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A New Supramolecular Cd(II) Complex with Unusual Solid-State Properties Constructed from Rigid Coligand[1]

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Abstract—A new complex with chemical formulae $[Cd_2(L)(IP)_4(H_2O)_2 \cdot L \cdot 4H_2O]$ (**I**) (H_2L = terephthalic acid, IP = 1-*H*-imidazo[4,5-f][1,10]-phenanthroline) has been synthesized and structurally characterized by single-crystal X-ray diffraction analysis (CIF file CCDC no. 1004954). The structural determination revealed that **I** has a dimeric motif, which can be further linked into 2D network via the three different hydrogen bonding interactions. In addition, the luminescent behavior of compound **I** was also explored.

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INTRODUCTION

The flourishing realm of crystal engineering has provided a sound junction between aesthetics of crystalline architectures and their potential functions [1–4]. Thus, much effort has been devoted to controllable formation of desired 0–3D polymers with the concept of rational design and crystal engineering [5–7]. In some ways, the structures of coordination compounds are greatly affected by certain weak interactions, such as hydrogen bonding and stacking interactions [8, 9].

Chelating bipyridyl-like ligands, such as 1,10-phenanthroline (Phen) and 2,2'-bipyridine, are important in maintaining the one-dimensionality of the coordination polymers and may provide potential supramolecular recognition sites [10–13]. However, its derivative 1-*H*-imidazo[4,5-f][1,10]-phenanthroline (IP) is lack of research. It has two additional coordination sites when compared to Phen organic ligand. The remarkable feature for IP is not only a hydrogen-bond acceptor but also an excellent hydrogen-bond donor based on deprotonated –NH-group. In this work, we reported a new complex $[Cd_2(L)(IP)_4(H_2O)_2 \cdot L \cdot 4H_2O]$ (I) (H_2L = terephthalic acid) that was obtained by rigid dicarboxylate and IP co-ligand. Complex I shows a dimeric motif that is connected by one L linker, in which can be further linked into 2D network via the three different hydrogen bonding interactions. In addition, the luminescent behavior of compound I was also explored.

EXPERIMENTAL

Materials and method. All reagents were purchased from commercial sources and used as received. IR spectra were recorded with a PerkinElmer Spectrum One spectrometer in the region 4000–400 cm^{-1} using KBr pellets. Thermogravimetric analysis (TGA) was carried out with a Metter–Toledo TA 50 in dry dinitrogen (60 mL min^{-1}) at a heating rate of 5°C min^{-1}. X-ray powder diffraction (XRPD) data were recorded on a Rigaku RU200 diffractometer at 60 kV, 300 mA for CuK_α radiation (λ = 1.5406 Å) with a scan speed of 2°C/min and a step size of 0.013° in 2θ. Photoluminescence analyses were performed on a Perkin-Elmer LS55 luminescence spectrometer.

Synthesis of complex I. A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (0.1 mmol), H_2L (0.1 mmol), IP (0.2 mmol), CH_3OH (1 mL) and deionised water (10 mL) was stirred for 30 min in air. The pH of the resulting solution was adjusted to 7 using dilute NaOH (1 mol/L) and kept at 140°C (oven) for 72 h, and then cooled down to 25°C. The resulting crystals formed were filtered off, washed with water and dried in air.

For $C_{68}H_{52}N_{16}O_{14}Cd_2$

anal. calcd., %:	C, 52.96;	H, 3.40;	N, 14.53.
Found, %:	C, 52.77;	H, 3.27;	N, 14.60.

IR (KBr; ν, cm^{-1}): 3129 v.s, 1685 v.s, 1561 v.s, 1377 v.s, 1290 m, 1077 m, 710 v.s, 513 v.s.

X-ray crystallography. Single crystal X-ray diffraction analysis of complex **I** was carried out on a Bruker SMART APEX II CCD diffractometer equipped with

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Table 1. Crystallographic data and experimental details for compound **I**

Parameter	Value
Formula weight	1542.06
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a, Å	7.5677(11)
b, Å	14.093(2)
c, Å	14.788(2)
α, deg	91.729(2)
β, deg	103.126(2)
γ, deg	90.135(2)
Volume, Å^3; Z	1535.2(4); 1
ρ_{calcd}, kg/m^3	1.668
F(000)	780
Absorption coefficient, mm^{-1}	0.778
Index ranges	$-9 \le h \le 8, -18 \le k \le 16, -12 \le l \le 12$
θ Range for data collection, deg	1.45–27.10
Reflections collected	9288
Independent reflection (R_{int})	6657 (0.0493)
GOOF	1.002
Reflections refined	475
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0380, wR_2 = 0.0803$
R indices (all data)	$R_1 = 0.0521, wR_2 = 0.0862$
Largest diff. peak/hole, e Å^{-3}	0.519/–0.518

a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using ϕ/ω scan technique at room temperature 298(2) K. Data were processed using the Bruker SAINT package and the structures solution and the refinement procedure was performed using SHELX-97 [14]. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The hydrogen atoms of lattice water molecules in compound **I** were located using the different Fourier method. Table 1 shows crystallographic data of **I**. Selected bond distances and bond angles are listed in Table 2. Supplementary material for **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 1004954; deposit@ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk).

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

Bond	d, Å	Bond	d, Å
Cd(1)–O(3w)	2.299(2)	Cd(1)–N(1)	2.313(3)
Cd(1)–O(1)	2.328(2)	Cd(1)–N(5)	2.334(3)
Cd(1)–N(6)	2.338(2)	Cd(1)–N(1)	2.338(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(2)Cd(1)O(2)	158.97(8)	O(3w)Cd(1)N(5)	157.27(8)
O(3w)Cd(1)N(1)	100.12(8)	N(6)Cd(1)N(1)	162.92(9)

RESULTS AND DISCUSSION

In the FT–IR spectra of the prepared products, the strong bands appeared around 3200 cm^{-1} should be assigned to the stretching vibrations of O–H, indicating the presence of free and/or coordinated water molecule. The infrared spectra of **I** exhibit two absorptions in the 1377–1680 cm^{-1} region which are associated with the stretching vibration modes of imidazo[4,5-f][1,10]-phenanthroline ring. In addition, the peaks observed at the range of 1561 and 1377 cm^{-1} are assigned to the stretching bands of ν_{as}(COO–) and ν_s(COO–), which indicates that the carboxyl groups in complex **I** is deprotonated [15].

As illustrated in Fig. 1, the asymmetric unit of **I** consists of one Cd^{2+} cation, one L anion, two IP ligands, one deprotonated L ligand, and two free water molecules. The Cd(II) atom is six-coordinated by one oxygen atom from the coordinated L ligand, four nitrogen atoms from two chelating IP ligands, one Cl anion and one oxygen atom from coordinated water molecule, respectively. The Cd–O bond distances range

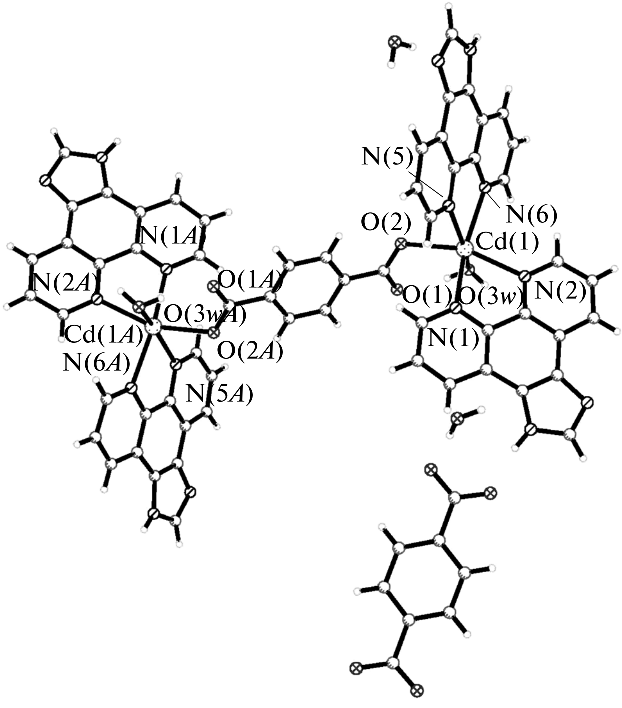

Fig. 1. Coordination environments of Cd^{2+} ions and organic ligands in **I** (symmetric code: (*A*) $-x + 2$, $-y + 1$, $-z + 1$).

from 2.299(2) to 2.328(2) Å, Cd–N bond distances range from 2.313(3) to 2.338(2) Å. The N(3) atom acts as a hydrogen donor for O(4) atom from free L ligand (N(4)···O(2) 2.699 Å, N(3)–H(3)···O(4) 168.89°) to form a hydrogen bonding chain (Fig. 2b). Also, the N(7) atom acts as a hydrogen donor for O(2) atom from coordinated L ligand (N(4)···O(2) 2.875 Å, N(7)–H(7)···O(2) 171.07°) to form a hydrogen bonding chain (Fig. 2b). Furthermore, the hydrogen bonds between the ligands and free water, and between the free water molecules extend the chains into a 2D weak linked layer (Fig. 2a and Table 3).

To study the stability of the polymer, TGA of complex **I** was performed (Fig. 3). The compound **I** shows two of weight loss steps. The first weight loss of 4.5% between 20 and 129°C is corresponding to the release of four free water molecules per formula unit (calcd. 4.6%) and the complex remains undecomposed up to 260°C. The second deposition finishes at about 750°C, which can be attributed to the elimination of organic ligands and two coordinated water moelcules (calcd. 79.5%). Additionally, to confirm the phase purity of compound, the original sample was characterized by XRPD at room temperature. The XRPD pattern of **I** is similar to that of simulated phase, although minor differences can be seen in the positions, intensities, and widths of some peaks.

As we all know, Cd(II) polymer can produce a variety of complexes that not only exhibit appealing structures but also possess PL properties [16]. The PL spectrum of complex **I** is investigated in the solid state at room temperature. As indicated in Fig. 4, the emission peak is 511 nm upon excitation at 338 nm. In order to understand the nature of emission band for **I**, the PL property of free ligand IP was analyzed, in which exhibits the strongest emission peak at about 460 nm. Compared with the PL spectrum of free ligand, the emission spectra of **I** might be attributable to the intraligand fluorescent emissions of IP [17, 18].

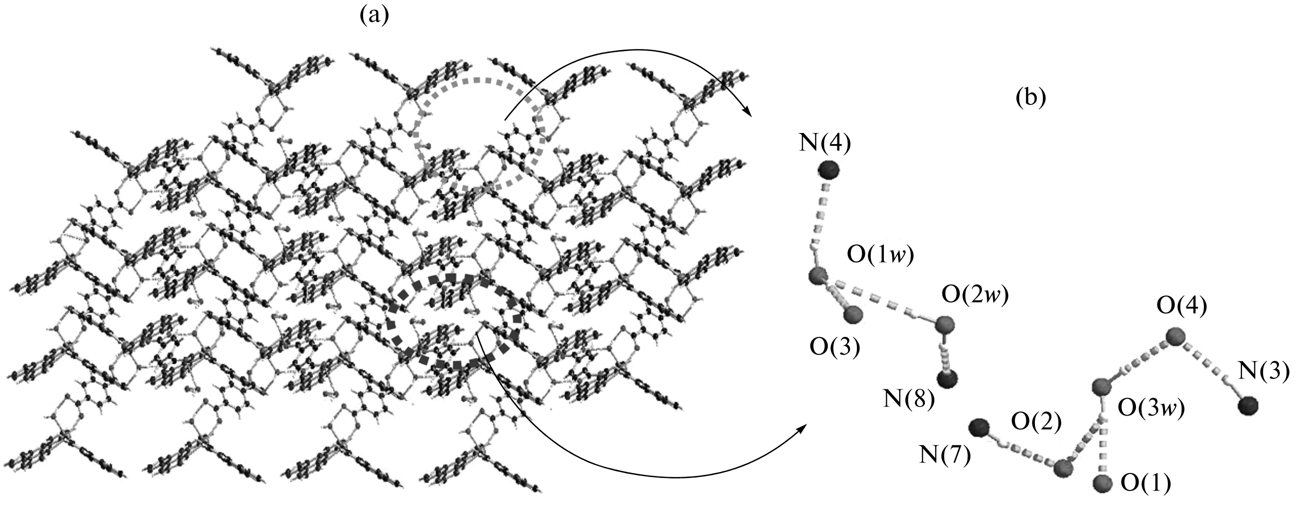

Fig. 2. The 2D supramolecular layer (a) and two different H-bonded interactions among the donor/acceptors sites (b).

Table 3. Geometric parametes of hydrogen bonds in **I**

Distance, Å				Angle DHA, deg
D–H···A	D–H	H···A	D···A	
O(3*w*)–H(3*B*)···O(1)	0.83	1.86	2.680(4)	168
O(3*w*)–H(3*C*)···O(4)	0.83	1.82	2.656(3)	177
N(7)–H(7)···O(2)	0.85	2.03	2.875(9)	171
O(1*w*)–H(1*B*)···O(3)	0.82	2.06	2.875(10)	174
O(3*w*)–H(3*B*)···O(2)	0.83	2.61	3.011(5)	111
N(3)–H(3)···O(4)	0.86	1.85	2.699(8)	169
O(1*w*)–H(1*A*)···N(4)	0.83	2.17	2.964(11)	167
O(2*w*)–H(2*A*)···N(8)	0.86	2.01	2.841(13)	164

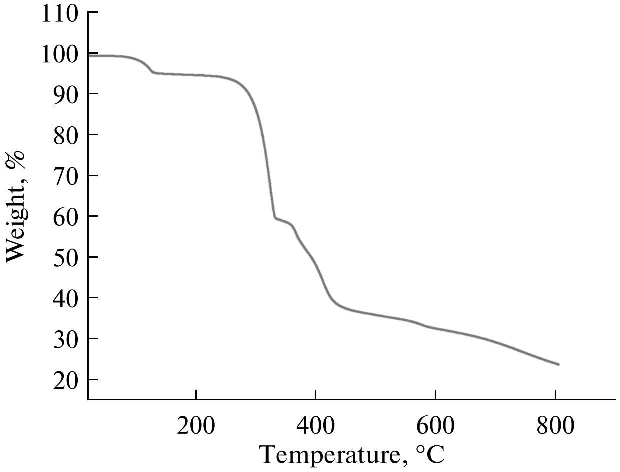

Fig. 3. TG curve of complex **I**.

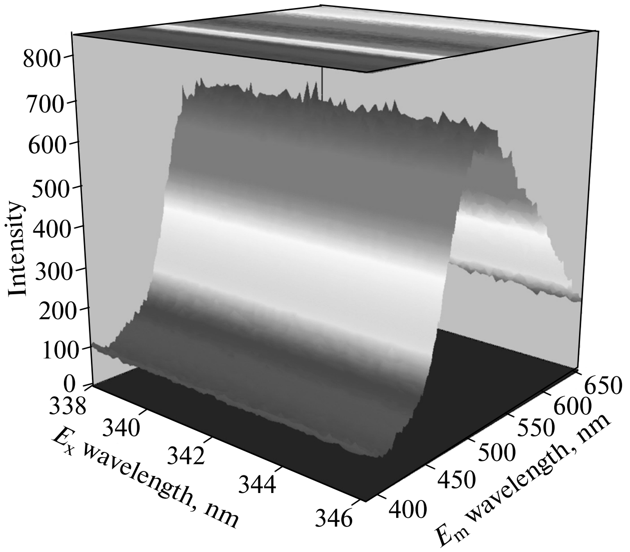

Fig. 4. View of the 3D fluorescence spectrum of **I** at room temperature.

Thus, we have presented a rational synthetic strategy that successfully achieved a new Cd(II) compound **I** with mixed ligands. In addition, complex **I** exhibits intense fluorescence emission and may be candidate for fluorescent materials.

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