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Syntheses, Structures, and Properties of Two Coordination Polymers Based on 2-Pyrimidineamidoxime[1]

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Abstract—Two coordination polymers, $\{[Cd(L^1)_2(L^2)] \cdot 0.25H_2O\}_n$ (**I**) and $\{[Cd(L^1)(L^3)H_2O] \cdot 2H_2O\}_n$ (**II**) (L^1 = 2-pyrimidineamidoxime, L^2 = 4-sulfobenzoate dianion and L^3 = 5-sulfosalicylate dianion), has been synthesized and structurally characterized by single-crystal X-ray diffraction (CIF files CCDC nos. 1565646 (**I**) and 1565728 (**II**)). Complex **I** crystallizes in monoclinic space group $P2_1/n$ with a = 10.1462(3), b = 16.0152(5), c = 14.0349(5) Å, β = 93.267(3)°, V = 2276.87(13) Å^3, $C_{68}H_{66}N_{32}O_{29}S_4Cd_4$, M = 2373.36, ρ_{calcd} = 1.731 g/cm^3, $\mu(MoK_\alpha)$ = 1.109 mm^{-1}, $F(000)$ = 1186, GOOF = 0.806, Z = 1, the final R_1 = 0.0287 and wR_2 = 0.0733 for $I > 2\sigma(I)$. Complex **II** crystallizes in monoclinic space group $P2_1$ with a = 6.882(2), b = 17.138(2), c = 7.883(2) Å, β = 103.83(3)°, V = 902.8(4) Å^3, $C_{12}H_{16}N_4O_{10}SCd$, M = 520.75, ρ_{calcd} = 1.916 g/cm^3, $\mu(MoK_\alpha)$ = 1.388 mm^{-1}, $F(000)$ = 520, GOOF = 1.047, Z = 2, the final R_1 = 0.0739 and wR_2 = 0.2041 for $I > 2\sigma(I)$. Crystal structural analysis reveals that complex **I** possesses the corrugated 1D chain structure extending along the $[\bar{1}01]$ direction. However, complex **II** displays a 2D coordination network lying on the *ab* crystal plane, which can be simplified as a binodal 3-connected 6^3 topological network by considering Cd^{2+} ions and L^3 ligands as 3-connected nodes. Their photoluminescent and thermal properties were also investigated.

Keywords: polymer, structure, fluorescence, cadmium
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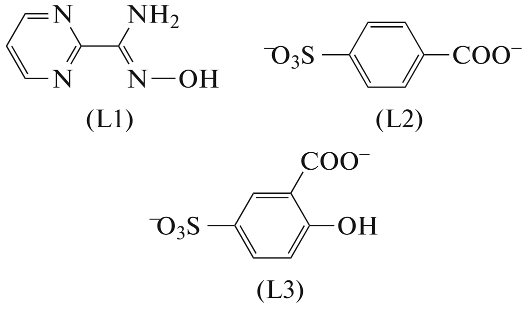
INTRODUCTION

Coordination polymers (CPs) are a kind of compounds assembled from the metal ions or metal clusters and functional organic ligands. Over the past two decades, CPs have attracted remarkable attention and have been heavily synthesized due to their intriguing structural variety, promising functional properties and potential applications in a variety of fields such as magnetism [1, 2], luminescence [3], drug delivery and biomedical imaging [4], sensor [5–8], gas storage [9, 10], catalysis [11], etc. The oxime ligands are well known to been extensively used in the synthesis of metal clusters. Take monoanionic 2-pyridylaldoxime/ketoximes, (Py)C(R)NOH (R = H, Me, Ph, etc.) and 2-pyridineamidoxime for example, they form homo- or heterometallic clusters with fascinating magnetic properties [12–14]. Compared with those extensively used oxime ligands, the reported complexes based on the ligand 2-pyrimidineamidoxime (L^1) are still limited. Ligand L^1 (Scheme 1) possesses not only the coordinated nitrogen and oxygen atoms but also hydrogen bonding donor ($-OH$, $-NH_2$) and acceptor ($=N-$). Furthermore, sulfobenzoates with sulfonate and carboxylate groups are useful synthetic synthons which can develop multimodal and polydentate coordinative systems. The complex based on both 2-pyrimidineamidoxime and sulfobenzoates is still not reported.



Scheme 1.

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Herein, the reactions of $Cd(Ac)_2 \cdot 2H_2O$ and 2-pyrimidineamidoxime with 4-sulfobenzoic acid potassium salt or 5-sulfosalicylic acid dihydrate offered two CPs, $\{[Cd(L^1)_2(L^2)] \cdot 0.25H_2O\}_n$ (**I**) and $\{[Cd(L^1)(L^3)H_2O] \cdot 2H_2O\}_n$ (**II**), respectively. The two compounds were characterized by single crystal X-ray diffraction (SC-XRD), elemental analyses (EA), powder X-ray diffraction (PXRD), infrared spectroscopy (IR), thermogravimetric (TG) analysis and photoluminescent spectroscopy (PL).

EXPERIMENTAL

The chemicals used in this work are of analytical grade and available commercially and were used without further purification. The ligand L^1 was prepared using a slightly modified method of the reported procedure [14, 15]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer (USA). Infrared spectra were recorded with KBr pellets in the 400–4000 cm^{-1} region on a Perkin-Elmer FT-IR spectrometer (USA). PXRD investigation on polycrystalline samples were carried out with a Bruker D8 advanced diffractometer (Germany) equipped with a diffracted-beamed monochromator set for CuK_α (λ = 1.5418 Å) radiation. The data were collected at room temperature in the 2θ range from 5° to 50° at an angular rate of 0.2 s/step with a scan step width of 0.02°. The TGA were performed in a SHIMADZU DTG-60 simultaneous DTA-TG apparatus instrument (Japan), under dynamic N_2 atmosphere (20 mL/min) and heating rate of 10°C/min from room temperature to 800°C. Photoluminescent spectra were measured using a Perkin-Elmer LS55 fluorescence spectrometer (USA).

Synthesis of complex I. $Cd(Ac)_2 \cdot 2H_2O$ (0.2 mmol, 53 mg) was dissolved in 10 mL methanol, and solid L^1 (0.4 mmol, 55.2 mg) was added to it in portions. 4-Sulfobenzoic acid potassium salt (0.4 mmol, 96 mg) dissolved in 10 mL water was added to the above mixture solution. The resulting deep brown solution was stirred for 10 min at room temperature and then filtered. Colorless block single crystals of complex **I** were obtained by slow evaporation from the filtrate for one day. The yield of **I** was 35% (based on cadmium).

IR (KB; ν, cm^{-1}): 3490 m, 3454 m, 3362 m, 3094 w, 2868 w, 1684 s, 1577 s, 1541 w, 1482 m, 1391 s, 1251 s, 1158 s, 1112 s, 1030 s, 1005 m, 830 m, 783 w, 738 s, 701 w, 644 s, 571 w, 482 w.

For $C_{68}H_{66}N_{32}O_{29}S_4Cd_4$			
Anal. calcd., %	C, 34.41	H, 2.80	N, 18.89
Found, %	C, 34.56	H, 2.68	N, 19.02

Synthesis of complex II. $Cd(Ac)_2 \cdot 2H_2O$ (0.1 mmol, 26.6 mg) was dissolved in 10 mL methanol, and solid L^1 (0.4 mmol, 55.2 mg) was added to it in portions. 5-Sulfosalicylic acid dihydrate (0.4 mmol, 101.7 mg) dissolved in 10 mL water was added to the above mixture solution. The resulting colorless solution was stirred for 10 min at room temperature and then filtered. Colorless block single crystals of complex **II** were obtained by slow evaporation from the filtrate for one day. The yield of **II** was 42% (based on cadmium).

IR (KB; ν, cm^{-1}): 3440 s, 3317 w, 1686 m, 1654 w, 1629 w, 1577 s, 1561 m, 1479 m, 1444 m, 1388 m, 1347 w, 1259 m, 1229 m, 1166 s, 1131 m, 1081 w, 1041 s, 1000 w, 825 w, 676 m, 602 s, 587 w, 484 w, 427 w.

For $C_{12}H_{16}N_4O_{10}SCd$			
Anal. calcd., %	C, 27.68	H, 3.10	N, 10.76
Found, %	C, 27.54	H, 3.25	N, 10.59

X-ray structure determination. The colorless block single crystals of complex **I** and **II** with dimensions of 0.10 × 0.13 × 0.14 and 0.11 × 0.14 × 0.15 mm were mounted on a Bruker Smart Apex CCD area detector diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) using the φ–ω scan mode in the range $3.174° \le \theta \le 25.049°$ and $3.272° \le \theta \le 24.995°$ at 293(2) K, respectively. Raw frame data were integrated with the SAINT program [16]. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [17]. An empirical absorption correction was applied with the program SADABS [18]. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms on water molecules (O(8), O(9) and O(10)) in complex **II** were directly included in the molecular formula. The other hydrogen atoms were placed in calculated positions and refined as riding mode. The final R_1 = 0.0287 and wR_2 = 0.0733 for 3433 observed reflections with $I > 2\sigma(I)$ ($w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 5.0026P]$, where $P = (F_o^2 + 2F_c^2)/3$), $(\Delta\rho)_{max}$ = 0.644 e/Å^3, $(\Delta\rho)_{min}$ = –0.351 e/Å^3 and $(\Delta/\sigma)_{max}$ = 0.000 for **I**. The final R_1 = 0.0739 and wR_2 = 0.2041 for 2066 observed reflections with $I > 2\sigma(I)$ ($w = 1/[\sigma^2(F_o^2) + (0.2000P)^2 + 0.6814P]$, where $P = (F_o^2 + 2F_c^2)/3$), $(\Delta\rho)_{max}$ = 1.556 e/Å^3, $(\Delta\rho)_{min}$ = –1.079 e/Å^3 and $(\Delta/\sigma)_{max}$ = 0.000 for **II**. Crystallographic details for complexes **I** and **II** have been summarized in Table 1. Selected bond lengths and angles for complexes **I** and **II** are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1565646 (**I**) and 1565728 (**II**)); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) or can be obtained from the authors.

RESULTS AND DISCUSSION

The complex **I** was readily obtained by the reaction of $Cd(Ac)_2 \cdot 2H_2O$, solid L^1 and 4-sulfobenzoic acid potassium salt in 1 : 2 : 2 molar ration in the mixed solution of methanol and H_2O under mild condition. The complex **II** was obtained by the reaction of $Cd(Ac)_2 \cdot 2H_2O$, solid L^1 and 5-sulfosalicylic acid dihydrate in 1 : 4 : 4 molar ration in the mixed solution of methanol and H_2O under mild condition. Their crystals were obtained by the solvent evaporation method. Both the complexes **I** and **II** are stable in air.

As shown in Fig. 1a, the asymmetric unit of **I** contains one crystallographically independent Cd^{2+} ion, two L^1 ligands, one coordination divalent anion L^2 and one quarter of free water molecule. The Cd^{2+} ion is six-coordinated by two oxygen atoms (O(3) and $O(6)^i$) from two coordination divalent anions L^2 and four nitrogen atoms (N(1), N(2), N(5) and N(6)) from two L^1 ligands to form the distorted octahedral coordination geometry. The bond lengths of Cd–N and Cd–O range from 2.286(3) to 2.444(3) Å and from 2.278(2) to 2.260(2) Å, respectively, which are all comparable to those found in other Cd(II) complexes [19, 20]. Ligand L^1 acts as bidentate neutral blocking $N^{\wedge}N$ donor to form a stable five member chelate ring. L^2 ligand acts as μ_2 bridging ligand to link two Cd^{2+} ions through a carboxylate oxygen atom and a sulfonic oxygen atom. Each Cd^{2+} ion is coordinated to two L^2 ligands and each μ_2 bridging L^2 ligand links two Cd^{2+} ions to lead to a series of parallel-arranged corrugated 1D chains extending along the $[\bar{1}01]$ direction (Fig. 1b).

As shown in Fig. 2a, the asymmetric unit of **II** contains one crystallographically independent Cd^{2+} ion, a L^1 ligand, one coordination divalent anion L^3, a coordinated water molecule and two free water molecules. The Cd^{2+} ion is six-coordinated by three oxygen atoms (O(2), $O(5)^i$ and $O(6)^{ii}$) from three coordination divalent anions L^3, an oxygen atom from the coordinated water and two nitrogen atoms (N(1) and N(4)) from a L^1 ligand to form the distorted octahedral coordination geometry. The bond lengths of Cd–N and Cd–O range from 2.279(17) to 2.43(3) Å and from 2.16(2) to 2.288(13) Å, respectively, which are all comparable to those found in other Cd(II) complexes [19, 20]. Ligand L^1 acts as bidentate neutral blocking $N^{\wedge}N$ donor to form a stable five member chelate ring. L^3 ligand acts as μ_3 bridging ligand to link three Cd^{2+} ions through a carboxylate oxygen atom and two sulfonic oxygen atoms. Each Cd^{2+} ion is coordinated to three L^3 ligands and each μ_3 bridging L^3 ligand links three Cd^{2+} ions to lead to a 2D coordination network lying on the *xy* crystal plane (Fig. 2b), which can be simplified as a binodal 3-connected 6^3 topological networks by considering Cd^{2+} ions and L^3 ligands as 3-connected nodes.

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

Parameter	**I**	**II**
Fw	2373.36	520.75
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$
a, Å	10.1462(3)	6.882(2)
b, Å	16.0152(5)	17.138(2)
c, Å	14.0349(5)	7.883(2)
β, deg	93.267(3)	103.83(3)
V, $Å^3$	2276.87(13)	902.8(4)
Z	1	2
ρ_{calcd}, g cm^{-3}	1.731	1.916
μ, mm^{-1}	1.109	1.388
F(000)	1186	520
Reflections collected	9209	3306
Unique reflections	4026	2288
R_{int}	0.0231	0.0843
GOOF (F^2)	0.806	1.047
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0287, 0.0733	0.0739, 0.2041
R_1, wR_2 (all data)*	0.0374, 0.0827	0.0849, 0.2478
$\Delta\rho_{max}/\Delta\rho_{min}$, e $Å^{-3}$	0.644/–0.351	1.556/–1.079

$* R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

In order to check the phase purities of complexes **I** and **II**, the PXRD of the compounds were recorded at room temperature. The peak positions of the simulated patterns closely match those of the experimental patterns, indicating phase purities of the as-synthesized samples. The differences in reflection intensity between the simulated and experimental patterns are due to the variation in crystal orientation of the powder samples.[2]

TG analyses were performed to check the thermal stabilities of complexes **I** and **II** (Fig. 3). For complex **I**, between room temperature and 270°C, the gradual weight loss is 0.62%, corresponding to the loss of one quarter of guest water molecule (calcd. 0.76%). The compound **I** begin to decompose upon 280°C. For complex **II**, the first gradual weight loss of 10.41% occurs between 70 and 245°C (calcd.

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[2] Data of PXRD are available from the authors on request.

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

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
			I		
Cd(1)–O(3)	2.278(2)	Cd(1)–O(6)$^{\text{i}}$	2.260(2)	Cd(1)–N(1)	2.374(3)
Cd(1)–N(2)	2.352(3)	Cd(1)–N(5)	2.286(3)	Cd(1)–N(6)	2.444(3)
			II		
Cd(1)–O(2)	2.16(2)	Cd(1)–O(5)$^{\text{i}}$	2.275(15)	Cd(1)–O(6)$^{\text{ii}}$	2.288(13)
Cd(1)–O(8)	2.270(13)	Cd(1)–N(1)	2.43(3)	Cd(1)–N(4)	2.279(17)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
			I		
O(6)$^{\text{i}}$Cd(1)O(3)	84.68(9)	O(6)$^{\text{i}}$Cd(1)N(5)	102.95(9)	O(3)Cd(1)N(5)	110.75(10)
O(6)$^{\text{i}}$Cd(1)N(2)	104.58(9)	O(3)Cd(1)N(2)	94.12(9)	N(5)Cd(1)N(2)	144.28(10)
O(6)$^{\text{i}}$Cd(1)N(1)	82.15(10)	O(3)Cd(1)N(1)	155.36(9)	N(5)Cd(1)N(1)	92.50(10)
N(2)Cd(1)N(1)	69.40(9)	O(6)$^{\text{i}}$Cd(1)N(6)	171.57(9)	O(3)Cd(1)N(6)	95.93(9)
N(5)Cd(1)N(6)	68.94(9)	N(2)Cd(1)N(6)	83.78(9)	N(1)Cd(1)N(6)	100.13(10)
			II		
O(2)Cd(1)O(5)$^{\text{i}}$	80.9(8)	O(2)Cd(1)O(6)$^{\text{ii}}$	86.4(7)	O(2)Cd(1)O(8)	89.4(9)
O(2)Cd(1)N(1)	173.9(6)	O(2)Cd(1)N(4)	102.6(7)	O(5)$^{\text{i}}$Cd(1)O(6)$^{\text{ii}}$	165.0(7)
O(5)$^{\text{i}}$Cd(1)O(8)	87.2(6)	O(5)$^{\text{i}}$Cd(1)N(1)	96.8(7)	O(5)$^{\text{i}}$Cd(1)N(4)	96.5(7)
O(6)$^{\text{ii}}$Cd(1)O(8)	84.7(5)	O(6)$^{\text{ii}}$Cd(1)N(1)	96.6(5)	O(6)$^{\text{ii}}$Cd(1)N(4)	94.0(6)
O(8)Cd(1)N(1)	96.2(9)	O(8)Cd(1)N(4)	167.8(9)	N(1)Cd(1)N(4)	71.9(8)

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

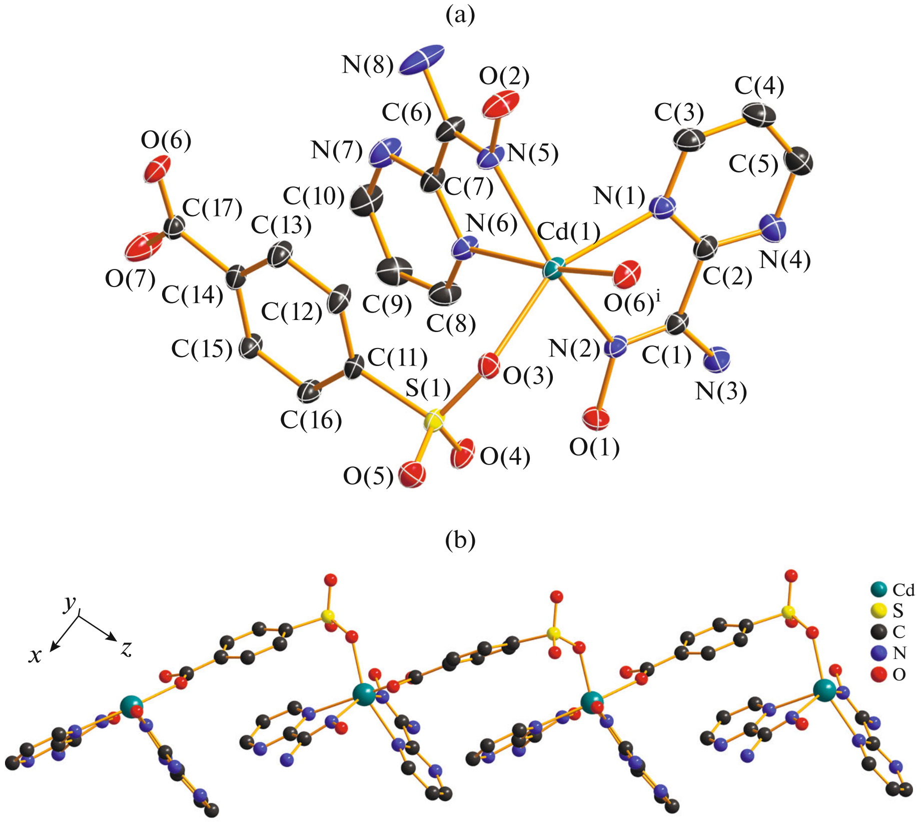

Fig. 1. View of the asymmetric unit of complex **I** with the thermal ellipsoids drawn at the 30% probability level (a); the 1D corrugated chain extending along the [$\bar{1}$01] direction (symmetry code: $^{\text{i}}$ $x - 1/2, -y + 1/2, z + 1/2$) (b).

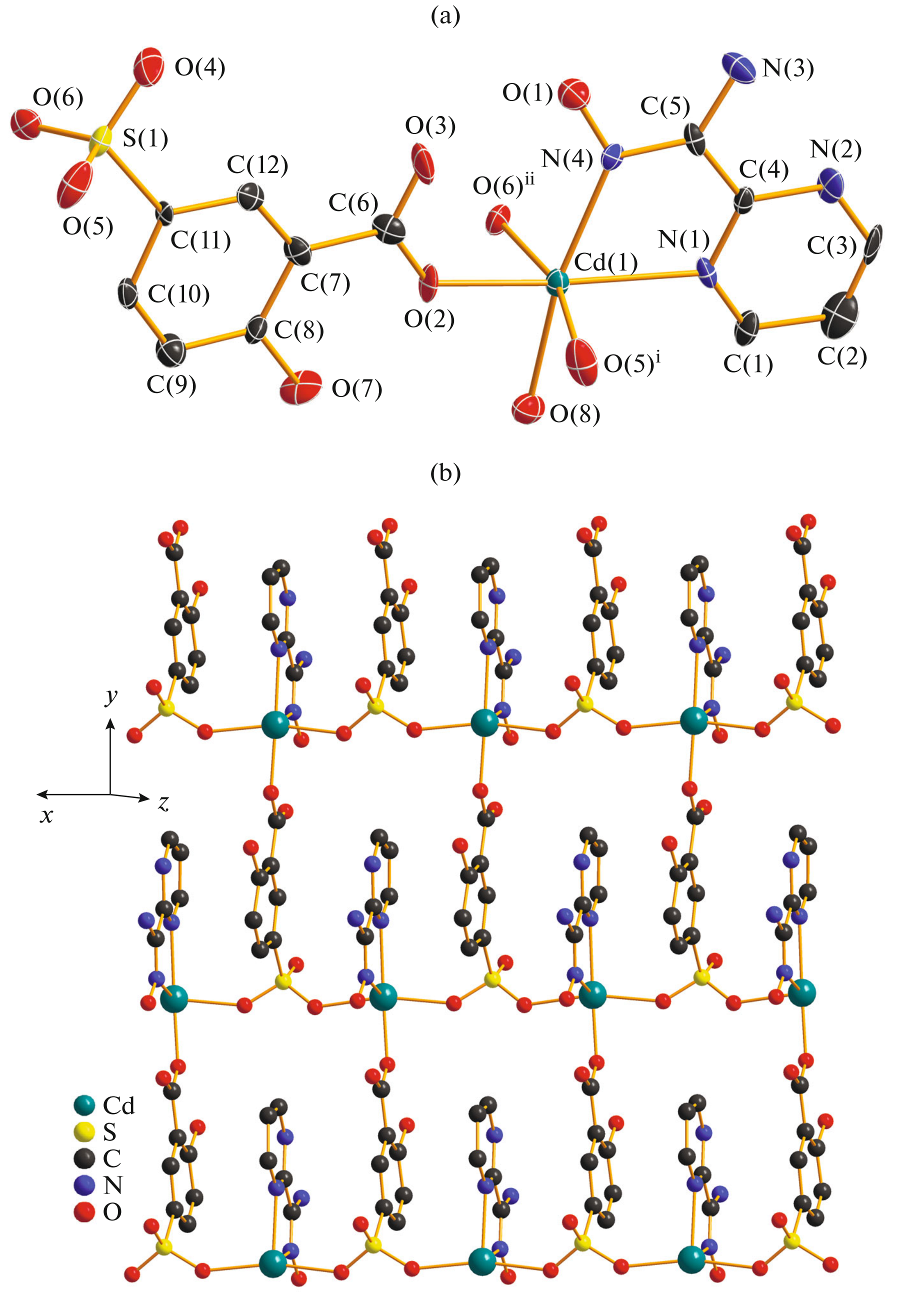

Fig. 2. View of the asymmetric unit of complex **II** with the thermal ellipsoids drawn at the 30% probability level (a); the 2D coordination network lying on the *xy* crystal plane (symmetry codes: ^{i} $-x + 2$, $y + 1/2$, $-z + 2$; ^{ii} $-x + 1$, $y + 1/2$, $-z + 2$) (b).

10.38%), corresponding to the loss of two guest water molecules and a coordinated water molecule. Further decomposition took place at 250°C, and finally the weight of the remainder is 24.71% (calcd. 24.66%) and the residues are CdO at 800°C.

As shown in Fig. 4, the luminescence properties of L^1, complexes **I** and **II** were studied in solid state at room temperature. The emission spectra of ligands L^2 and L^3 have been reported in [21, 22]. The free L^1 ligand emits blue-violet light with the broad emission peak and the emission maximum at 390 nm with a shoulder peak centered at 289 nm upon excitation at the maximum excitation wavelength of 240 nm. The free L^2 ligand shows an emission peak at 387 nm with a shoulder peak centered at 313 nm. The free L^3 ligand shows an emission peak at 404 nm with a shoulder peak centered at 318 nm. The complexes **I** and **II** exhibit the almost same emission behavior as

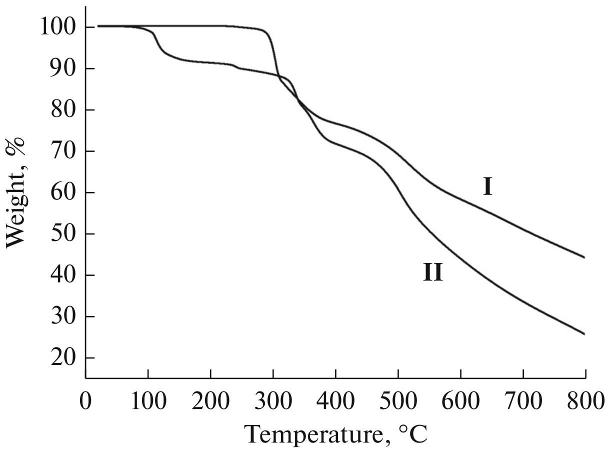

Fig. 3. TGA curves of **I** and **II**.

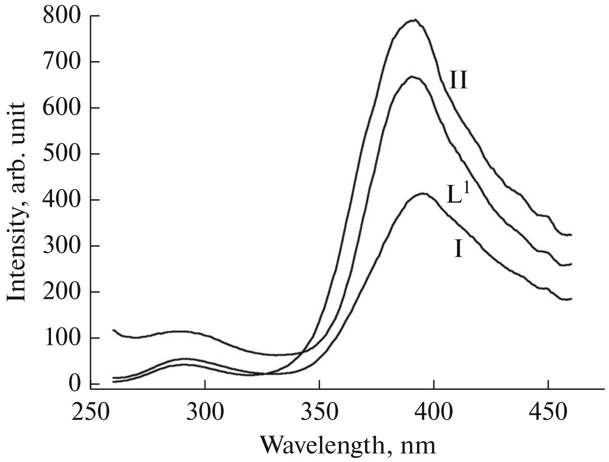

Fig. 4. Emission spectra of L^1, **I** and **II**.

L^1 ligand except for the change of relative intensities of peaks at 390 and 289 nm. So the emissions of complexes **I** and **II** should be originated from the coordinated L^1 ligands.

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REFERENCES

1. Brooker, S., *Chem. Soc. Rev.*, 2015, vol. 44, p. 2880.
2. Zhou, X.H., Chen, Q.Q., Liu, B.L., et al., *Dalton Trans.*, 2017, vol. 46, p. 430.
3. Cui, Y.J., Yue, Y.F., and Qian, G.D., *Chem. Rev.*, 2012, vol. 112, p. 1126.
4. Rocca, J.D., Liu, D.M., and Lin, W.B., *Acc. Chem. Res.*, 2011, vol. 44, p. 957.
5. Li, L., Chen, Q., Niu, Z.G., et al., *J. Mater. Chem. C*, 2016, vol. 4, p. 1900.
6. Li, A., Li, L., Lin, Z., et al., *New J. Chem.*, 2015, vol. 39, p. 2289.
7. Li, L., Zhu, Y.L., Zhou, X.H., et al., *Adv. Funct. Mater.*, 2016, vol. 26, p. 8677.
8. Zhou, X.H., Zhu, Y.L., Li, L., et al., *Sci. China Chem.*, 2017, vol. 60, p. 1130.
9. Oh, H., Maurer, S., Balderas-Xicohtencatl, R., et al., *Int. J. Hydrogen Energy*, 2017, vol. 42, p. 1027.
10. Li, J.R., Kuppler, R.J., and Zhou, H.C., *Chem. Soc. Rev.*, 2009, vol. 38, p. 1477.
11. Dang, D.B., Wu, P.Y., He, C., et al., *J. Am. Chem. Soc.*, 2010, vol. 132, p. 14321.
12. Dendrinou-Samara, C., Psomas, G., Iordanidis, L., et al., *Chem.-Eur. J.*, 2001, vol. 7, p. 5041.
13. Ishikawa, N., Otsuka, S., and Kaizu, Y., *Angew. Chem., Int. Ed.*, 2005, vol. 44, p. 731.
14. Gole, B., Chakrabarty, R., Mukherjee, S., et al., *Dalton Trans.*, 2010, vol. 39, p. 9766.
15. Fish, P.V., Allan, G.A., Bailey, S., et al., *J. Med. Chem.*, 2007, vol. 50, p. 3442.
16. *SAINT-Plus, Version 6.02*, Madison: Bruker Analytical X-ray System, 1999.
17. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
18. Sheldrick, G.M., *SADABS*, *An Empirical Absorption Correction Program*, Madison: Bruker Analytical X-ray Systems, 1996.
19. Zhou, X.H., Zhu, Y.L., Li, L., and Huang, W., *Chin. J. Chem.*, 2017, vol. 35, p. 1869.
20. Zhou, X.H. and Chen, Q., *Crystallogr. Rep.*, 2017, vol. 62, p. 238.
21. Zhu, W.Q., Li, Z., Wang, J.P., et al., *Basic Sci. J. Textile Univ.*, 2013, vol. 4, p. 521.
22. Ma, A.Q. and Zhu, L.G., *RSC Adv.*, 2014, vol. 4, p. 14691.