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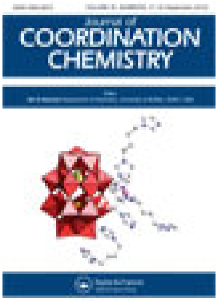

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Complexes of unsymmetric bis-hydrazide ligands: crystal structures and properties

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Accepted author version posted online: 04 Jul 2012.Published online: 27 Jul 2012.

To cite this article: Ying-Xia Zhou , Rui-Fang Yuan , Cai-Ling Fan , Li-E Liu , Ben-Lai Wu & Hong-Yun Zhang (2012) Complexes of unsymmetric bis-hydrazide ligands: crystal structures and properties, Journal of Coordination Chemistry, 65:17, 3133-3146, DOI: 10.1080/00958972.2012.708411

To link to this article: http://dx.doi.org/10.1080/00958972.2012.708411

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Journal of Coordination Chemistry
Vol. 65, No. 17, 10 September 2012, 3133–3146

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Complexes of unsymmetric bis-hydrazide ligands: crystal structures and properties

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(*Received 25 March 2012; in final form 21 May 2012*)

Two unsymmetric bis-aroyl-hydrazines, N′-(2-hydroxybenzoyl)isonicotinohydrazide (L1) and N′-(2-hydroxybenzoyl)nicotinohydrazide (L2), were synthesized through reactions of salicyl hydrazide with isonicotinoyl chloride and nicotinoyl chloride, respectively. Reactions of metal salts with L1 or L2 gave three new complexes, $[Cd(L1)_2(SCN)_2]_n$ (**1**), $[Zn(L1)_2Cl_2] \cdot H_2O$ (**2**), and $[Zn(L2)_2Cl_2]$ (**3**). Complex **1** features a 1-D double-chain structure built by SCN^- bridging six-coordinate Cd^{II} centers while **2** and **3** are mononuclear Zn^{II} complexes. In **1**–**3**, isomeric ligands L1 and L2 coordinate with metal ions in a terminal coordination mode. Ligands L1 and L2 through O–H···N and N–H···O hydrogen-bonding interactions in **1**–**3** are crucial for the structure extension into 3-D supramolecular structures of **1** and **2**, or 2-D sheet of **3**. Complexes **1**–**3** emit interesting blue-green luminescence. Thermal behaviors of **1**–**3** as well as the specific rotation of **2** were also investigated.

Keywords: Bis-hydrazide ligand; d^{10} Metal complex; Crystal structure; Fluorescence; Thermogravimetric analysis

1. Introduction

Hydrazine derivatives have been investigated because of their coordinative and biological activities as well as their use in analytical chemistry as metal-extracting agents [1–4]. Hydrazides based on $–CONHNH_2$ and their derivatives contain trigonal N- and O-donors, making them potential chelating ligands. Hydrazide derivatives and complexes have supramolecular interactions because they include hydrogen-bonding donors (amino-groups) and acceptors (carbonyl), and thus hydrogen-bonding plays an important role in extending and stabilizing the structures of the resultant complexes [5]. Hydrazide derivatives which have heteroatoms and various conformers may provide

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.708411

additional coordinative properties [6, 7]. Herein, as part of our continuing study, two unsymmetric pyridyl bis-hydrazides based on –CONHNHCO– were synthesized as spacers in this article. In the search for molecular-based materials with new and unusual properties, a marked increase in both interest and research activity has been given to extended solids of metals with d^{10} configuration because of their various coordination configurations and coordination numbers [8–14]. Therefore, three complexes of bis-hydrazide with d^{10} metal ions (Zn^{II} and Cd^{II}) were synthesized and characterized.

2. Experimental

2.1. *Materials and physical measurements*

Reagent grade chemicals were purchased from Zhengzhou Zhongliang Chemical Reagent Company and most were used without purification. The solvents were dried using standard methods when required [15].

IR spectra were recorded with an FTS-40 infrared spectrometer as KBr pellets from 4000 to 400 cm^{-1}. Thermal decomposition experiments were carried out using an NETZSCH TG 209 instrument in air from room temperature to 800°C with a flow rate of $20\,mL \cdot min^{-1}$ and a heating rate of $10^\circ C \cdot min^{-1}$. Luminescence spectra in solid samples were determined with a Fluoro Max-p spectrophotometer at room temperature with slit width of 0.5 nm. ^1H NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300 MHz.

Data collection was on a Rigaku Raxis-IV X-ray diffractometer at 291(2) K using graphite monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm). All structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL [16]. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. Hydrogen atoms of N and O were located from difference Fourier maps and included in the final refinement by using geometrical restraints, while the other hydrogen positions were generated geometrically and allowed to ride on their parent. Details of the crystal structure determinations of **1**–**3** are listed in table 1, and selected bond distances and angles are in table 2.

2.2. *Syntheses of ligands*

2.2.1. Synthesis of L1. Salicyl hydrazide was synthesized according to the reported method [17]. A mixture of isonicotinic acid (3.94 g, 32 mmol) and thionyl chloride (25 mL) in a round-bottomed flask was refluxed for 7 h with stirring. Excess thionyl chloride was removed under reduced pressure until yellow crystals of isonicotinoyl chloride were obtained. A solution of the prepared isonicotinoyl chloride and chloroform (30 mL) was dropped into a solution of salicyl hydrazide (5.02 g, 33 mmol), triethylamine (6 mL), and chloroform (30 mL) with vigorous stirring at 0–5°C. After addition, the resulting mixture was allowed to react for another 2 h at the same temperature. Finally, white solid product of L1 was obtained by filtration, washed with water, and recrystallized with ethanol. Yield: 61%; m.p.: 228–229°C.

Table 1. Crystal data and structure refinement for **1–3**.

Complex name	**1**	**2**	**3**
Empirical formula	$C_{28}H_{22}N_8O_6S_2Cd$	$C_{26}H_{24}Cl_2N_6O_7Zn$	$C_{26}H_{22}Cl_2N_6O_6Zn$
Formula weight	743.08	668.77	650.77
Temperature (K)	291(2)	291(2)	291(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$C222_1$	$C2/c$
Unit cell dimensions (Å, °)			
a	16.591(2)	7.6776(15)	8.668(2)
b	5.8816(8)	11.806(2)	11.513(3)
c	14.9320(19)	29.145(6)	26.406(6)
β	97.809(2)		96.848(3)
Volume (Å^3), Z	1443.6(3), 2	2641.8(9), 4	2616.4(11), 4
Calculated density ($Mg \cdot m^3$)	1.709	1.681	1.652
$F(000)$	748	1368	1328
Crystal size (mm^3)	0.44 × 0.37 × 0.19	0.30 × 0.20 × 0.20	0.45 × 0.27 × 0.20
θ range for data collection (°)	2.48–25.0	2.79–25.50	1.55–24.99
Limiting indices	$-19 \le h \le 19$,	$-9 \le h \le 9$,	$-9 \le h \le 10$,
	$-6 \le k \le 6$,	$-14 \le k \le 14$,	$-13 \le k \le 13$,
	$-17 \le l \le 15$	$-34 \le l \le 34$	$-31 \le l \le 26$
Reflections collected	2524	2342	2123
Independent reflection	6950 [R(int) = 0.0179]	13,377 [R(int) = 0.0474]	5750 [R(int) = 0.0332]
Data/restraints/parameters	2524/0/205	2342/0/207	2123/0/187
Goodness-of-fit on F^2	1.071	1.059	1.107
R_1	0.0222	0.0393	0.0929
wR_2	0.0559	0.0798	0.2431
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ ($e \cdot Å^{-3}$)	0.303 and −0.288	0.310 and −0.242	1.193 and −0.695

Table 2. Selected bond distances (Å) and angles (°) for **1–3**.

1		**2**		**3**	
Cd(1A)–N(1B)	2.285(2)	Zn(1)–N(1A)	2.057(2)	Zn(1)–N(1)	2.061(6)
Cd(1A)–N(1A)	2.285(2)	Zn(1)–N(1)	2.057(2)	Zn(1)–N(1A)	2.061(6)
Cd(1A)–N(2F)	2.3887(17)	Zn(1)–Cl(1)	2.2120(9)	Zn(1)–Cl(1)	2.206(2)
Cd(1A)–N(2A)	2.3887(17)	Zn(1)–Cl(1A)	2.2120(9)	Zn(1)–Cl(1A)	2.206(2)
Cd(1A)–S(1B)	2.7240(7)	N(1)–Zn(1)–N(1A)	113.44(14)	N(1)–Zn(1)–N(1A)	105.8(4)
Cd(1A)–S(1E)	2.7240(7)	N(1A)–Zn(1)–Cl(1A)	106.84(11)	N(1)–Zn(1)–Cl(1A)	110.3(2)
N(1A)–Cd(1A)–N(2F)	89.19(7)	N(1A)–Zn(1)–Cl(1)	104.65(11)	N(1)–Zn(1)–Cl(1)	105.57(18)
N(1A)–Cd(1A)–N(2A)	90.81(7)	Cl(1A)–Zn(1)–Cl(1)	120.74(5)	N(1A)–Zn(1)–Cl(1A)	105.57(18)
N(2F)–Cd(1A)–N(2A)	180.00(2)	N(1)–Zn(1)–Cl(1)	104.65(11)	N(1A)–Zn(1)–Cl(1)	110.3(2)
N(1A)–Cd(1A)–S(1B)	91.63(5)	N(1)–Zn(1)–Cl(1A)	106.84(11)	Cl(1A)–Zn(1)–Cl(1)	118.62(13)
N(2A)–Cd(1A)–S(1B)	89.65(5)	C(3)–N(1)–Zn(1)	118.3(3)	C(4)–N(1)–Zn(1)	119.5(5)
N(2A)–Cd(1A)–S(1E)	90.35(5)	C(3)–N(1)–Zn(1)	123.0(2)	C(1)–N(1)–Zn(1)	122.4(5)
N(1F)–Cd(1A)–N(1A)	180.0(8)				
N(1F)–Cd(1A)–S(1B)	88.37(5)				
S(1B)–Cd(1A)–S(1E)	180.0				

Symmetry codes: A = $-x+1$, $-y+1$, $-z+1$, B = x, $y+1$, z , E = $-x$, $-y+1$, $-z+1$, and F = $-x$, $y+1/2$, $-z+1/2$ for **1**; A = $-x+2$, y, $-z+3/2$ for **2**; A = $-x$, y, $-z+1/2$ for 3.

Elem. Anal. Found (%): C, 60.34; H, 4.35; N, 16.21. Calculated for $C_{13}H_{11}N_3O_3$ (257.1) (%): C, 60.70; H, 4.31; N, 16.33. IR (KBr, cm^{-1}): 3421 (m), 3281 (m), 1626 (s), 1476 (m), 1306 (m), 749 (m). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 12.16 [1H, OH], 11.03 [2H, NH], 7.53–8.86 [4H, py], 6.76–7.46 [4H, Ar].

2.2.2. Synthesis of L2. The synthesis of L2 is similar to that of L1 only with isonicotinic acid being substituted by nicotinic acid. White solid product of L2 was obtained. Yield: 67%; m.p.: 238–239°C. Elem. Anal. Found (%): C, 60.92; H, 4.24; N, 16.50. Calculated for $C_{13}H_{11}N_3O_3$ (257.1) (%): C, 60.70; H, 4.31; N, 16.33. IR (KBr, cm^{-1}): 3420 (m), 3217 (m), 1632 (s), 1530 (m), 1484 (m), 1303 (s), 706 (m). ^1H NMR (300 MHz, DMSO-d_6) δ: 12.16 [1H, OH], 11.03 [2H, NH], 7.65–9.05 [4H, py], 6.76–7.45 [4H, Ar].

2.3. *Syntheses of complexes*

2.3.1. Synthesis of $[Cd(L1)_2(SCN)_2]_n$ (1). A solution of L1 (0.10 mmol) in methanol (5 mL) was mixed with a solution of $CdSO_4 \cdot H_2O$ (0.10 mmol) in water (5 mL), and then a solution of KSCN (0.10 mmol) in methanol (5 mL) was added dropwise. The resulting mixture was stirred for a half-hour and filtered. After keeping the filtrate at room temperature for two weeks, pale yellow block crystals suitable for X-ray analysis were formed. Yield: 0.032 g (36%). IR (KBr, cm^{-1}): 3282 (m), 1637 (s), 1528 (m), 1480 (m), 1066 (m), 764 (m).

2.3.2. Synthesis of $[Zn(L1)_2Cl_2] \cdot H_2O$ (2). A solution of L1 (0.2 mmol) in methanol (5 mL) was added dropwise to a solution of $ZnCl_2$ (0.2 mmol) in water (5 mL) with the resulting mixture stirred for a half-hour. The solution was filtered and the filtrate was kept at room temperature. After three weeks, yellow block crystals suitable for X-ray analysis were formed. Yield: 0.037 g (36%). IR (KBr, cm^{-1}): 3404 (m), 3278 (m), 1635 (s), 1530 (m), 1487 (m), 1091(m), 756 (m).

2.3.3. Synthesis of $[Zn(L2)_2Cl_2]$ (3). The synthesis process of **3** is similar to that of **2** only with the L1 being substituted by L2. Colorless block crystals of **3** suitable for X-ray analysis were formed. Yield: 0.030 g (31%). IR (KBr, cm^{-1}): 3446 (m), 3253 (m), 1615 (s), 1567 (m), 1488 (m), 1099 (m), 742 (m).

3. Results and discussion

3.1. *Description of the crystal structures*

3.1.1. Crystal structure of $[Cd(L1)_2(SCN)_2]_n$ (1). Complex **1** is a 1-D two-stranded chain and crystallizes in the monoclinic space group $P2_1/c$. The coordination environment of Cd^{II} is shown in figure 1. Selected bond lengths and angles are given in table 2. The centrosymmetric unit of **1** consists of one Cd^{II} atom, two SCN^- anions, and two L1 ligands with Cd^{II} located at the inversion center *i*. The coordinated sphere around every Cd^{II} is a distorted octahedron constructed by two nitrogen atoms from two L1 ligands, two nitrogen atoms from two bridging SCN^- anions, and two sulfur atoms from another two bridging SCN^- anions. In **1**, N(1A), N(1D), S(1 C), S(1B), and Cd(1A) are coplanar with Cd–N and Cd–S being 2.285(2) and 2.7240(7) Å, respectively (table 2). N(2A), Cd(1A), and N(2D) are in a straight line with the angle

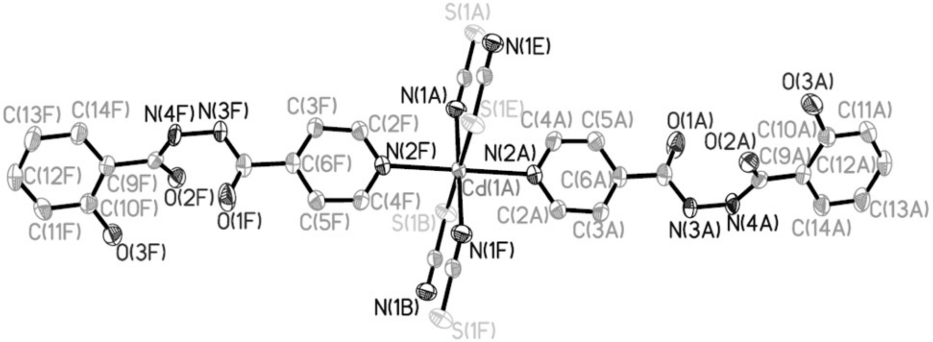

Figure 1. View of the coordination environment of Cd^{II} in **1** (hydrogen atoms are omitted for simplicity) Symmetry codes: $A = -x+1, -y+1, -z+1$, $B = x, y+1, z$, $E = -x, -y+1, -z+1$, and $F = -x, y+1/2, -z+1/2$ for **1**.

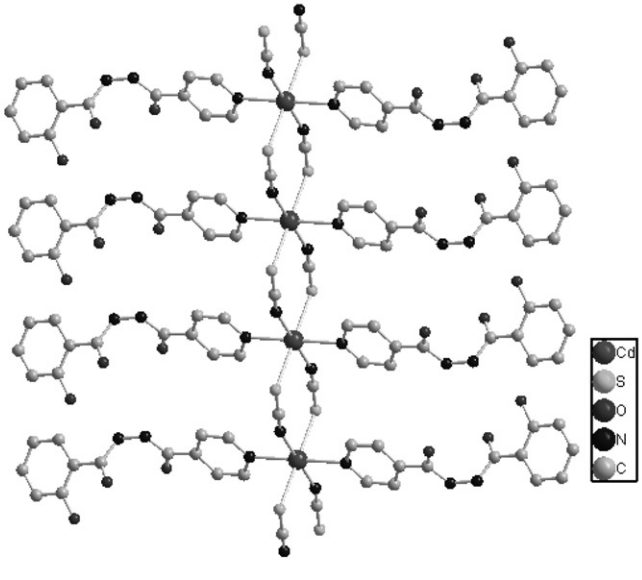

Figure 2. View of 1-D chain in **1** (hydrogen atoms are omitted for simplicity).

N(2D)–Cd(1A)–N(2A) of 180.0(9)° and the Cd–N bond distances of 2.3887(17) Å; this line is almost perpendicular to the plane N(1A)N(1D)S(1C)S(1B). The overall structural feature of **1** is a two-stranded chain along the *b*-axis constructed from two SCN^- anions simultaneously bridging two adjacent Cd^{II} atoms (figure 2). All Cd^{II} atoms are linear with angle of Cd(1A)···Cd(1B)···Cd(1C) 180° (figure 2).

In the crystal structure of **1**, there are intraligand hydrogen bonds with O(3)···O(2) being 2.680(2) Å between O–H and the oxygen from carbonyl near the benzene ring in L1 (table 3 and figure 3). Besides these intraligand hydrogen bonds, the amino N–H near the benzene ring of L1 with the oxygen from carbonyl near the pyridine ring of the adjacent chain form interchain hydrogen bonds with N(4)···O(1) being 2.847(2) Å, and the O–H with the oxygen from carbonyl near the benzene ring of the

Table 3. Hydrogen bond distances (Å) and angles (°) for **1–3**.

D–H···A	d(D···A)	∠(DHA)
1		
N(4)–H(4A)···O(1F)	2.847(2)	168.3
N(3)–H(3B)···O(2E)	2.926(2)	156.4
O(3)–H(3A)···O(2)	2.680(2)	139.3
2		
N(2)–H(2A)···O(4B)	2.938(5)	161.4
O(3)–H(3A)···O(2C)	2.878(4)	169.4
O(4)–H(4A)···O(1)	2.910(3)	158.5
N(3)–H(3B)···O(3)	2.626(5)	138.4
3		
N(3)–H(3A)···O(3)	2.599(8)	139.0
N(2)–H(2A)···O(2B)	2.928(8)	154.2
O(3)–H(3B)···O(1C)	2.705(8)	158.6

Symmetry codes: A = $-x+1, -y+1, -z+1$, B = $x, y+1, z$, E = $-x, -y+1, -z+1$ and F = $-x, y+1/2, -z+1/2$ for **1**; A = $-x+2, y, -z+3/2$, B = $x+1/2, y-1/2, z$, and C = $x+1/2, y+1/2, z$ for **2**; A = $-x, y, -z+1/2$, B = $-x+1/2, -y-1/2, -z$, and C = $-x+1/2, -y+1/2, -z$ for **3**.

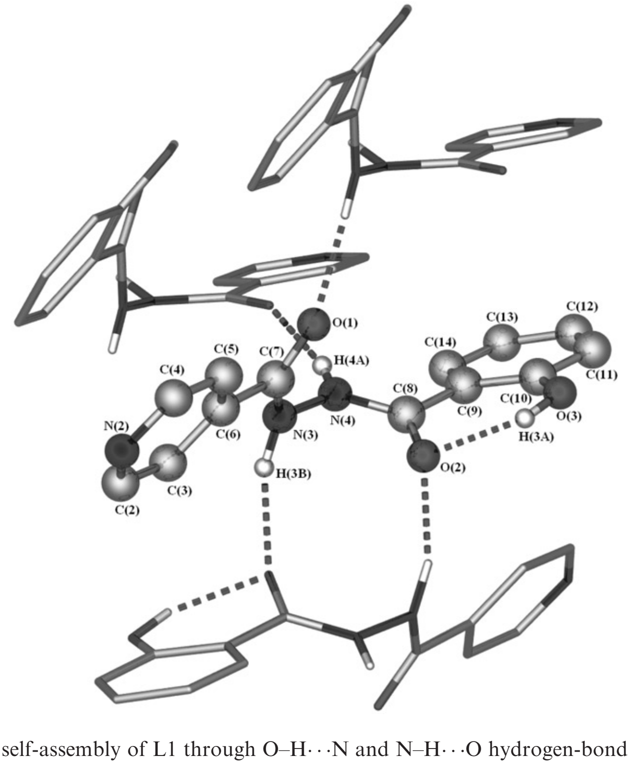

Figure 3. View of self-assembly of L1 through O–H···N and N–H···O hydrogen-bonding interactions in **1** (hydrogen atoms are omitted for simplicity). Symmetry codes: A = $-x+1, -y+1, -z+1$, B = $x, y+1, z$.

neighboring chain form interchain hydrogen bonds with N(3)···O(2) being 2.926(2) Å (table 3 and figure 3). In this manner, the two-stranded chains are connected with neighboring chains by two interchain hydrogen bonds to form a 3-D supramolecular framework in **1** (figure 4).

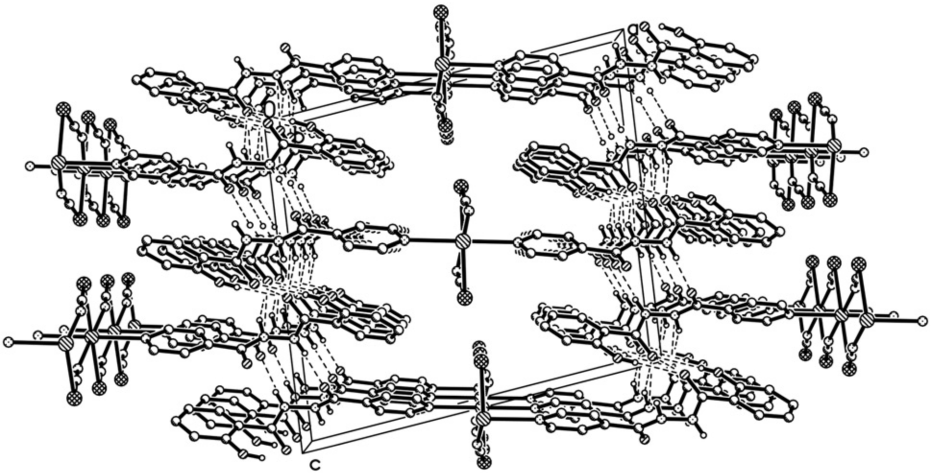

Figure 4. View of 3-D supramolecular network of **1** (hydrogen atoms are omitted for simplicity).

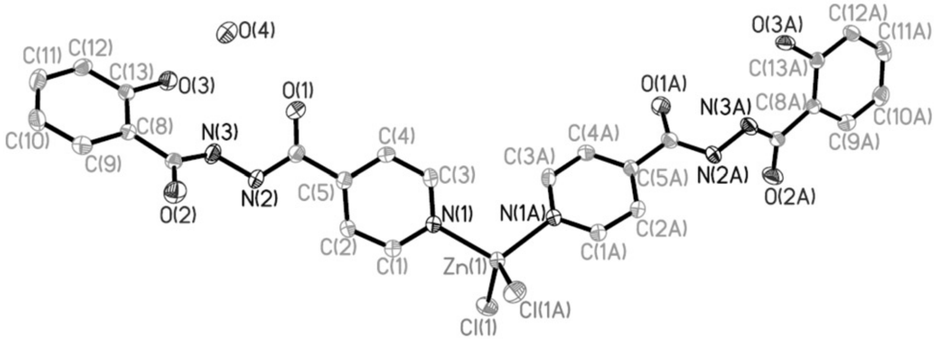

Figure 5. The molecular structure of **2** (hydrogen atoms are omitted for simplicity). Symmetry code: A = $-x+2$, y, $-z+3/2$.

3.1.2. Crystal structure of [Zn(L1)$_2$Cl$_2$]$\cdot$H$_2$O (2). Complex **2** is a monomer crystallizing in the orthorhombic chiral space group *C*222$_1$ with the Flack parameter of 0.058(1). The crystal structure unit of **2** is shown in figure 5. The crystallographic data and selected bond lengths and angles are listed in tables 1 and 2, respectively. Complex **2** is a chiral structure, and its structural unit consists of one Zn^{II} atom, two L1 ligands, and two Cl$^-$ atoms with a two-fold axis passing through Zn^{II} and halving the structural unit. Zn^{II} is ligated by two nitrogen atoms from L1 and two Cl$^-$ atoms, forming a distorted tetrahedral coordination geometry. In **2**, two L1 ligands form a distorted V-shaped structure constructed from coordination between Zn^{II} and nitrogen of pyridine with the torsion angle C(3A)–N(1A)–Zn(1)–N(1) of $-29.02°$, and the two rings of N(1)C(1)C(2)C(5)C(4)C(3) and C(8)C(9)C(10)C(11)C(12)C(13) from the same L1 are twisted with dihedral angle of 13.6°. This distortion phenomenon also exists in **1** for the bis-hydrazide group (–CONHNHCO–) bridging the pyridine ring and the benzene ring is rotatable and flexible.

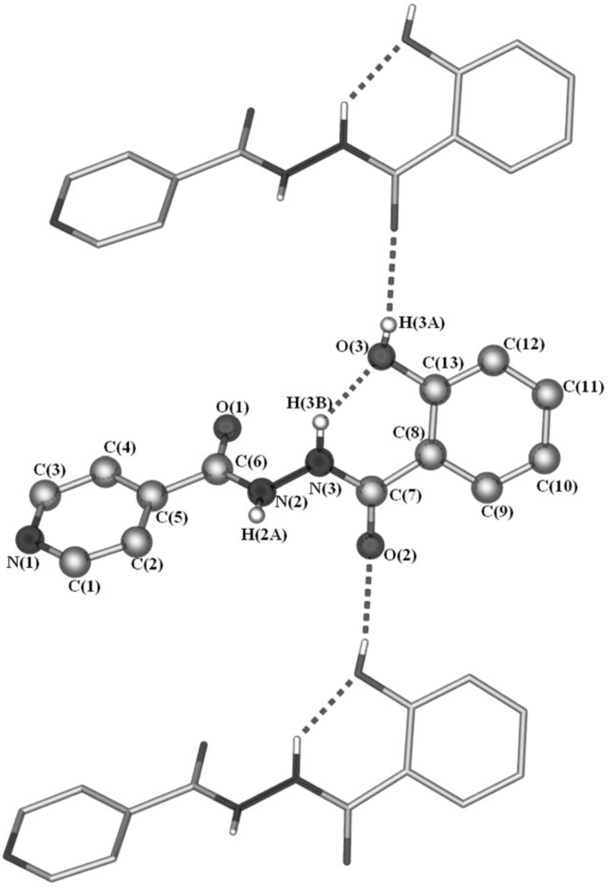

Figure 6. View of self-assembly of L1 through O–H···N and N–H···O hydrogen-bonding interactions in **2** (hydrogen atoms are omitted for simplicity). Symmetry codes: A = $-x+2$, y, $-z+3/2$ and B = $x+1/2$, $y-1/2$.

Every lattice water molecule among structural units of **2** is a tetrahedral supramolecular connector, connecting with amido near the pyridine ring and oxygen atoms of carbonyl near the pyridine ring from four different units through intermolecular hydrogen bonds with N(2)···O(4) being 2.938(5) Å and O(4)···O(1) being 2.910(3) Å, respectively. Another intermolecular hydrogen bond O(3)···O(2) occurs between O–H and oxygen from carbonyl near the benzene ring of the neighboring unit at 2.878(4) Å. In addition, there is an intramolecular hydrogen bond between the amino N–H near the benzene ring and hydroxyl group from the same unit with N(3)···O(3) being 2.626(5) Å. Figure 6 is a view of self-assembly of L1 through O–H···N and N–H···O hydrogen-bonding interactions in **2**. As a result, the structural units of **2** extend into a 3-D supramolecular framework by the complicated hydrogen-bonding network (figure 7 and table 3). Through regular intermolecular hydrogen-bonding interactions homochiral monomers of **2** recognize each other to form chiral crystals although the whole complex is racemic mixtures of enantiopure crystals.

Vertical face-to-face distances between pyridine rings and benzene rings of the neighboring unit are 3.679 Å, indicating the existence of π–π stacking interactions.

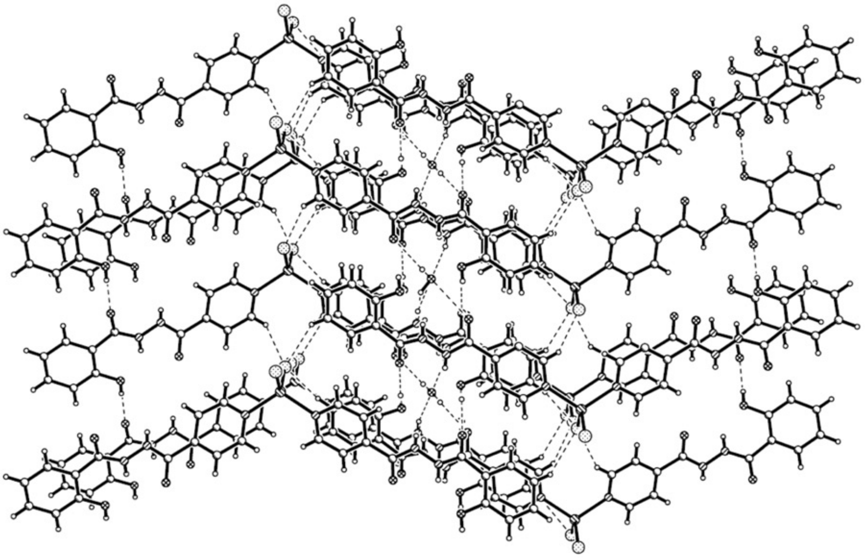

Figure 7. View of 3-D framework supported by hydrogen-bonding net in **2**.

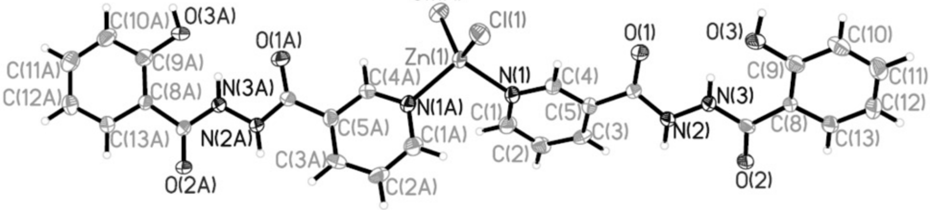

Figure 8. The molecular structure of **3**. Symmetry code: A = $-x$, y, $-z + 1/2$.

The π–π stacking interactions and intermolecular hydrogen bonds mentioned above play an important role in stabilization of the 3-D supramolecular framework of **2**.

3.1.3. Crystal structure of [Zn(L2)$_2$Cl$_2$] (3). The structural unit of **3** consists of one Zn^{II} atom, two L2 ligands, and two Cl$^-$ atoms as shown in figure 8. The crystal structure parameters and selected bond lengths and angles are listed in tables 1 and 2, respectively. In **3**, Zn^{II} is four-coordinate by two nitrogen atoms from L2 and two Cl$^-$ atoms, forming a distorted tetrahedron, similar to that of **2**. In **3**, the two rings of N(1)C(1)C(2)C(3)C(5)C(4) and C(8)C(9)C(10)C(11)C(12)C(13) from the same L2 are distorted with dihedral angle of 12.4° and torsion angle C(1)–N(1)–Zn(1)–N(1A) of 39.83°. Although **3** is similar to **2**, in shape, **2** is V-like while **3** is linear. The structure of **3** is similar to that of [Zn(Py)$_2$Cl$_2$] [18]. The shape difference mainly originates from the different bite angles of L1 and L2, which results in crystal packing as presented below.

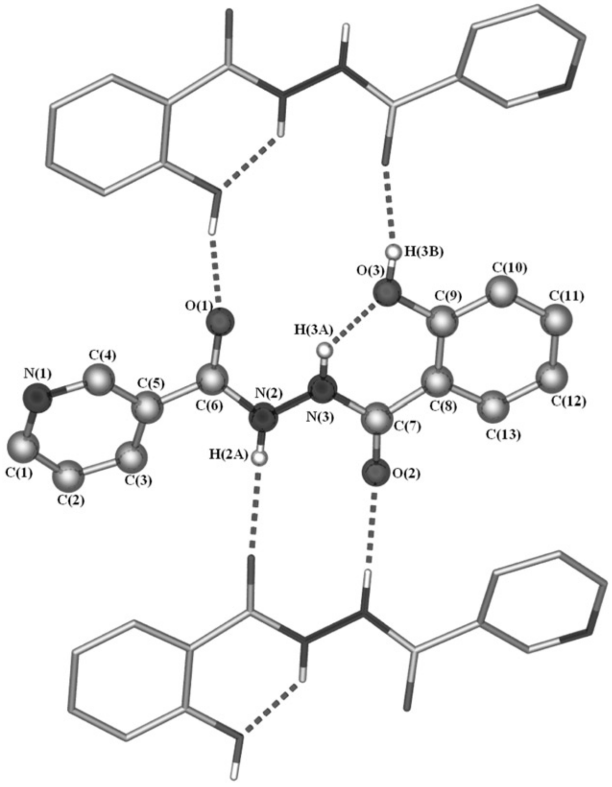

Figure 9. View of self-assembly of L2 through O–H···N and N–H···O hydrogen-bonding interactions in **3** (hydrogen atoms are omitted for simplicity). Symmetry codes: A = $-x$, y, $-z+1/2$ and B = $-x+1/2$, $-y-1/2$.

Hydrogen bonds exist in **3** (table 3 and figure 9), also. There is an intramolecular hydrogen bond between the amino N–H near the benzene ring and hydroxyl group from the same unit with N(3)···O(3) being 2.599(8) Å, similar to that in **2**. The N(2)···O(2) intermolecular hydrogen bond between N–H near the pyridine ring of L2 and carbonyl near the benzene ring of the neighboring unit is 2.928(8) Å, and the O(3)···O(1) intermolecular hydrogen bond between O–H group and carbonyl near the pyridine ring of the neighboring unit is 2.705(8) Å. These intermolecular hydrogen bonds join the monomer units to give a 2-D sheet as shown in figure 10. In **3**, there are π–π stacking interactions between pyridine rings and benzene rings of neighboring layers with vertical face-to-face distances of 3.657 Å. The π–π interaction stabilizes the complexes.

As discussed above, **2** and **3** are 0-D and **1** shows a 1-D structure. The three complexes propagate into metal–organic supramolecular architectures by various intermolecular interactions, such as hydrogen-bonding and π–π stacking interactions. The hydrogen bonds are the main forces sustaining the crystal framework. In **1**, the polymeric chains are connected into a 3-D supramolecular framework through interchain hydrogen bonds occurring between L1 (shown in figure 3) while the monomer units are extended into a 3-D supramolecular structure of **2** or 2-D sheet of **3** *via* complicated hydrogen-bonded self-assembly of L1 or L2 (shown in figures 6 and 9).

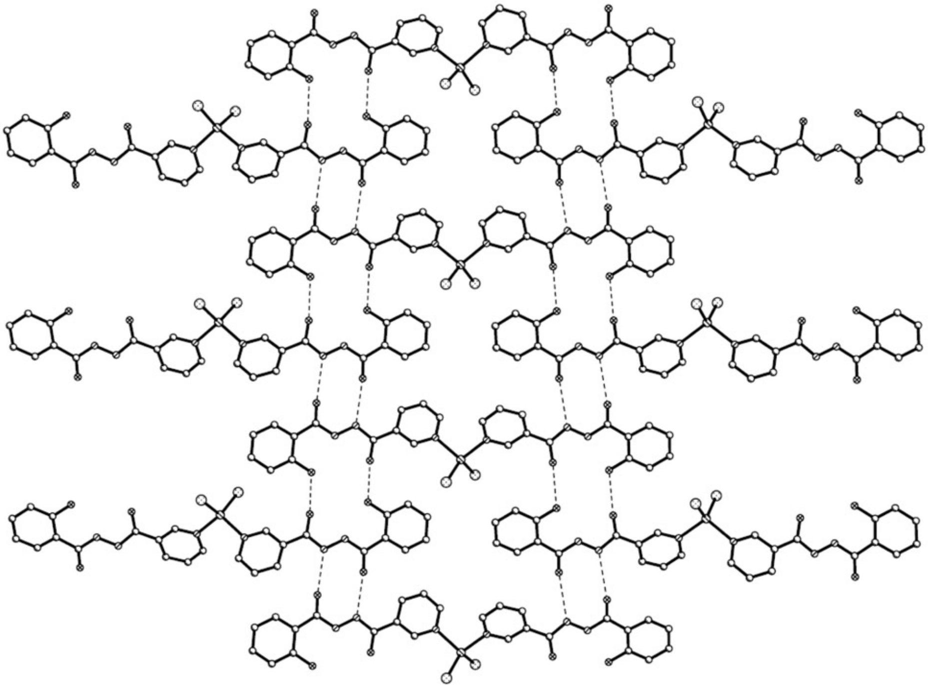

Figure 10. View of 2-D framework of **3** connected by hydrogen bonds (hydrogen atoms are omitted for simplicity).

Formation of the 3-D supramolecular structure of **2** is aided by water-mediated hydrogen-bonding interactions.

It is familiar that π–π stacking interaction exists in metal complexes of aromatic ligands, and the usual π–π interaction is an offset or slipped stacking, i.e. the rings are parallel displaced, the ring normal, and the vector between the ring centroids form an angle of about 20° up to centroid–centroid distances of 3.8 Å [19]. In **2** and **3**, the π–π stacking interactions exist and the π–π interactions also play an important role in stabilizing the crystal packing.

3.2. *Fluorescent properties of 1–3*

The photoluminescence properties of **1**–**3** as well as L1 and L2 were investigated in the solid state at room temperature. L1 displays weaker emissions centered at 470 and 517 nm, probably attributable to $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transitions [20–23]. However, **1** and **2** give relatively strong fluorescence under the same experimental conditions. The enhancement may be due to the introduction of the metal ions enhancing the rigidity of L1 which causes increase in the conjugation of the whole molecule, thereby reducing the non-radiative decay of the intraligand ($\pi \rightarrow \pi^*$) excited state [24, 25]. Spectral bands of **1** and **2** are blue-shifted compared with free L1. This may be related to the coordination environment, hydration level, and crystal packing, which could result in an increase in HOMO–LUMO energy gap of the complex [26–28]. Compared with free L2, the fluorescence intensity of **3** is slightly enhanced and the emitting wavelength is close to L2, which indicates that the coordination of Zn^{II} and Cl^- does not affect the rigidity of L2. The energy transfer in neutral guest–host systems accords with the relative energy level spacings of the luminescing donor and acceptor molecules [29]. The fluorescence behaviors suggest that emissions of **1**–**3** are neither MLCT nor LMCT, and can be mainly assigned to intraligand charge transfer (ILCT) because Cd^{II} and Zn^{II} are difficult to oxidize or reduce due to d^{10} configurations [30–32].

3.3. *Thermogravimetric analysis*

Thermogravimetric (TG-DSC) analysis was performed on polycrystalline samples for **1**–**3**. There are three transitions in the decomposition of **1**. The first starts at 200°C and ends at 360°C, due to loss of two molecular fragments of salicyl hydrazide from the structure (Found: 51.5%, Calcd: 48.3%). The second transition from 360°C to 660°C (26.8%) containing an exothermic peak at 546°C is related to loss of two molecular fragments of isonicotinoyl chloride (Calcd: 28.5%). The third transition from 660°C to 780°C of 8.4% is related to loss of two SCN^- anions (Calcd: 6.9%). The total mass loss to 800°C is 86.7%, which agrees with the theoretical value (84.4%) calculated by taking CdO as the final product.

There are three transitions in the decomposition of **2** or **3**. The first from 200°C to 460°C is due to loss of one H_2O molecule and two molecular fragments of salicyl hydrazide. The second transition from 460°C to 620°C is due to loss of two molecular fragments of isonicotinoyl chloride for **2** and nicotinoyl chloride for **3**. During the third weight loss process from 620°C to 700°C, **2** and **3** lost two HCl. The total weight loss of decomposition is 89.5% for **2** (calculated by taking ZnO as the final product, 89.7%) and 90.9% for **3** (calculated by taking ZnO as the final product, 90.0%).

3.4. *Polarimetric analysis of 2*

Polarimetric analysis of **2** was also investigated. A solution of 15 mg of **2** in 10 mL of DMF was added to an optical tube, and polarimetric measurements were carried out on an America AA-10 apparatus (26°C, 589 nm). The observed value of $[\alpha]_{589}^{26}$ is $0^\circ\ \mathrm{dL \cdot cm^{-1} \cdot g^{-1}}$. Although the single crystal of **2** is a chiral structure, the solution of **2** in DMF has no optical activity, showing that **2** is a racemic mixture.

4. Conclusions

Two isomeric ligands, L1 and L2, coordinate with d^{10} metal ions in terminal coordination, and different coordination modes of the ligands and environments around the metal ions offer distinctive supramolecular interaction sites for each structural unit. Therefore, **1**, **2**, and **3** have specific unit structures and crystal-packing modes.

For polymer **1** and monomers **2** and **3**, hydrogen bonds and π–π interactions are the main forces holding complex molecules together and sustaining the crystal framework.

Coordination of metal ions and anions change rigidity of ligands, thus fluorescence behaviors of complex were changed. The luminescence mechanisms of **1**–**3** are mainly ILCT.

Supplementary material

The supplementary crystallographic data for the structural analyses of this article have been deposited *via* the Cambridge Crystallographic Data Centre, CCDC Reference Nos: 847487 (for **1**), 847488 (for **2**), and 847489 (for **3**). Copies of these can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/data_request/cif).

Acknowledgments

The authors acknowledge financial support from the National Natural Science Foundation of China (20771094).

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