ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 7, pp. 517–523. © Pleiades Publishing, Ltd., 2019.

Two Zinc(II)/Cadmium(II) Coordination Polymers Constructed by Semirigid Carboxylic Acid Ligand: Syntheses, Structures, and Photoluminescence Properties

Y. P. Li[a, b, c], F. Y. Ju[a, b, c], G. L. Li[a, b, c], L. Y. Xin[a, b, c], X. L. Li[a, b, c], and G. Z. Liu[a, b, c, *]

[a] *College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang, 471934 P.R. China*
[b] *Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang, 471934 P.R. China*
[c] *School of Food and Drug, Luoyang Normal University, Luoyang, 471934 P.R. China*
**e-mail: gzliuly@126.com*

Received May 28, 2018; revised January 4, 2019; accepted January 30, 2019

Abstract—Two new coordination polymers $\{[Zn(HL)(HBpp)] \cdot H_2O\}_n$ (**I**) and $[Cd(HL)(HBpe)]_n$ (**II**) (H_4L = 5-(2,3-dicarboxy phenoxy) isophthalic acid, Bpp = 1,3-bis(4-pyridyl)propane, Bpe = 1,2-bis(4-pyridyl)ethylene) were prepared and characterize by element analysis, powder XRD and single crystal X-ray diffraction (CCDC nos. 1836060 (**I**), 1844999 (**II**)). The single-crystal X-ray diffractions reveal that the complex **I** is a 2D carboxylate layer with the HBpp suspension arms, in which the zinc(II) is four-coordinated with a tetrahedral geometry. Compound **II** is a 1D Cd(II)-carboxylate chains, in which the cadmium(II) is seven-coordinated with a distorted pentagonal bipyramidal geometry. Complexes **I** and **II** are further extended into three-dimensional supramolecular framework via hydrogen bonds. The solid state luminescent properties of compounds **I** and **II** have been investigated.

Keywords: mixed ligand, coordination polymer, fluorescence

DOI: 10.1134/S1070328419070054

INTRODUCTION

Coordination polymers (CPs) as a new class of crystalline multifunctional materials have become a very attractive area of research in coordination chemistry aiming to construct fascinating architectures with multiple novel topologies and explore their extensive application prospect in a great diversity of scientific fields, such as porous absorption, heterogeneous catalysis, luminescence, magnetism, chemical sensing and drug carrier, etc. [1–9]. Over the last decade, much effort has been invested in the purposeful design and controllable synthesis of these functional complexes [10–15]. According to the literature, organic ligands play vital roles in directing the final structures and properties due to the versatile coordination modes of carboxyl group, such as monodentate, bidentate, chelated and their combinations. Amongst many factors for constructing coordination polymers, the self-assembly of polycarboxylate anions and N-heterocyclic neutral ligands with metal ions under hydrothermal or solvothermal conditions has become one of the most effective ways [16, 17].

We choose the semi-rigid tetracarboxylic acid named 5-(2,3-dicarboxy phenoxy) isophthalic acid (H_4L) and auxiliary ligand 1,3-bis(4-pyridyl)propane (Bpp) as the building block to construct new coordination polymers. The reasons are described as follows: (i) eight potential coordination sites and may be completely or partially deprotonated. This property brings about various coordination modes and higher dimensionality structures; (ii) a rotatable-O-group links two rigid benzene rings, which allows the ligand with subtle conformational adaptation; (iii) the hydrogen bond acceptor–donor, depending on the degree of deprotonation [18–21].

According to the above facts, we reported the coordination polymer $\{[Zn(HL)(HBpp)] \cdot H_2O\}_n$ (**I**) and $[Cd(HL)(HBpe)]_n$ (**II**) based on H_4L. The synthesis, crystal structures, thermal stabilities, powder X-ray diffraction, and IR and photoluminescent properties of the complex have been discussed in detail.

EXPERIMENTAL

Materials and methods. All chemicals for synthesis were of reagent grade and used as received without further purification. Elemental analyses for C, H, and N were carried out using a Flash 2000 organic elemental analyzer. Infrared spectra (4000–600 cm^{-1}) were recorded on powdered samples using a NICOLET 6700 FT-IR spectrometer. The thermogravimetric analyses were performed on a SII EXStar 6000

TG/DTA6300 analyzer with a heating rate of 10°C/min up to 800°C under N_2 atmosphere. Powder X-ray diffraction (PXRD) patterns were taken on a Bruker D8-ADVANCEX ray diffractometer with CuK_α radiation (λ = 1.5418 Å). The luminescence spectra were performed on an Aminco Bowman Series 2 luminescence spectrometer at room temperature.

Synthesis of I. The mixture of $Zn(OAC)_2 \cdot 2H_2O$ (0.027 g, 0.1 mmol), H_4L (0.018 g, 0.05 mmol), Bpp (0.010 g, 0.05 mmol) and H_2O (6 mL) was placed in a 23 mL Teflon-lined autoclave at 120°C for 4 days, and then cooled at 5°C/h to room temperature. Colorless blocked crystals were obtained.

For $C_{29}H_{24}N_2O_{10}Zn$

Anal. calcd., %	C, 55.63	H, 3.88	N, 4.49
Found, %	C, 55.65	H, 3.86	N, 4.48

IR spectrum (KBr; ν, cm^{-1}): 3424 m, 3098 w, 2930 w, 1712 m, 1619 s, 1571 s, 1504 m, 1451 w, 1370 s, 1272 m, 1247 m, 994 w, 817 w, 773 m, 493 w.

Synthesis of II. The mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.031 g, 0.1 mmol), H_4L (0.018 g, 0.05 mmol), Bpe (0.010 g, 0.05 mmol) were dissolved in a mixed solvent of absolute ethyl alcohol (2.00 mL) and deionized water (4.00 mL) giving colorless block crystals after the hydrothermal reaction at 160°C for 6 days.

For $C_{28}H_{18}N_2O_9Cd$

Anal. calcd., %	C, 52.64	H, 2.84	N, 4.38
Found, %	C, 52.68	H, 2.82	N, 4.36

X-ray crystallography. The crystallographic data collections for the complex was carried out a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) by using the ϕ/ω scan technique at room temperature. The structures were solved by direct methods followed by successive difference Fourier syntheses, and a full-matrix least-squares refinement on F^2 was carried out using the SHELX-97 program package with anisotropic thermal parameters for all non-hydrogen atoms [22]. All non-hydrogen atoms were easily found from the Fourier difference maps, whereas the H atoms were placed in calculated positions and refined isotropically with a riding model except for water H atoms, which were initially located in a difference Fourier map and included in the final refinement by use of geometrical restraints with O–H = 0.85 Å and $U_{iso} = 1.5U_{eq}(O)$. Crystallographic data and structural refinement results for compounds **I** and **II** were summarized in Table 1. Selected bond distances and angles are listed in Table 2.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1836060 (**I**), 1844999 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Single-crystal X-ray analysis shows that the structure of complex **I** features a two-dimensional coordination polymer. The asymmetric unit contains one crystallographically Zn^{2+} ion, one incompletely deprotonated HL^- anion, one protonated $HBpp^+$ ion, and one lattice water molecule as shown in Fig. 1a. In this complex, Zn cation is four-coordinated in a tetrahedral bonding structure [$ZnNO_3$] by one N atom from one Bpp ligand, three oxygen atoms from three symmetry-related incompletely deprotonated HL^- anion. The Zn–O bond lengths are 1.9418(14), 1.9744(15), and 1.9800(15) Å, and the Zn–N bond lengths are 2.0367(17) Å.

The adjacent Zn ions are connected by HL^- anions adopting monodentate coordination mode to form a 1D carboxylate chain along *a* direction with the Zn···Zn distance of 8.0137(4) Å. Adjacent carboxylate chains are connectted together through HL^- anion with the Zn···Zn separation of 9.4034(4) Å to form a two-dimensional carboxylic acid layer (Fig. 1b) with the protonated $HBpp^+$ ions as suspension booms. The adjacent layers are assembled into a three-dimensional supramolecular (Fig. 1c) via two types of H-bonding interactions: (i) between lattice water molecules and carboxylate O atoms; (ii) between the N atoms of HBpp ion and carboxylate O atoms from HL^-. The detailed hydrogen bonds data are listed in Table 3. Besides, face to face π–π interactions between two benzene ring of HL^- ligands from the adjacent layer (centroid distance: 3.954 Å, Fig. 1d) further consolidate the stability of the resultant 3D network.

The direct assembly of Cd(II) and HL^- anion results in **II** with 1D Cd(II)-carboxylate chains. The asymmetric unit contains one Cd^{2+} ion, one incompletely deprotonated HL^- anion, one protonated Hbpe ion, as depicted in Fig. 2a. The Cd cation is seven-coordinated with a distorted pentagonal bipyramidal geometry [$CdNO_6$] formed by one HBpe N atoms and six carboxylate oxygen atoms from three symmetry-related HL^- anions. The Cd(1)–O bond lengths range from 2.273(2) to 2.532(2) Å and one Cd(1)–N bond lengths is 2.299(3) Å.

Two adjacent [$CdNO_6$] are connected together by a pair of HL^- anions adopting chelate coordination mode to form a [$Cd_2(CO_2)_6N_2$] with the Cd···Cd distance of 5.6873(4) Å. The [$Cd_2(CO_2)_6N_2$] are extended by a couple of HL^- anions to produce an infinite one-dimensional chain along the *b* direction with the protonated HBpe ions as suspension booms (Fig. 2b). The structure of compound **II** extends into 3D supermo-

Table 1. Crystallographic data and structure refinement for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	625.87	638.84
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a, Å	12.5749(4)	12.3401(4)
b, Å	17.2029(5)	9.3297(4)
c, Å	24.0304(7)	21.3577(10)
β, deg	90	92.008(4)
V, Å^3	5198.4(3)	2457.39(17)
Z	8	4
ρ_{calcd}, g cm^{-3}	1.599	1.727
μ, mm^{-1}	1.011	0.951
F(000)	2576	1280.0
θ Range, deg	1.69 to 25.45	3.304 to 25.49
Reflections collected/unique	32496/4774	13491/4496
R_{int}	0.0340	0.0325
Completeness, %	99.3	99.8
Data/restraints/parameters	4774/0/380	4496/27/386
Goodness-of-fit	1.055	1.038
R_1, wR_2 ($I > 2\sigma(I)$)	0.0292, 0.0725	0.0346, 0.0648
R_1, wR_2 (all data)	0.0363, 0.0758	0.0462, 0.0690
Largest peak and hole, e Å^{-3}	0.288 and –0.334	0.34 and –0.38

lecular (Fig. 2c) array through two types of hydrogen bonds: (a) between N atoms from $Hbpe^+$ ions and carboxylate O atoms; (b) between the two carboxyl O atoms of HL^- ion. The detailed hydrogen bonds data are listed in Table 3.

PXRD of the complexes have been studied at room temperature, which are in good agreement with the pattern simulated from the respective single-crystal data, implying the good phase purity of the complex.

Thermogravimetric analysis (TGA) of the complex was performed on crystalline samples from room temperature to 800°C with a heating rate of 10°C min^{-1} under nitrogen atmosphere, as shown in Fig. 3. An initial mass loss (3.47%) from room temperature to 103°C is in agreement with the removal of one solvent water molecule (calcd. 2.88%). There is a plateau covering a temperature range of 120–256°C, indicating the framework maintains its integrity after losing the guest water. Subsequently, the organic ligands decompose up 800°C. Complex **II** is thermally stable up to almost 340°C. After that, the framework begins to collapse rapidly up to 490°C owing to the decomposition of organic ligands. Its mass remnant of 23.58% may be CdO (calcd. 20.10%) and unburned carbon.

The solid-state photoluminescence of the compound, the free H_4L, Bpp and Bpe ligands were examined at ambient temperature, as illustrated in Fig. 4. Two complexes display a wide range of emission behaviors with a maximum at 431 nm (λ_{ex} = 357 nm) for **I**, 420 nm (λ_{ex} = 300 nm) for **II**, respectively. In

Table 2. Selected bond lengths (Å) and angles (deg) for the compound **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
Zn(1)–O(2)	1.9418(14)	Zn(1)–O(5)$^{\#1}$	1.9744(15)
Zn(1)–O(3)$^{\#2}$	1.9800(15)	Zn(1)–N(1)	2.0367(17)
		II	
Cd(1)–O(1)	2.496(3)	Cd(1)–O(2)	2.273(2)
Cd(1)–O(3)$^{\#1}$	2.441(2)	Cd(1)–O(4) $^{\#1}$	2.337(2)
Cd(1)–O(6)$^{\#2}$	2.532(2)	Cd(1)–O(7)$^{\#2}$	2.348(2)
Cd(1)–N(1)	2.299(3)		
Angle	ω, deg	Angle	ω, deg
		I	
O(2)Zn(1)O(5)$^{\#1}$	106.64(6)	O(2)Zn(1)O(3)$^{\#2}$	100.83(7)
O(5)$^{\#1}$Zn(1)O(3)$^{\#2}$	102.48(6)	O(2)Zn(1)N(1)	116.52(7)
O(5)$^{\#1}$Zn(1)N(1)	115.09(7)	O(3)$^{\#2}$Zn(1)N(1)	113.46(7)
		II	
O(1)Cd(1)O(6)$^{\#2}$	95.27(8)	O(2)Cd(1)O(1)	54.15(8)
O(2)Cd(1)O(3)$^{\#1}$	89.07(8)	O(2)Cd(1)O(4)$^{\#1}$	101.68(9)
O(2)Cd(1)O(6)$^{\#2}$	81.08(8)	O(2)Cd(1)O(7)$^{\#2}$	133.17(8)
O(2)Cd(1)N(1)	127.89(10)	O(3)$^{\#1}$Cd(1)O(1)	143.13(7)
O(3)$^{\#}$1Cd(1)O(6)	74.18(7)	O(4)$^{\#1}$Cd(1)O(1)	128.73(9)
O(4)$^{\#1}$Cd(1)O(3)$^{\#1}$	54.10(7)	O(4)$^{\#1}$Cd(1)O(6)$^{\#2}$	127.95(8)
O(7)$^{\#2}$Cd(1)O(1)	113.88(9)	O(7)$^{\#2}$Cd(1)O(3)$^{\#1}$	88.40(7)
O(7)$^{\#2}$Cd(1)O(4)$^{\#1}$	114.07(8)	O(7)$^{\#2}$Cd(1)O(6)$^{\#1}$	53.38(7)
N(1)Cd(1)O(1)	84.59(9)	N(1)Cd(1)O(1)$^{\#1}$	126.55(9)
N(1)Cd(1)O(4)$^{\#1}$	78.89(9)	N(1)Cd(1)O(6)$^{\#2}$	139.13(8)
N(1)Cd(1)O(7)$^{\#2}$	89.32(9)		

* Symmetry codes for compound: $^{\#1}$ $-x+2, y+1/2, -z+1/2$; $^{\#2}$ $x+1/2, y, -z+1/2$ (**I**); $^{\#1}$ $1-x, 1-y, 1-z$; $^{\#2}$ $1-x, -y, 1-z$ (**II**).

addition, the free H_4L ligand shows intense emission with a maximum at 417 nm (λ_{ex} = 300 nm), the Bpp and Bpe molecules show weak emission with a maximum at 439 nm (λ_{ex} = 348 nm) and 366 nm (λ_{ex} = 334 nm), respectively. In comparison with the emission peak of both free ligands, due to very weak fluo-

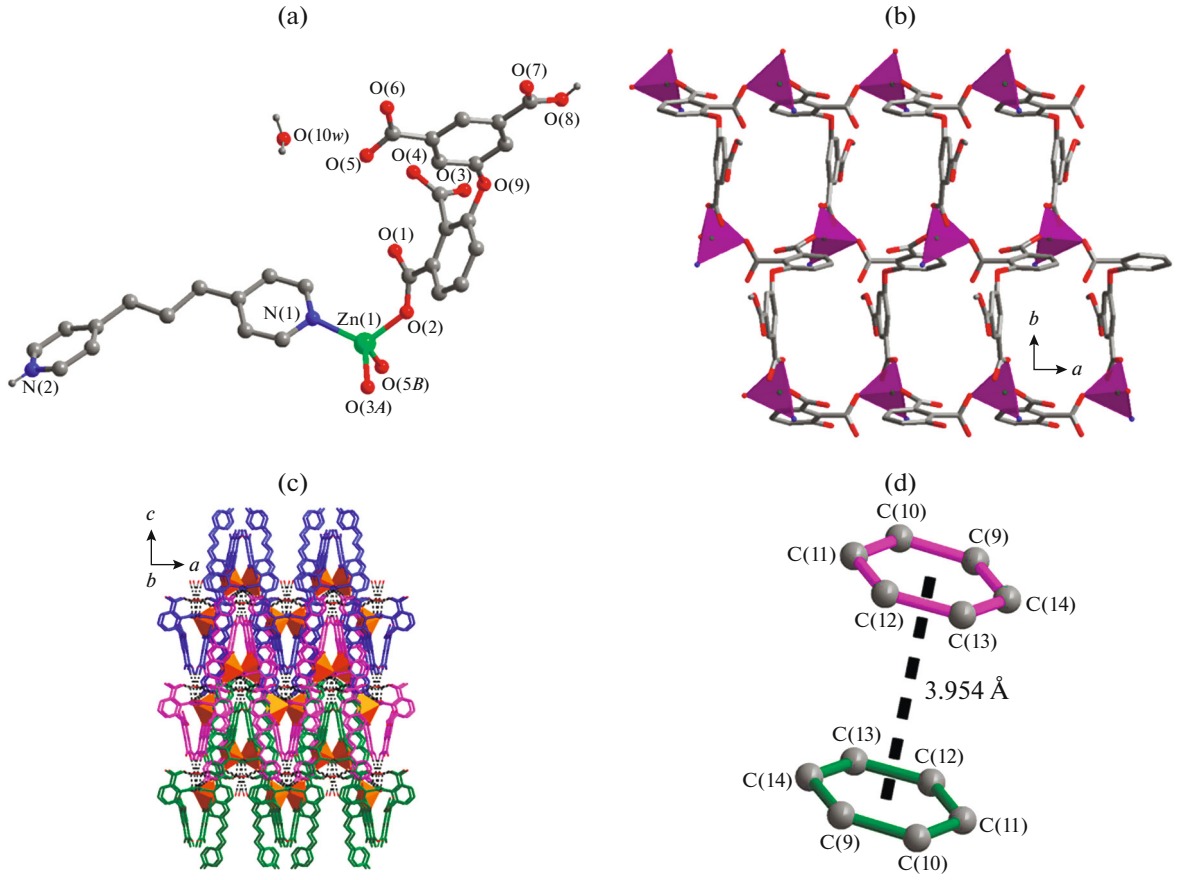

Fig. 1. View of the coordination environment of Zn atom for complex **I**, symmetry codes: (*A*) 0.5 + *x*, *y*, 0.5 – *z*; (*B*) 2 – *x*, 0.5 + *y*, 0.5 – *z* (a); view of a 2D layer, all hydrogen atoms of carbon atoms are omitted for clarity (b); view of 3D supramolecular structure showing the stacking of adjacent layers via H-bonding (c); π–π interactions in the compound (d).

Table 3. Geometric parameters of hydrogen bond for **I*** and **II****

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
I				
N(2)–H(2)···O(4)$^{\#4}$	0.86	1.86	2.683(2)	159
O(8)–H(8)···O(10*w*)$^{\#5}$	0.82	1.85	2.663(2)	174
O(10*w*)–H(1*w*)···O(2)$^{\#3}$	0.85	2.08	2.918(2)	169
O(10*w*)–H(2*w*)···O(1)$^{\#6}$	0.85	2.15	2.929(3)	153
O(10*w*)–H(2*w*)···O(3)$^{\#6}$	0.85	2.56	3.068(2)	120
II				
O(9)–H(9)···O(7)$^{\#1}$	0.82	1.85	2.659(3)	168
N(2)–H(2)···O(3)$^{\#2}$	0.83(4)	2.00(4)	2.756(4)	151
N(2)–H(2)···O(6)$^{\#3}$	0.83(4)	2.66(4)	3.094(4)	114

* Symmetry codes for compound: $^{\#3}$ –*x* + 2, *y* – 1/2, –*z* + 1/2; $^{\#4}$ –*x* + 2, –*y* + 1, –*z*; $^{\#5}$ –*x* + 3/2, –*y* + 1, *z* + 1/2; $^{\#6}$ –*x* + 3/2, *y* – 1/2, *z* (**I**).
** Symmetry codes: $^{\#1}$ 2 – *x*, *y* + 1/2, –*z* + 3/2; $^{\#2}$ –*x*, 2 – *y*, 1 – z; $^{\#3}$ *x*, 1 – *y*, 1 – *z*.

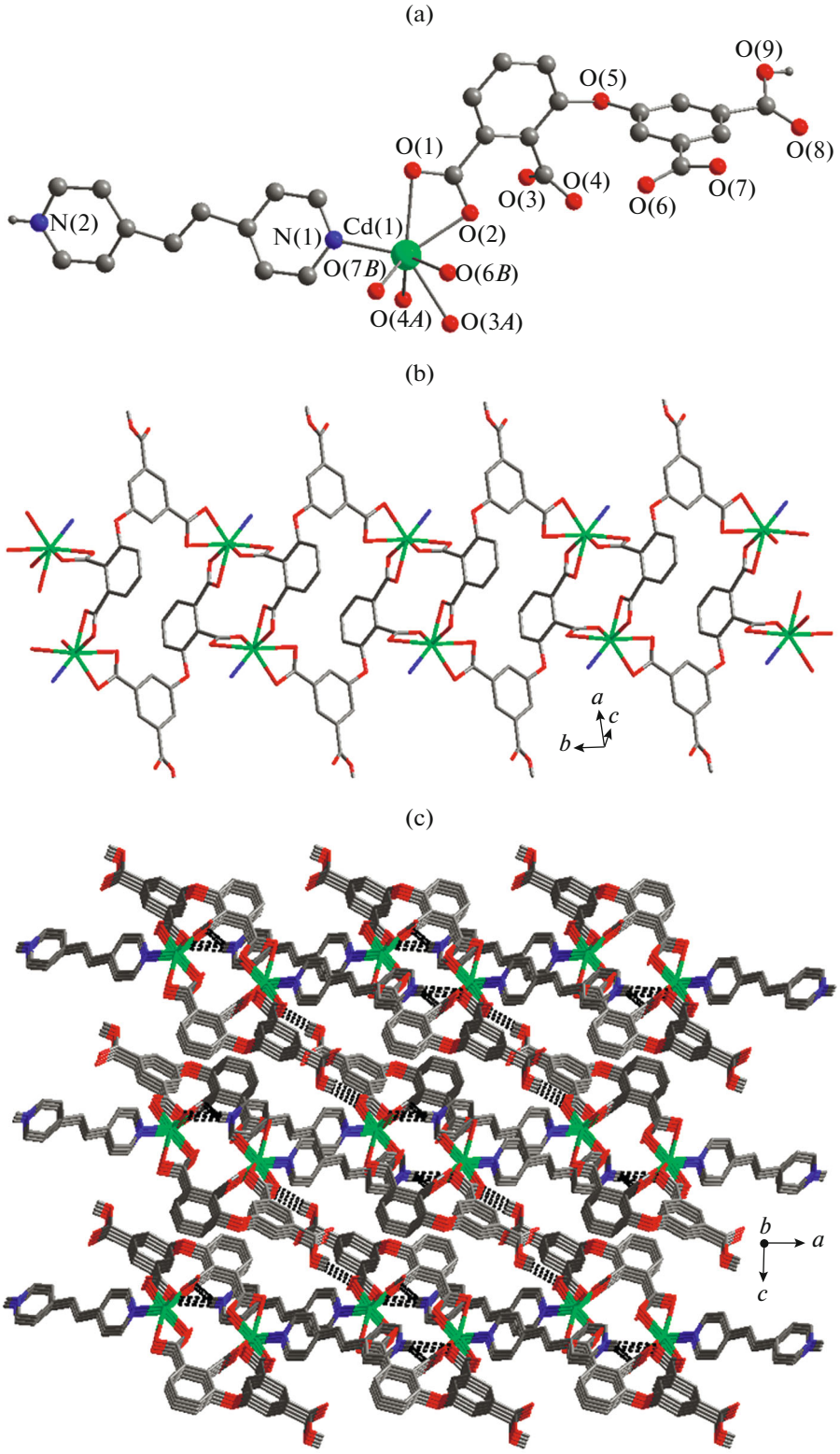

Fig. 2. View of the coordination environment of Cd(II) for the complex **II**, symmetry codes: (*A*) $1 - x$, $1 - y$, $1 - z$; (*B*) $1 - x$, $-y$, $1 - z$ (a); view of a 1D chain (b); view of 3D supramolecular structure via H-bonding (c).

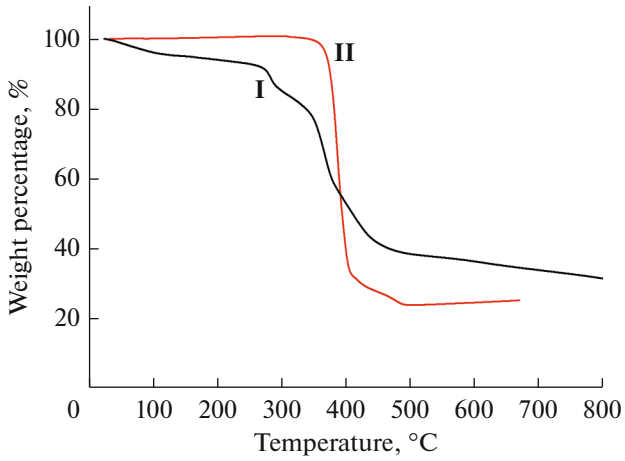

Fig. 3. The TGA curves for **I** and **II**.

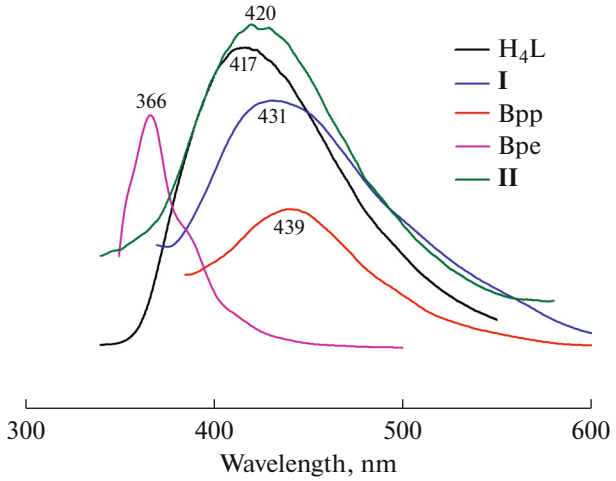

Fig. 4. The solid-state emission spectra of the compounds **I** (*1*), **II** (*2*), Bpp (*3*), Bpe (*4*) and the free H_4L ligand (*5*) at room temperature.

rescent emission of the Bpp and Bpe coligands, the peak of the compound **I** and **II** may be related to the emission of free H_4L ligand, these emission bands can be attributed to a ligand-centered charge transfer ($n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$) [23, 24]. The nature of metal ions has no obvious effect on such ligand-based photoluminescence, showing that the inorganic motifs are independent on the electronic state of luminescence centers. The emission peak at 431 nm for the complex **I** is little red-shifted compared with that of the H_4L ligand, the reason for this may be attributed to the coordination effect of the ligand with the metal centers, which increases the conjugation upon metal coordination [25].

FUNDING

This work was supported by the National Natural Science Foundation of China (no. 21571093) and the Foundation of Science and Technology of Henan Province (no. 162102210304).

REFERENCES

1. Li, Y.L., Zhao, Y., Wang, P., et al., *Inorg. Chem.*, 2016, vol. 55, p. 11821.
2. Fei, H.H., Shin, J.W., Meng, Y.S., et al., *J. Am. Chem. Soc.*, 2014, vol. 136, p. 4965.
3. Zhang, X., Hu, Q., Xia, T.F., et al., *ACS Appl. Mater. Interfaces*, 2016, vol. 8, p. 32259.
4. Wang, K., Du, L., Ma, Y., and Zhao, Q., *Inorg. Chem. Commun.*, 2016, vol. 68, p. 45.
5. Rojas, S., Carmona, F.J., Maldonado, C.R., et al., *Inorg. Chem.*, 2016, vol. 55, p. 2650.
6. Sadakiyo, M., Kasai, H., Kato, K., et al., *J. Am. Chem. Soc.*, 2014, vol. 136, p. 1702.
7. Li, T., Kozlowski, M.T., Doud, E.A., Blakely, M.N., et al., *J. Am. Chem. Soc.*, 2013, vol. 135, p. 11688.
8. Li, G.L., Liu, G.Z., Xin, L.Y., et al., *J. Inorg. Organomet. Polym.*, 2015, vol. 25, p. 694.
9. Ju, F.Y., Li, Y.P., Li, G.L., and Liu, G.Z., *Chin. J. Struct. Chem.*, 2016, vol. 35, p. 404.
10. Furukawa, H., Cordova, K.E., O'Keeffe, M., et al., *Science*, 2013, vol. 341, p. 1230444.
11. Mason, J.A., Veenstra, M., and Long, J.R., *Chem. Sci.*, 2014, vol. 5, p. 32.
12. Taylor, J.M., Dawson, K.W., and Shimizu, G.K., *J. Am. Chem. Soc.*, 2013, vol. 135, p. 1193.
13. Choi, M.H., Park, H.J., Hong, D.H., and Suh, M.P., *Chemistry*, 2013, vol. 19, p. 17432.
14. He, Y.P., Tan, Y.X., and Zhang, J., *Chem. Commun.*, 2013, vol. 49, p. 11323.
15. Li, D.S., Wu, Y.P., Zhao, J., et al., *Coord. Chem. Rev.*, 2014, vol. 261, p. 1.
16. Ni, T., Xing, F., Shao, M., et al., *Cryst. Growth Des.*, 2011, vol. 11, p. 2999.
17. Xing, F., Bai, Y., He, X., et al., *CrystEngComm*, 2012, vol. 14, p. 4312.
18. Wang, C.C., Zhang, Y.Q., Zhu, T., et al., *Polyhedron*, 2015, vol. 90, p. 58.
19. Si, C.D., Hu, D.C., Fan, Y., et al., *Cryst. Growth Des.*, 2015, vol. 15, p. 2419.
20. Yang, D.L., Zhang, X., Yang, J.X., et al., *Inorg. Chim. Acta*, 2014, vol. 423, p. 62.
21. Li, X.L., Liu, G.Z., Xin, L.Y., and Wang, L.Y., *J. Solid State Chem.*, 2017, vol. 246, p. 252.
22. Sheldrick, G.M., *SHELXS-97, Program for Crystal Structure Solution*, Göttigen: Univ. of Göttigen, 1997.
23. Guo, X.D., Zhu, G.S., Fang, Q.R., et al., *Inorg. Chem.*, 2005, vol. 44, p. 3850.
24. Tao, J., Tong, M.L., Shi, J.X., et al., *Chem. Commun.*, 2000, vol. 20, p. 2043.
25. Xin, L.Y., Liu, G.Z., Ma, L.F., and Wang, L.Y., *J. Solid State Chem.*, 2014, vol. 206, p. 233.