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Syntheses, Structure, and Luminescence of Two New 1D Cd(II) Complexes[1]

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Abstract—Two Cd-based complexes with chemical formulae $\{[Cd(L)(2,2'\text{-Bipy})] \cdot 0.5H_2O\}_n$ (**I**) and $[Cd(L)(3\text{-Mp})_2]_n$ (**II**) (H_2L = 3,5-dibromosalicylaldehyde salicylhydrazone; 2,2'-Bipy = 2,2'-pyridine, 3-Mp = 3-methylpyridine), have been synthesized and structurally characterized by X-ray single-crystal diffraction (CIF files CCDC nos. 1044341 (**I**), 1044342 (**II**)). Furthermore, the luminescence properties of compounds **I** and **II** have been investigated.

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INTRODUCTION

Hydrazone complexes are of interest for their various applications in analytical chemistry, catalysis, nonlinear optical materials and biochemistry. In a variety of synthetic fluorescent chemosensors, acylhydrazone Schiff base [1–6], which contains the group –CONHN=CH–, have been proved to be good fluorescent receptor. The formation of complexes with a coplanar structure is conducive to the production of fluorescence: the reaction of a metal ion with a chelating agent induces rigidity in the resulting molecule and tends to produce fluorescence [7, 8]. From the viewpoint of structure, the ligands with the necessary NNS coordination sites can play an important role in assembling different coordination structures and even interesting supramolecular frameworks [9–13]. Our strategy is to explore the linking of multidentate hydrazone ligand with aromatic systems in cadmium coordination chemistry, and investigate the effect of chelating N-donor ligands on the resulting motifs. In this paper, 3,5-dibromosalicylaldehyde salicylhydrazone (H_2L), which acts as a good fluorescent and colorimetric detector for d^{10} Cd(II) system. We choose the L as the fluorophore base on the fact that it possesses desirable photophysical properties, such as a large Stocks Shift, visible excitation and emission wavelength. Herein, we report two complexes $\{[Cd(L)(2,2'\text{-Bipy})] \cdot 0.5H_2O\}_n$ (**I**) and $[Cd(L)(3\text{-Mp})_2]_n$ (**II**), where 2,2'-Bipy = 2,2'-pyridine, 3-Mp = 3-methylpyridine. Their structures have been characterized by X-ray single-crystal diffraction, FTIR and elemental analysis. The thermal and luminescence of properties were also investigated of complexes **I** and **II**.

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. 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 (PXRD) 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.

X-ray crystallography. Single crystal X-ray diffraction analysis of compounds **I** and **II** was carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using ϕ/ω scan technique at room temperature. 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 molecule in compound **I** were not located using the different Fourier method. Crystallographic data of **I** and **II** are given in Table 1. Selected bond distances and bond angles are listed in Table 2.

Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. CCDC 1044341 (**I**), 1044342 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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[1] The article is published in the original.

Table 1. Crystallographic data and structural refinement details of complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	1379.27	710.70
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c_1$
Crystal color	Yellow	Yellow
a, Å	12.359(7)	9.164(5)
b, Å	9.262(5)	24.512(13)
c, Å	22.460(11)	13.395(6)
β	100.290(9)	116.05(3)
V, Å^3	2530(2)	2703(2)
Z	2	4
ρ_{calcd}, g/cm^3	1.811	1.746
μ, mm^{-1}	4.057	3.798
F(000)	1340	1392
θ Range, deg	2.38–25.43	2.32–22.78
Index ranges hkl	$-14 \le h \le 14$, $-10 \le k \le 11$, $-27 \le l \le 23$	$-11 \le h \le 10$, $-29 \le k \le 28$, $-9 \le l \le 16$
Reflection collected	12806	13956
Independent reflections (R_{int})	0.0452	0.0529
Reflections with $I > 2\sigma(I)$	4592	4903
Number of parameters	308	327
GOOF	1.161	0.815
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0495, 0.1494	0.0386, 0.1007
R_1, wR_2 (all data)**	0.0721, 0.1635	0.0779, 0.1283
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	1.773, –1.050	0.455, –0.699

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

Synthesis of complex I. A DMF solution (15 mL) of the Schiff base (1 mmol) and 2,2'-Bipy (1.5 mmol) were added with stirring to a DMF solution (15 mL) of $Cd(Ac)_2$ (1 mmol). After adding two drops of triethylamine, the reaction solution were stirred at room temperature for 2 h. X-ray quality single crystals were formed by slow evaporation of the solutions in air after a few days.

For $C_{48}H_{34}N_8O_7Br_4Cd_2$ (M = 1379.27)

anal. calcd., %:	C, 41.80;	H, 2.48;	N, 8.12.
Found, %:	C, 41.39;	H, 2.37;	N, 8.44.

IR (KBr; ν, cm^{-1}): 3421 v.s, 2842 m, 1682 v, 1609 m, 1440 v.s, 1142 v, 1012 m, 759 v.s, 697 v.s, 562 m.

Synthesis of complex II was carried out by the same synthetic method used for the preparation of **I** except that 2,2'-Bipy was replaced by 3-Mp (1.5 mmol).

For $C_{26}H_{22}N_4O_3Br_2Cd$ (M = 710.70)

anal. calcd., %:	C, 43.94;	H, 3.12;	N, 7.88.
Found, %:	C, 43.56;	H, 3.10;	N, 7.59.

IR (KBr; ν, cm^{-1}): 3043 m, 2881 v, 1609 m, 1485 v.s, 1424 m, 1333 m, 1131 m, 759 m, 703 v.s, 578 v.

RESULTS AND DISCUSSION

The results of crystallographic analysis revealed that the asymmetric unit of complex **I** contains one

Table 2. Selected bond distances (Å) and angles (deg) of structure **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
		I	
Cd(1)–O(3)	2.198(5)	Cd(1)–O(1)	2.216(4)
Cd(1)–N(1)	2.306(5)	Cd(1)–N(3)	2.307(5)
Cd(1)–N(2)	2.346(6)	Cd(1)–O(2)	2.349(5)
		II	
Cd(1)–O(1)	2.190(4)	Cd(1)–O(3)	2.201(4)
Cd(1)–O(2)	2.328(4)	Cd(1)–N(1)	2.348(5)
Cd(1)–N(4)	2.366(4)	Cd(1)–N(3)	2.370(5)
Angle	**ω, deg**	**Angle**	**ω, deg**
		I	
O(3)Cd(1)O(1)	104.63(18)	O(3)Cd(1)N(1)	91.48(19)
O(1)Cd(1)N(1)	100.07(18)	O(3)Cd(1)N(3)	105.77(18)
O(1)Cd(1)N(3)	78.37(17)	N(1)Cd(1)N(3)	162.6(2)
O(3)Cd(1)N(2)	157.57(18)	O(1)Cd(1)N(2)	91.5(2)
N(1)Cd(1)N(2)	70.1(2)	N(3)Cd(1)N(2)	92.55(19)
O(3)Cd(1)O(2)	85.44(17)	O(1)Cd(1)O(2)	148.11(17)
		II	
O(1)Cd(1)O(3)	119.97(14)	O(1)Cd(1)O(2)	147.80(14)
O(3)Cd(1)O(2)	91.36(13)	O(1)Cd(1)N(1)	78.50(14)
O(3)Cd(1)N(1)	161.27(14)	O(2)Cd(1)N(1)	69.93(13)
O(1)Cd(1)N(4)	90.13(16)	O(3)Cd(1)N(4)	86.12(16)
O(2)Cd(1)N(4)	84.37(15)	N(1)Cd(1)N(4)	91.01(16)
O(1)Cd(1)N(3)	95.18(18)	O(3)Cd(1)N(3)	89.96(16)
O(2)Cd(1)N(3)	91.87(17)	N(4)Cd(1)N(3)	174.49(18)

Cd(II) atom, one L ligand, one 2,2'-Bipy ligand and half lattice water molecule (Fig. 1a). The Cd^{2+} ion in compound **I** is surrounded by two phenol oxygen atom, a salicyloyl oxygen atom and a hydrazine nitrogen atom from one L ligand, and two nitrogen atoms from one chelating 2,2'-Bipy ligand, forming a distorted CdN_3O_3 octahedral configuration. In the equatorial plane, one N(2) (2,2'-Bipy) atom and one O(2) (Acyl) atom, and two hydroxyl oxygen atoms of O(1) and O(3) are coordinated to the Cd center in trans arrangement. The Cd(II)–N/O distances are 2.346(6) and 2.349(5) Å, respectively. The axial positions are occupied by two N atoms (N(1) and N(3)) with the large distance of 2.307(5) Å to the Cd center. Hence, the octahedron is obviously elongated in the axial direction due to Jahn–Tellar distortion. In addition, the carbonyl-O of the L ligand enolizes during complexation and deprotonates to bond through carbonylate-O. So, phenolate-O bridges between adjacent metal atoms result into a 1D chain structure in **I** (Fig. 2a).

The results of crystallographic analysis revealed that the asymmetric unit of complex **II** contains one Cd(II) atom, one L ligand, two 3-Mp ligands (Fig. 1b). The Cd^{2+} ion is coordinated to one bi-anionic ligand through a carbonyl-O, azomethine-N and two phenolate-O of a L ligand, and two N atoms from two 3-Mp ligands. The molecular structure shows a distorted octahedral geometry around metal ion.

The Cd–O(2) (carbonyl-O), Cd–O(3)/Cd–O(1) (phenolate-O), Cd–N(1) (azomethine-N) bond lengths are 2.328(4), 2.201(4), 2.190(4) and 2.348(5) Å, respectively [15]. The bond distances of Cd–N(3)/Cd–N(4) are 2.370(5), 2.366(4) Å, respectively. These bond lengths fall in the normal range of many octahedral Cd(II) complexes with N,O-donor ligands. The shorter Cd–O(3) bond length as compared to Cd–O(2) indicates that the phenolate-O bond is more stronger than the carbonyl oxygen [16]. The observed bond angles of O(2)Cd(1)O(1), 147.80(14)°, N(1)Cd(1)O(1), 78.50(14)°, N(3)Cd(1)N(4) 174.49(18)° indicate that the octahedral geometry is slightly distorted due to chelation effect [17]. The phenolate-O bridges between adjacent metal atoms also result into a 1D chain structure in **II** (Fig. 2b).

In the FTIR spectra, ν(N–H) observed at 3249 cm^{-1} in the IR spectrum of free ligand [18], occurs nearly at the same or at a slightly shifted position in the Cd(II)-based complexes, indicating the non-involvement of NH group in bonding. The ν(C=O) band observed at 1638 cm^{-1} in the ligand, is shifted to lower wave number by ca. 1018 cm^{-1} in its Cd(II) complexes, indicating coordination of the C=O group to the metal ion. The appearance of a new ν(C–O)$^{-}$ band in the two complexes in the range 1360–1350 cm^{-1}, suggests bonding of the ligand to metal through a phenolate-O. The ν(C=N) band observed at 1610 cm^{-1} in the spectra of ligand, shifts to low frequency in **I** and **II**, suggesting coordination of azomethine-N. The non-ligand bands in the 560–590 and 500–430 cm^{-1} ranges have been tentatively assigned to ν(Cd–O) and ν(Cd–N).

To study the stability of the complexes, thermogravimetric analyses (TGA) of complexes **I** and **II** were performed (Fig. 3). The TGA diagram of **I** shows three weight loss steps. The first weight loss starts at 35°C and completed at 105°C. The observed weight loss of 1.5% is corresponding to the loss of the water molecules (calcd. 1.3%). The second weight loss occurs in the range 126–210°C, which can be attributed to the elimination of 2,2'-Bipy ligands. The complex **II** has two weight loss steps. The first weight loss began at 300°C and completed at 350°C. The observed weight loss of 25.6% is corresponding to the loss of the two 3-Mp (calcd. 26.2%). Soon after, the deposition of all the ligands starts on, which indicates that the full framework will be decomposed when the coordinative 3-Mp were lost.

Additionally, to confirm the phase purity and stability of compounds **I** and **II**, both the original samples were characterized by PXRD. Although the experimental patterns have a few unindexed diffractions lines and some are slightly broadened in comparison to those simulated from single-crystal models, it can still to be considered that the bulk synthesized materials and as-grown crystal are homogeneous for compounds **I** and **II**.

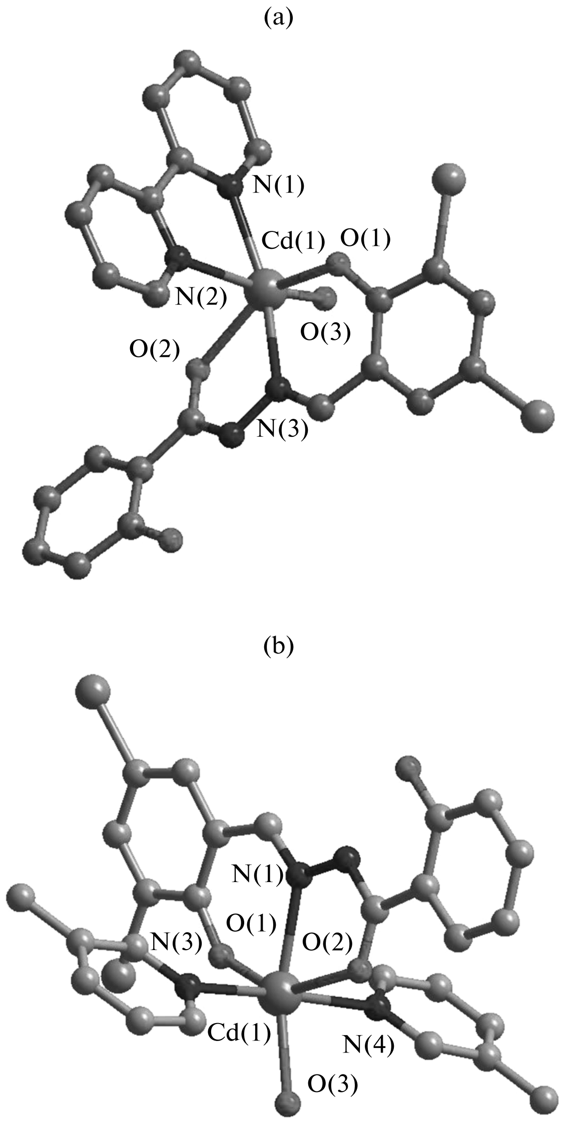

Fig. 1. The coordination geometries of the metal centers and the ligands geometries in **I** (a) and **II** (b). Displacement ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity.

Luminescent properties of compounds **I** and **II** were investigated under the same situation. Excitation of the solid samples at λ = 320 nm leads to strong blue-fluorescent emission bands with the maximum intensity at 466 nm for **I** and 469 nm for **II**, which can be seen in Fig. 4. The free H_2L ligand exhibits emission bands at 509 nm upon excitation at λ = 320 nm, while no clear photoluminescence emission can be observed for the ligand at room temperature. It is clear that in comparison with other compounds, such as $[Zn_2(Fshz)_2(Bipy) \cdot 2DMF)]_n$ [6, 19], a hypsochromic shift of emissions occurs in the compounds **I** and **II**. This is probably due to the differences of the central metal ions, because the photoluminescence behavior is closely associated with the metal ions and the

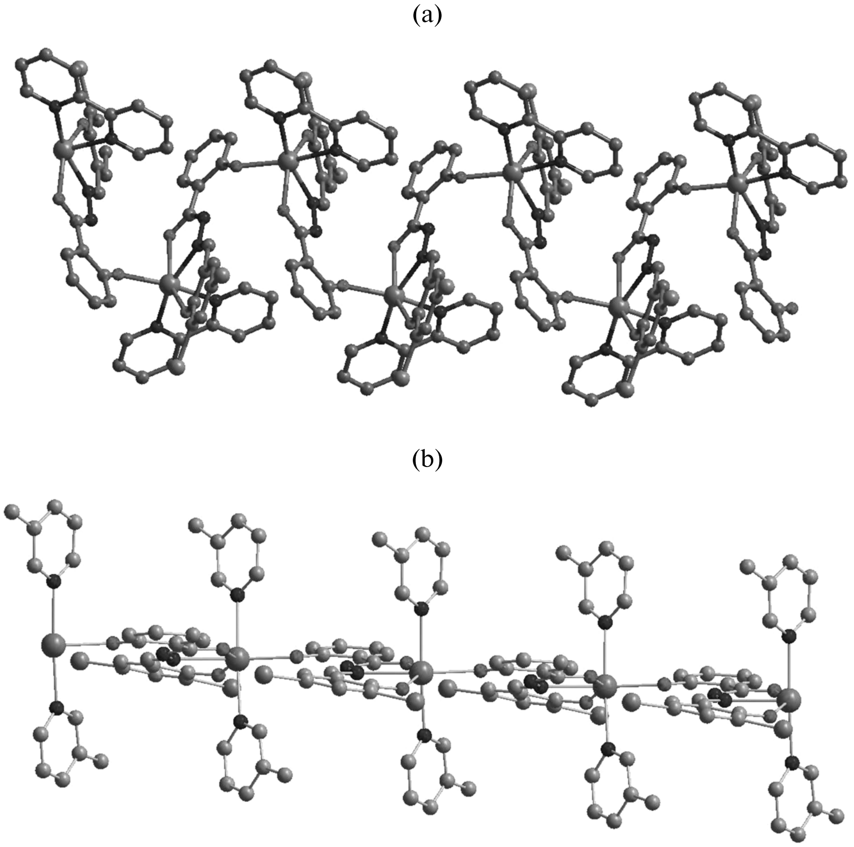

Fig. 2. View of the 1D packing chain directing by L linkers along *x* axis in **I** (a) and along the *y* axis in **II** (b).

ligands coordinated around them. The enhancement of the emission intensity for **I** and **II** compared with those of the free ligands may be ascribed to the increase of the ligand conformational rigidity due to their coordination to d^{10} ions.

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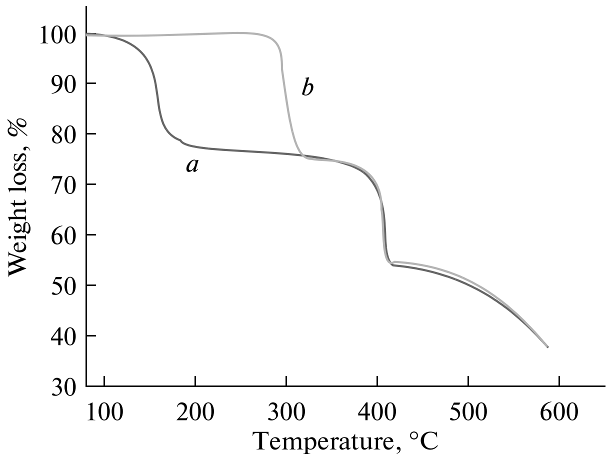

Fig. 3. TG curves of the complexes **I** (*a*) and **II** (*b*).

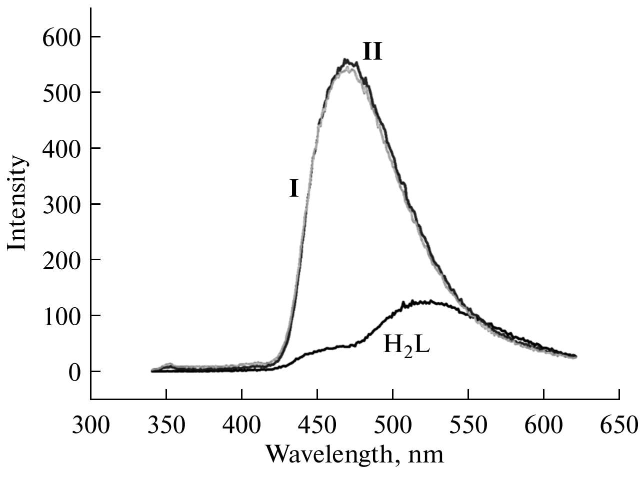

Fig. 4. View of the fluorescence spectra of H_2L, **I**, and **II** at room temperature.

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