.94(11)°, which slightly deviates from the angle of 109.47° in a perfect tetrahedron. The Zn—O bond lengths range from 1.943 (2)∼1.971 (2) Å, with an average value of about 1.957 Å, and Zn—N bond distances are 2.054 (3) and 2.046 (3) Å, respectively, which are within

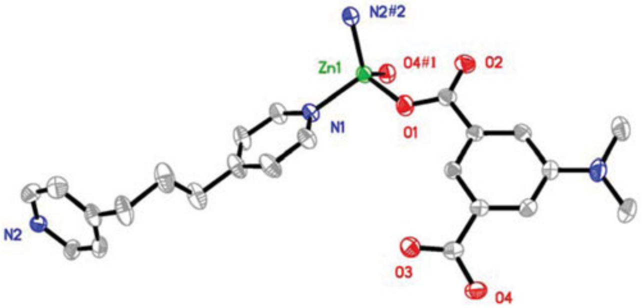

Figure 1. View of the coordination environment of Zn^{2+} ions of **1** (symmetry code for **1**: #1 $x, -y + 0.5, z +$ 0.5; #2 $2-x, y - 0.5, 1.5 -$).

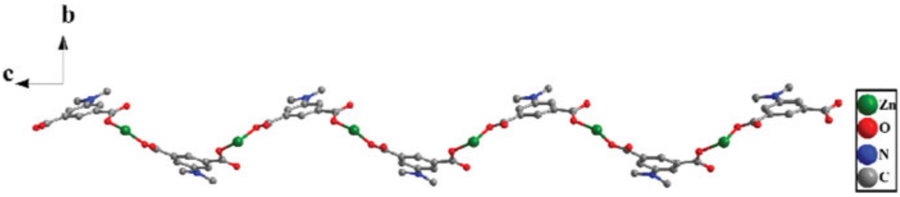

Figure 2. A view of the one-dimensional coordination chain of **1**, linked *via* bridging L^{2-} ligands.

the normal ranges in other Zn^{2+} complexes [17,18]. Each L^{2-} anion adopts a κ^1-κ^1-μ_2 coordination mode, linking adjacent Zn^{2+} ions to form a one-dimensional (1D) $[ZnL]_n$ chain along the c axial (Fig. 2), with the Zn···Zn distance of 8.7482 Å. Then, flexible bpp ligands further expand the 1D chains into a corrugated 2D network by linking neighboring Zn^{2+} ions (Fig. 3(a)). The bpp in the anti-gauche (TG) conformation separate Zn···Zn distance is 12.7571 Å along b axial. From the viewpoint of topology, the network can be rationalized to a 2D uninodal four-connected non-interpenetrated sql/Shubnikov tetragonal plane net with $\{4^4.6^2\}$ topology, in which the Zn^{2+} ions can be viewed as four-connected nodes, L^{2-} anions and bpp ligands are simplified as linear connectors (Fig. 3(b)). Notably, all four-connecting nodes in **1** adopt the tetrahedral geometries and, thus, result in a nonplanar feature of the 2D layer. The potential void space of the crystal, as calculated by PLATON software, was found to be 129.8 $Å^3$, which is approximately 5.6% of the unit cell volume.

Intramolecular O—H···O interactions (Fig. 4(a)) are observed between coordinated H2O molecules (O5) and carboxylate O2/O4 atoms of L^{2-} anions. Moreover, this structure also contains three kinds of strong C—H···π supramolecular interactions with an edge-to-face orientation ($d = 2.821$, 2.852, and 2.91Å; $A = 145$, 153, and 161°; d and A stand for H···π separations and C—H···π angles in the C—H···π patterns, respectively) as calculated by the PLATON program, which further result in an overall three-dimensional (3D) supramolecular network (Fig. 4(b)). To our knowledge, C—H···π stacking is a common interaction in the assembly of supramolecular compounds. However, three C—H···π stacking modes coexisting in one supramolecular complex are very limited.

In order to check the bulk purity of **1**, powder X-ray diffraction technique (PXRD) has been measured and compared with the result simulated from the single-crystal structure. The measured PXRD pattern is in good accord with the result simulated from the respective single-crystal data, indicative of pure product (Fig. 5). The differences in intensity may be owing to the variation in the preferred orientation of the powder sample. **1** is air-stable and insoluble in common solvents such as water, acetone, methanol, ethanol, toluene, acetonitrile, and N, N-dimethylformamide at room temperature. In the IR spectra of **1**, the characteristic

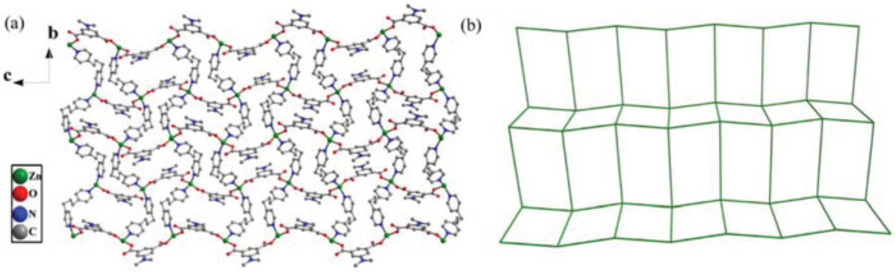

Figure 3. (a) A view of the two-dimensional network of **1**, extending in the *bc* plane. H atoms have been omitted for clarity; (b) A view of the topological structure of **1**.

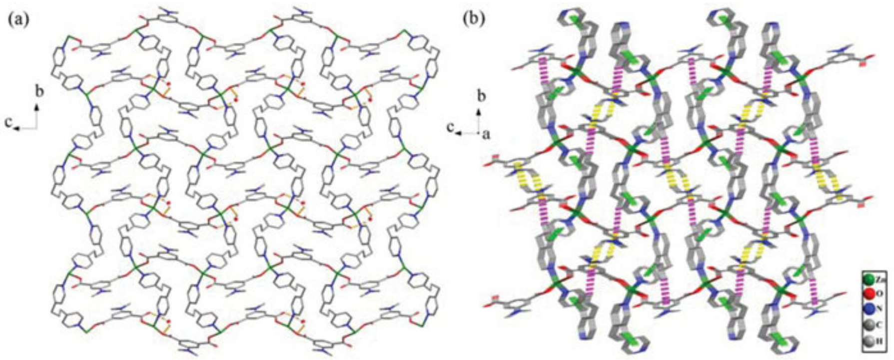

Figure 4. (a) Intramolecular H-bonding indicated by light orange dotted lines. (b) 3D supramolecular structure formed *via* C—H···π interactions indicated by yellow, bright green, and pink dotted lines, respectively. All H atoms except those related to C—H···π interactions have been omitted for clarity.

stretching vibrations of the carboxylate groups, of which the absorbance peaks in the range of 1582~1632 cm^{-1} and 1322~1496 cm^{-1}, are attributed to the asymmetric stretching and symmetric stretching, respectively. The absence of bands at the region of 1675~1710 cm^{-1} suggests the complete deprotonation of carboxylate groups in H_2L, which are in agreement with the crystallographic structural analysis. The broad medium intensity bands from about 3116 cm^{-1} could be assigned to the lattice water molecules. Thermal property of **1** was investigated by thermogravimetric analysis (TGA) experiments. The TGA curve of **1** suggests that the first weight loss of 3.65% occurs between 70°C and 86°C, which corresponds to the expulsion of one lattice water molecule (calculated: 3.68%). The main framework keeps stable up to 320°C followed by an intense weight loss, which is attributed to the decomposition of the framework (Fig. 6(a)).

It is well known that CPs with d^{10} metal configuration could be used as candidates for potential photoactive materials. Therefore, solid-state fluorescent property of **1** has been investigated at room temperature. The free ligand bpp displays photoluminescence with emission maxima at 446 nm excited at 348 nm, assigned to $\pi*\rightarrow\pi$ or $\pi*\rightarrow$n transition. To the best of our knowledge, the emission of dicarboxylate belongs to $\pi*\rightarrow$n transition, which is very weak compared to that of the $\pi*\rightarrow\pi$ transition of bib, so the polycarboxylates almost have no contribution to the fluorescent emission of as-synthesized CPs. At room temperature,

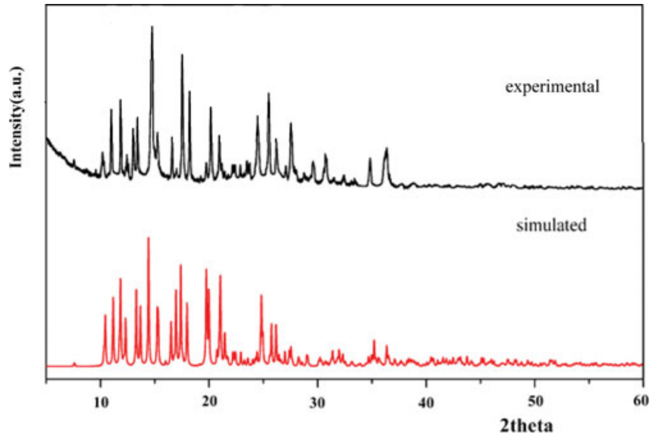

Figure 5. View of powder X-ray diffraction patterns of **1**.

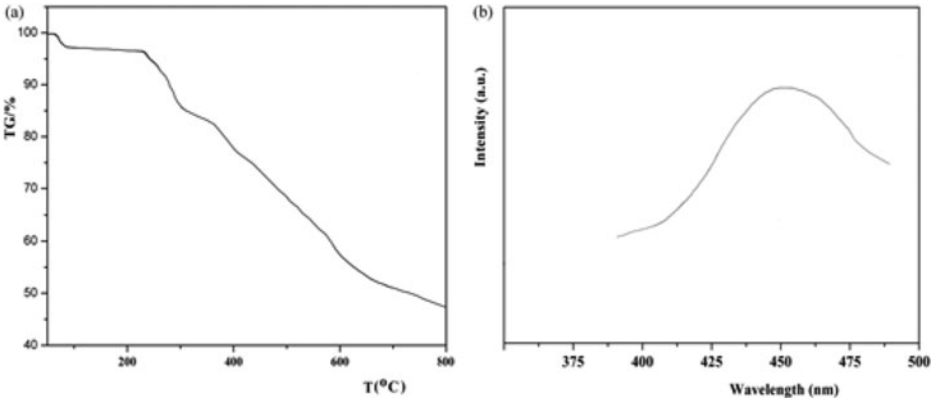

Figure 6. (a) TGA curve of **1**. (b) Solid-state emission spectra for **1**.

the emission spectra exhibit a maximum emission peak at 450 nm for **1** under excitation at 350 nm (Fig. 6(b)). What is more, the Zn(II) ion is difficult to oxidize or reduce because of the d^{10} configuration. As a result, the emission of **1** is neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer in nature. Thus, it could be assigned to a mixture characteristic of intraligand and ligand-to-ligand charge transition.

Conclusion

In summary, a new zinc complex has been prepared under hydrothermal conditions using 5-dimethylamino-isophthalic acid and 1,3-bis(4-pyridyl)propane mixed ligands. In the complex, Zn^{2+} ions are connected together by mixed ligands to get a 2D four-connected layer network, which are further stacked through $C—H\cdots\pi$ interaction to form a 3D supramolecular structure.

Funding

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Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center with registration number CCDC 1026419 (**1**). Copies of this information 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.

References

[1] Cairns, A. J. *et al.* (2008). *J. Am. Chem. Soc.*, *130*, 1560.
[2] Cook, T. R., Zheng, Y. R., & Stang, P. J. (2013). *Chem. Rev.*, *113*, 734.
[3] Hee, K. C., Jaheon, K., Olaf, D. F., O'Keeffe, M., & Yaghi, O. M. (2003). *Angew. Chem. Int. Ed.*, *42*, 3907.
[4] Lacroix, P. G. *et al.* (2001). *Chem. Mater.*, *13*, 441.
[5] Li, Z. *et al.* (2013). *CrystEngComm.*, *15*, 2745.

[6] Lan, A. *et al.* (2009). *Angew. Chem. Int. Ed.*, *48*, 2334.
[7] Mahata, P., & Natarajan, S. (2005). *Eur. J. Inorg. Chem.*, 2156.
[8] Xue, L., Li, Z., & Miao, S. (2012). *Chin. J. Struct. Chem.*, *6*, 791.
[9] Bo, Q., Wang, H., & Wang, D. (2013). *New J. Chem.*, *37*, 380.
[10] Chen, L. *et al.* (2011). *Dalton Trans.*, *40*, 9731.
[11] Ma, S., Sun, D., Wang, X., & Zhou, H. (2007). *Angew. Chem. Int. Ed.*, *46*, 2458.
[12] Pan, L. *et al.* (2006). *J. Am. Chem. Soc.*, *128*, 4180.
[13] Sun, N., Yan, Y., & Chen, J. (2013). *J. Mol. Struct.*, *1047*, 324.
[14] Lagnoux, D., Delort, E., Douat-Casassus, C., Esposito, A., & Reymond, J. (2004). *Chem. Eur. J.*, *10*, 1215.
[15] Sheldrick, G. M. (1997). *SADABS*, University of Göttingen: Göttingen.
[16] Sheldrick, G. M. (1997). *SHELXTL97: Program for Refining Crystal Structure Refinement*, University of Göttingen: Göttingen.
[17] Yang, W. *et al.* (2013). *Inorg. Chem.*, *52*, 2736.
[18] Yan, S., Shi, L., Sun, F., & Wu, C. (2010). *Cryst. Eng. Comm.*, *12*, 3437.