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Synthesis, Structures, and Properties of Two Coordination Polymers with Chelating Carboxylic and Triazolyl Derivatives

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Abstract—Two coordination polymers, $[Zn(Btec)_{0.5}(H_2L)]_n$ (**I**) and $[Cd_{0.5}(Tp)_{0.5}(H_2L')(H_2O)]_n \cdot nH_2O$ (**II**) (H_2L = 3-(1H-pyrazol-4-yl)-5-(pyridin-2-yl)-1,2,4-triazole; H_4Btec = 1,2,4,5-benzenetetracarboxylic acid; H_2L' = 3-(1H-pyrazol-4-yl)-5-(pyridin-3-yl)-1,2,4-triazole; H_2Tp = terephthalic acid), have been synthesized under hydrothermal conditions. The title compounds were structurally characterized by elemental analysis, single crystal X-ray diffraction analysis, infrared spectra. Compounds **I** and **II** crystallize in the orthorhombic and triclinic, space group *Pbca* and $P\bar{1}$, respectively. Compound **I** displays a two-dimensional plane structure, those are connected by N···H···O hydrogen bonds to generate 3D frameworks. Compound **II** is constructed a 1D chain structure by Tp^{2-} ligands, which are connected into 2D structure by the hydrogen bonds. In addition, the fluorescent property of **I** has been studied in the solid state at room temperature. The thermal analysis of **I** has also been investigated.

Keywords: coordination polymers, structure, fluorescent property

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INTRODUCTION

Recently, coordination polymers (CPs), as solid-state materials, have been widely explored in luminescence, gas storage/separations, heterogeneous catalysis, and magnetic and electronic applications, due to their fascinating structures and molecular topologies [1–4]. Various new ligands and their combinations are being exploited for the design and construct of novel CPs. The variety of metal ions, organic linkers, and structural motifs affords an essentially infinite number of possible combinations in which the structures of CPs are controlled by the geometries of organic ligands. Among the plenty of ligands employed in the construction of CPs, the multidentate N- and/or O-donor building blocks have received extensive attention [5–7]. The use of asymmetrical triazole derivatives ligands containing various spacers in combination with several aromatic polycarboxylic acid and transition metals is one of the well exploited strategies that resulted in many CP-based functional materials [8–10].

Recently, we have focused on coordination assemblies of a family of pyrazol/pyrazine/pyridyl-substituted triazolyl ligands [11–13], which can be considered as excellent building blocks for their multiple binding sites and diverse conformations upon complexation. Our initial results show that a mixed ligand is a good choice for the construction of new frameworks. However, it is accompanied with even more uncertain elements. Thus, the prediction of mixed-ligand architectures is a challenging scientific striving.

With this concept in mind, to expand our research on coordination polymers, we successfully obtained two new coordination polymers based on triazolyl derivatives and carboxylic ligands, namely, $[Zn(Btec)_{0.5}(H_2L)]_n$ (**I**) and $[Cd_{0.5}(Tp)_{0.5}(H_2L')(H_2O)]_n \cdot nH_2O$ (**II**).

EXPERIMENTAL

Materials and methods. All reagents used in the syntheses were of analytical grade. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Vario EL III elemental analyzer. Infrared spectra (IR) were obtained by a Nicolet 6700 FT-IR spectrophotometer over a range of 4000–600 cm^{-1}. Fluorescence measurements were recorded with a Hitachi F4500 fluorescence spectrophotometer. Thermogravimetric analyses (TGA) were carried out in nitrogen at a heating rate of 10°C $\min^{-1}$ using a TG/DTA 6300 integration thermal analyzer.

Synthesis of compound I. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2 mmol, 59.4 mg), H_2L (0.1 mmol, 21.2 mg) and H_4Btec (0.2 mmol, 50.8 mg) was dissolved in a solution of CH_3CN-H_2O (v : v = 1 : 3), dissolved in a glass vial (8 mL), then sealed in a 25 mL teflon-lined stainless steel vessel and heated at 150°C for 72 h. After cooling to room temperature, the colourless block crystals were obtained and then washed with distilled water for several times and filtered to give pure crystals of **I**.

For $C_{15}H_9N_6O_4Zn$

Anal. calcd., %	C, 44.74	H, 2.25	N, 20.87
Found, %	C, 44.57	H, 2.35	N, 20.71

IR spectrum (KBr; ν, cm^{-1}): 2986, 2910, 2357, 1750, 1710, 1552, 1510, 1470, 1348, 1042, 885, 808, 735, 674.

Synthesis of compound II. A mixture of H_2L' (21.2 mg, 0.10 mmol), H_2Tp (16.6 mg, 0.10 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (92.5 mg, 0.30 mmol) was stirred in the mixture of DMF–H_2O (v : v = 1 : 4). After that, the solution was placed in a bottle (10 mL), then sealed in a 25 mL Telfon reactor and heated at 140°C for 72 h, cooled to room temperature at a rate of 5°C h^{-1}. Light yellow block-shaped crystals of **II** were obtained.

For $C_{14}H_{14}N_6O_4Cd_{0.5}$

Anal. calcd., %	C, 43.51	H, 3.65	N, 21.74
Found, %	C, 43.70	H, 3.61	N, 21.76

IR spectrum (KBr; ν, cm^{-1}): 3351, 2882, 2984, 2363, 1760, 1715, 1550, 1390, 1055, 920, 810, 756, 670.

X-ray crystallography. Diffraction intensity data of the single crystals of **I** and **II** were collected on a Rigaku oxford diffraction equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using the X-scan technique at 293(2) K. The structures were solved by direct methods and refined F^2 by full matrix least squares using SHELXTL [14]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed during the structure refinement. Crystallographic data and details of refinement for compounds **I** and **II** are reported in Table 1. Selected bond distances and angles are given in Table 2.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1559420 (**I**), 1849275 (**II**) deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

As shown in Fig. 1a, the asymmetry unit contains one Zn(II) atom, half $Btec^{4-}$ ligand, and one H_2L ligand. Each Zn(II) center is penta-coordinated by three N atoms from two different H_2L ligands (Zn(1)–N(1) 2.148(6), Zn(1)–N(6)$^{\#2}$ 2.164(7), and Zn(1)–N(2) 2.174(6) Å) and two O atoms from two different $Btec^{4-}$ ligands (Zn(1)–O(1) 2.009(6), Zn(1)–O(3)$^{\#1}$ 2.027(5) Å) showing a distorted trigonal bipyramid coordination geometry. The OZnN bond angles vary from 88.9(2)° to 128.3(3)°. The bond angles of N(2)Zn(1)N(6)$^{\#2}$ and O(1)Zn(1)O(3)$^{\#1}$ are 168.0(3)° and 116.7(2)°, respectively, which are similar to other Zn-based complexes [15].

It is noteworthy that the H_4Btec is completely deprotonated in the formation of the compound **I**. The four carboxyl groups of H_4Btec ligand in compound **I** exhibit the same coordination modes (μ_1-η^1:η^0, μ_1-η^1:η^0, μ_1-η^1:η^0, μ_1-η^1:η^0) and link neighboring four Zn^{2+} ions forming two-dimensional $[Zn_4(Btec)]^{4-}$ unit with the Zn···Zn distances of 6.422 and 9.200 Å, respectively (Fig. 2a). On the other hand, H_2L ligands bind neighbouring Zn(II) ions forming 1D chain with the Zn···Zn separation of 6.422 Å. The H_2L ligands link the two-dimensional $[Zn_4(Btec)]^{4-}$ plane through Zn–N coordination ineractions to give a two-dimensional network as illustrated in Fig. 2a. In the crystal packing, there are H-bonding interactions between triazole nitrogen atom and carboxyl groups of H_4Btec ligand: (N(4)–H(4)···O(4)$^{\#1}$ (H···O/N···O distance = 1.92/2.742(9) Å; angle NHO = 160°, $^{\#1}$ 1/2 – x, 2 – y, 1/2 + z) and (N(5)–H(5)···O(2)$^{\#2}$ (H···O/N···O distance = 1.82/2.638(10) Å; angle NHO = 157°, $^{\#1}$ 1 – x, 1/2 + y, 3/2 – z). As a result, the 2D coordination layers are further interlinked via such secondary interactions to form a 3D supramolecular lattice (Fig. 2b).

As illustrated in Fig. 1b, every Cd(II) located at the inversion center reproduces the whole molecule through the asymmetric unit consisting of half of cadmium ion, one H_2L' ligand, a half Tp^{2-} ligand, one coordinated water molecule and one lattic water molecule. Each Cd^{2+} ions is a slightly distorted octahedron ligated by two N atoms from two different H_2L' ligands, two O atoms from two coordinated water molecules and two O atoms from two different Tp^{2-} ligands. Four O atoms (Cd(1)–O(1) 2.289(3), Cd(1)–O(3) 2.335(3) Å) form the equatorial plane.

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

Parameter	Value	
	I	**II**
Formula weight	402.65	386.51
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
a, Å	15.6614(16)	7.9930(4)
b, Å	11.7303(15)	8.9033(6)
c, Å	17.3327(15)	11.6219(8)
α, deg	90	111.222(6)
β, deg	90	92.771(5)
γ, deg	90	98.703(5)
Volume, Å^3	3184.3(6)	757.30(9)
Z	8	2
ρ_{calcd}, g/cm^3	1.680	1.695
Absorption coefficient, mm^{-1}	1.579	0.794
$F(000)$	1624.0	392
2θ Range for data collection, deg	6.684–56.22	6.516–50.896
Index ranges	$-20 \le h \le 18$, $-15 \le k \le 9$, $-15 \le l \le 22$	$-9 \le h \le 7$, $-9 \le k \le 10$, $-13 \le l \le 11$
Reflections collected	9507	2674
Independent reflections (R_{int})	3343 (0.1555)	1861 (0.0242)
Data/restraints/parameters	3343/0/235	1861/0/236
Goodness-of-fit on F^2	1.031	1.065
Final R indexes ($I > 2\sigma(I)$)	$R_1 = 0.0990$, $wR_2 = 0.2333$	$R_1 = 0.0357$, $wR_2 = 0.0805$
Final R indexes (all data)	$R_1 = 0.1625$, $wR_2 = 0.2738$	$R_1 = 0.0381$, $wR_2 = 0.0816$
Largest diff. peak and hole, e Å^{-3}	2.02 and –1.31	0.47 and –0.48

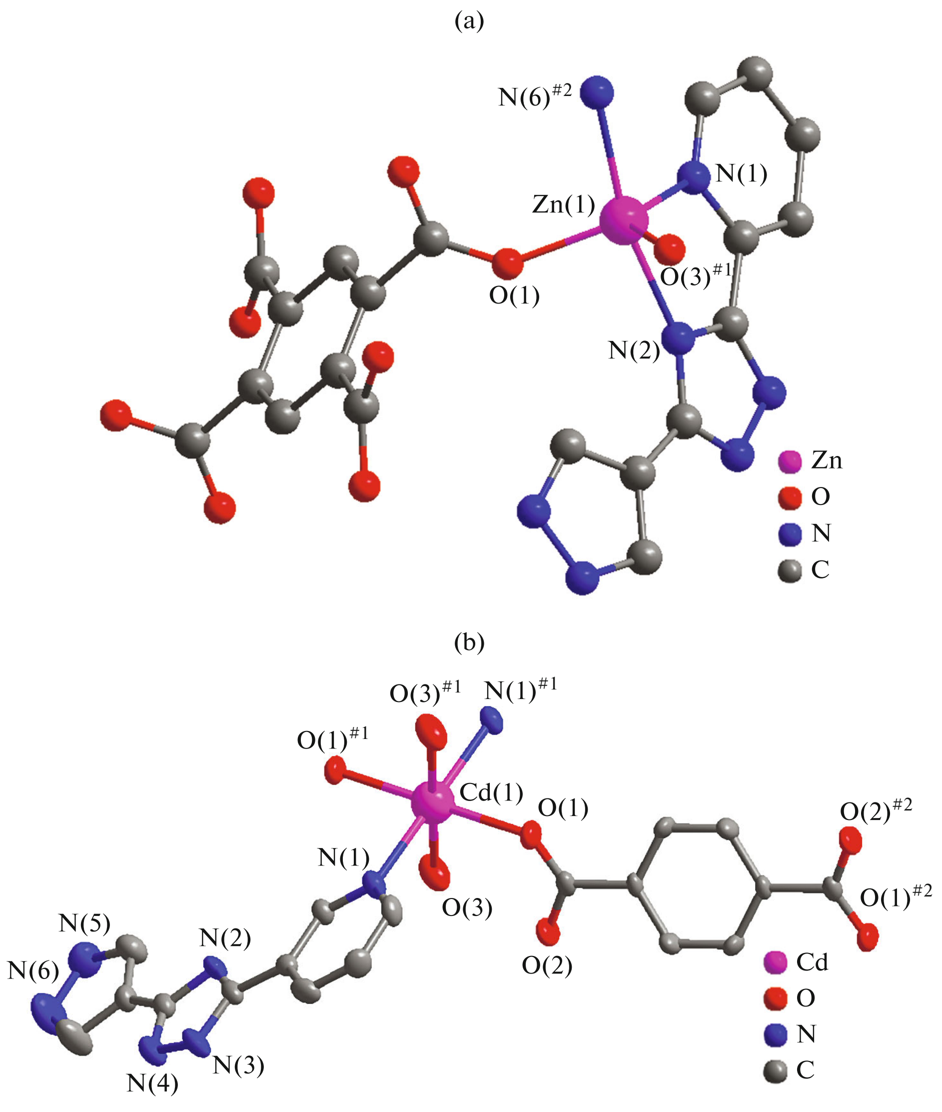

Fig. 1. Coordination environments of the Zn^{2+} ion in **I** (a) and Cd^{2+} ion in **II** (b).

The two N atoms (Cd(1)–N(1) 2.307(3) Å) at the axial sites are almost perpendicular to the equatorial plane. The OCdO bond angles vary from 81.93(12)° to 180.0°. The OCdN bond angles vary from 86.71(11)° to 93.29(11)°. The bond angles of $N(1)Cd(1)N(1)^{\#1}$ are 180.0°, which are similar to other Cd-based complexes [16, 17]. The two carboxyl groups of H_2Tp ligand in compound **II** are completely deprotonated and link adjacent Cd^{2+} ions with coordination modes (μ_1-η^1:η^0, μ_1-η^1:η^0). The adjacent Cd^{2+} ions are bridged into one dimensional chain structure by oxygen atoms coming from Tp^{2-} ligands (Fig. 3a). The terminal H_2L' ligands suspend on the chains. Some hydrogen-bonding interactions such as O(water)···O(water) and O(water)···O(carboxyl), connect the adjacent chains into two-dimensional network (Fig. 3b).

Considering the excellent luminescent properties of coordination polymers with d^{10} transition metal ions, the luminescent properties of compound **I** and ligands have been determined in the solid state at room temperature. As shown in Fig. 4. The free ligands H_2L and H_4Btec display photoluminescence with emission maxima at 430 nm (λ_{ex} = 390 nm) and 390 nm (λ_{ex} = 360 nm), respectively, which are assigned to a $\pi^* \to \pi$ or $\pi^* \to n$ transition

Table 2. Selected bond distances and angles for **I** and **II***

Bond	d, Å	Bond	d, Å
		I	
Zn(1)–O(1)	2.009(6)	Zn(1)–N(2)	2.174(6)
Zn(1)–O(3)^1	2.027(5)	Zn(1)–N(6)^2	2.164(7)
Zn(1)–N(1)	2.148(6)		
		II	
Cd(1)–O(1)	2.289(3)	Cd(1)–N(1)	2.307(3)
Cd(1)–O(3)	2.335(3)		
Angle	**ω, deg**	**Angle**	**ω, deg**
		I	
O(3)^{1}Zn(1)N(2)	88.9(2)	O(1)Zn(1)O(3)^1	116.7(2)
O(3)^{1}Zn(1)N(6)^2	90.0(3)	O(1)Zn(1)N(1)	113.0(2)
N(1)Zn(1)N(2)	78.0(2)	O(1)Zn(1)N(2)	89.4(2)
O(3)^{1}Zn(1)N(1)	128.3(3)	O(1)Zn(1)N(6)^2	101.8(2)
N(6)^{2}Zn(1)N(2)	168.0(3)	N(1)Zn(1)N(6)^2	93.3(3)
		II	
O(1)^{1}Cd(1)O(1)	180.0	O(1)Cd(1)N(1)	92.78(12)
O(1)Cd(1)O(3)^1	81.93(12)	O(3)Cd(1)O(3)^1	180.0
O(1)Cd(1)O(3)	98.07(12)	O(3)Cd(1)N(1)^1	93.29(11)
O(1)^{1}Cd(1)O(3)	81.93(12)	N(1)Cd(1)O(3)	86.71(11)
O(1)^{1}Cd(1)N(1)	87.22(12)	N(1)Cd(1)N(1)^1	180.0

* Symmetry transformations used to generate equivalent atoms: ^{1} x, $3/2 - y$, $1/2 + z$; ^{2} $1 - x$, $-1/2 + y$, $3/2 - z$ (**I**); ^{1} $-x$, $1 - y$, $1 - z$ (**II**).

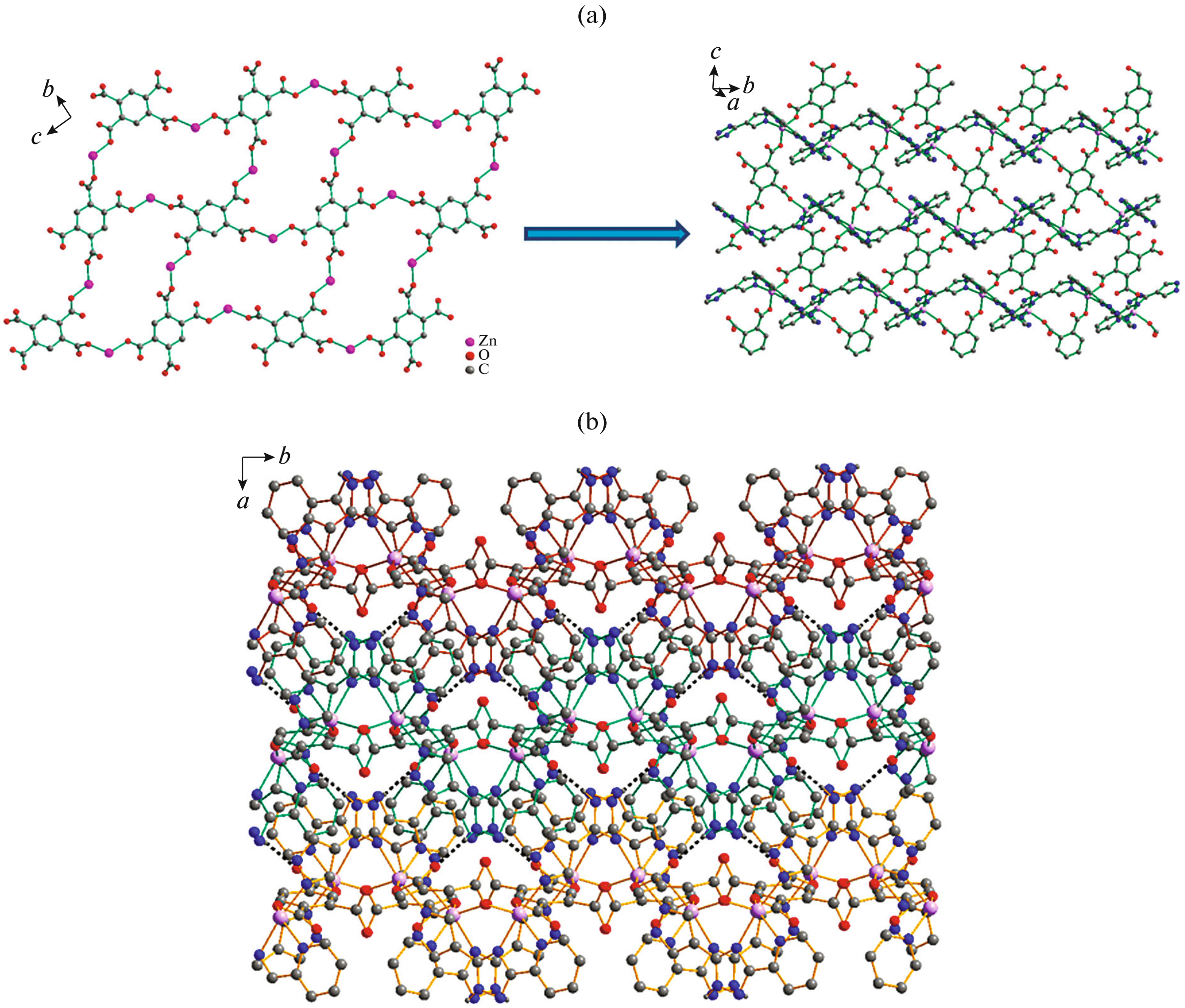

Fig. 2. The 2D layer $[Zn_4(Btec)]^{4-}$ and 2D network of **I** (a); the 3D supermolecule structure of **I** (b).

[18]. It was reported that the emission of aromatic dicarboxylate ligands belongs to $\pi^* \to n$ transitions, which is very weak compared to that of the $\pi^* \to \pi$ transition of H_2L, so the dicarboxylates almost have no contribution to the fluorescent emission of as-synthesized complexes [19]. The photoluminescent spectra of compound **I** shows the emission maxima at 410 nm ($\lambda_{ex} = 340$ nm). The Zn(II) atom is known to be difficult to oxidize or reduce because of its d^{10} configuration. As a result, the emissions of compound **I** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT), which are ascribed to a mixture character of intraligand and ligand-to-ligand charge transition (LLCT) [20]. The shift of the band in comparison to those of the free ligands may originate from coordination interactions between Zn(II) and ligands.

For the sake of discovering the thermal stability of the compound **I**, the thermal weight measurement was carried out in the range of 30–900°C under flowing air atmosphere (Fig. 5). The title compound is robust and stable from room temperature to 380°C. Then, a sharp continual weight loss occurred, which is attributed to the decomposition of the framework. The result shows that the compound **I** has high thermal stability.

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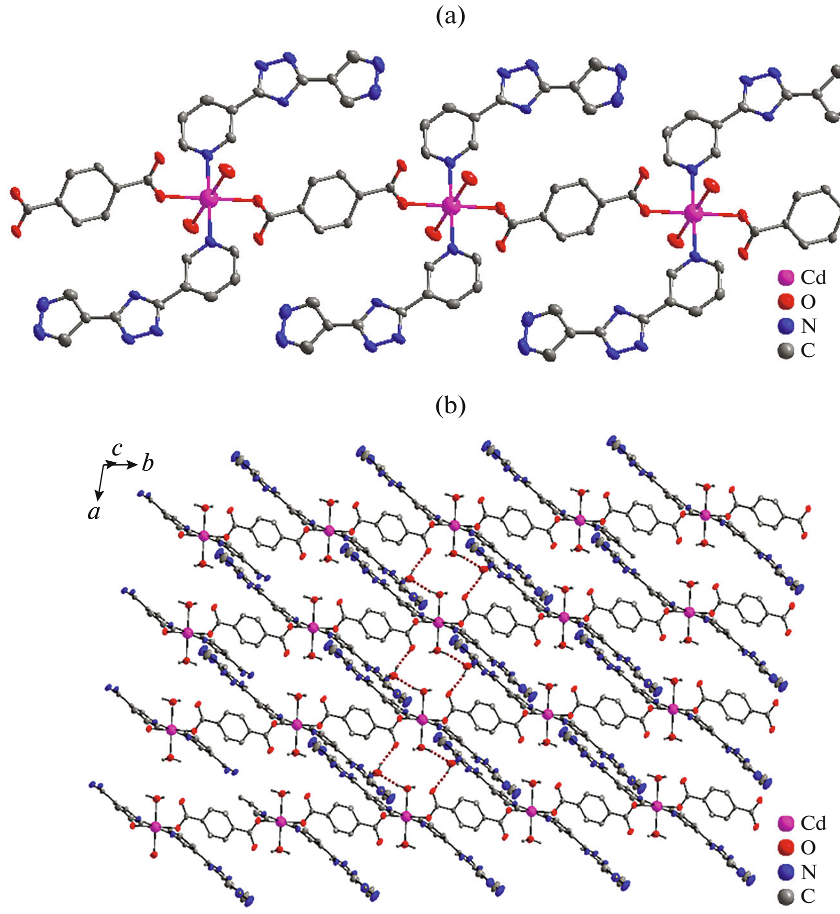

Fig. 3. The 1D chain structure of compound **II** (a) and the 2D network formed through the hydrogen bonds in **II** viewed along *c* axis (b).

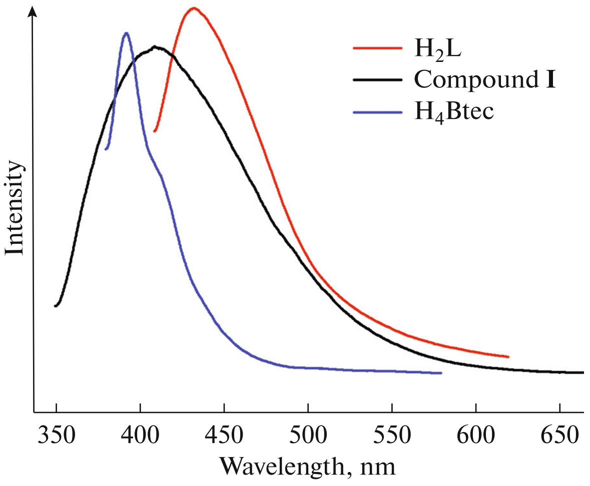

Fig. 4. The photoluminescent spectra of **I** and free ligand.

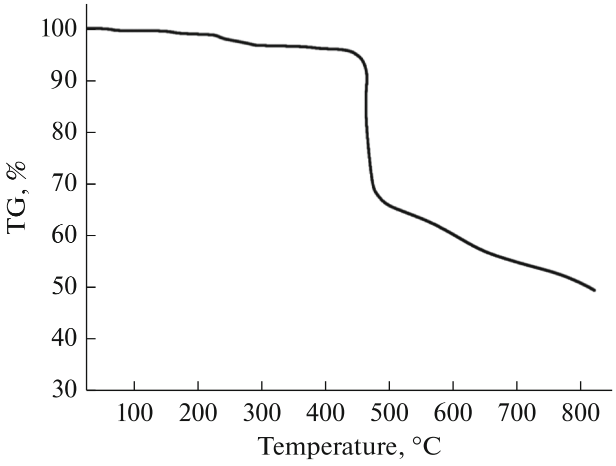

Fig. 5. The TGA curve of compound **I**.

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