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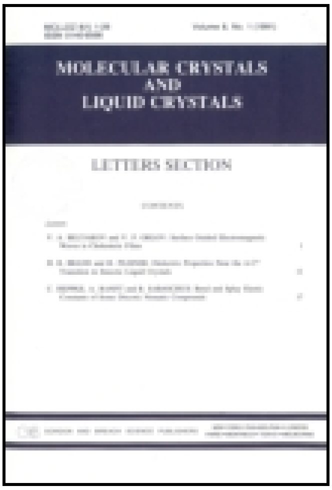

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Two d^{10} Coordination Complexes Based on the Substitutional Aromatic Multicarboxylate and N-Donor Co-Ligands: Syntheses, Structures, and Properties

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Two d^{10} Coordination Complexes Based on the Substitutional Aromatic Multicarboxylate and N-Donor Co-Ligands: Syntheses, Structures, and Properties

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Two new coordination complexes, formulated as $[Cd_2(3\text{-}NPA)(phen)_4(H_2O)_2]_2$ (**1**) *and* $[Zn(3\text{-}NPA)(phen)(H_2O)]_n$ (**2**) ($3\text{-}NPAH_2$ = *3-nitrophthalic acid, phen = 1,10-phenanthroline) have been synthesized by hydrothermal reactions of the rigid neutral ligand phen with metal ions in the presence of 3-NPAH. X-ray analysis shows that complex* **1** *is a 0D dinuclear structure that is arranged to form a 3D supramolecular framework through hydrogen bonds and* π–π *stacking interactions. In polymer* **2**, *the* $3\text{-}NPA^{2-}$ *anions coordinate the Cd(II) ions in a tridentate mode to form a 1D infinite chain structure, which is connected by the hydrogen bonds and* π–π *stacking interactions resulting in a 3D supramolecular architecture. In addition, the two complexes were characterized by infrared spectroscopy, elemental analysis, luminescent properties, thermo gravimetric analysis, and powder X-ray diffraction (PXRD).*

Keywords 3-Nitrophthalic acid; multi carboxylate; X-ray crystal diffraction

Introduction

The design and construction of inorganic–organic hybrid framework materials is of current great interest in the fields of crystal engineering and supramolecular chemistry, not only for the intriguing topological architectures, but also due to their potential applications in many fields, such as heterogeneous catalysis, gas storage, nonlinear optics, magnetism, and luminescent materials [1–11]. As it is known, it is still a big challenge to predict the final structures of desired crystalline products, since the self-assembly process of crystalline products is influenced by many factors, such as metal ions, organic ligands, counter ions, solvent system, temperature, and pH of reaction system [12–14]. In order to obtain new coordination complexes with various topological structures, multicarboxylates are often selected as bridging ligands to construct coordination complexes not only due to their versatile coordination modes to metal centers but also their strong ability to act as hydrogen bonding acceptors and donors [15–18]. Despite the fact that most coordination complexes

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based on the multicarboxylates has reported thus far, compared with the abundant compounds employed 1,2-benzenedicarboxylic acid (*o*-H_2bdc), those exploring the influences of the substituted groups of these ligands are rather limited in number [19–22]. On the other hand, in order to obtain coordination complexes with interesting structures as well as other functional properties, an important and useful strategy is to introduce a secondary N-donor ligands, such as 2,2′-bipy, 4,4′-bipy, 1,10-phenanthroline. With this understanding, to investigate the influence of the substitutional groups on the structure of coordination complexes, 3-nitrophthalic acid (3-NPAH_2) was chosen as the organic ligand, 1,10-phenanthroline was chosen as neutral co-ligand to construct new coordination complexes under the hydrothermal reaction. This paper presents the syntheses, structures, luminescent properties, thermal stabilities, and powder X-ray diffraction (PXRD) of two novel coordination complexes $[Cd_2(3\text{-NPA})(phen)_4(H_2O)_2]_2$ (**1**) and $[Zn(3\text{-NPA})(phen)(H_2O)]_n$ (**2**).

Experimental

All chemicals were commercial materials of analytical grade and used without purification. Elemental analysis for C, H, and N was carried out on a Perkin–Elmer 2400 II elemental analyzer. The FT-IR spectrum was obtained on a PE Spectrum One FT-IR Spectrometer Fourier transform infrared spectroscopy in the 4000–400 cm^{-1} regions, using KBr pellets. Perkin–Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG and DTG curves in the static air atmosphere at a heating rate of 10 K min^{-1} in the temperature range 25–1000°C using platinum crucibles. Fluorescence spectra were recorded with F-2500 FL Spectrophotometer analyzer. PXRD patterns were obtained using a pinhole camera (Anton Paar) operating with a point focused Ni-filtered Cu Kα radiation in the 2θ range from 5° to 50° with a scan rate of 0.08° per second.

Synthesis of Complex $[Cd_2(3 - NPA)(phen)_4(H_2O)_2]_2$ (1)

The reagents of $CdCl_2 \cdot 2/5H_2O$ (0.228 g, 1.00 mmol), 3-NPAH_2 (0.106 g, 0.500 mmol), phen (0.0991 g, 0.500 mmol) were dissolved in 15 mL mixed solvent of DMF/H_2O (volume ratio 1:2) and added eight drops of py then stirred 0.5 h. Then an aqueous solution of sodium hydroxide was added dropwise with stirring to adjust the pH value of the solution being 6. The resulting mixture was sealed in a 30 mL Teflon-lined stainless reactor, kept under autogenous pressure at 145 °C for 72 h, and then slowly cooled to room temperature at a rate of 5 °C per hour. The block crystals suitable for X-ray diffraction were isolated directly (Yield: 60%, based on Cd). Anal. Calcd for $C_{112}H_{74}Cd_4N_{18}O_{16}$ (%): C, 56.58; H, 3.14; N, 10.60. Found: C, 56.57; H, 3.15; N, 10.58. IR data (KBr pellets, cm^{-1}): 3409 (s), 3047 (w), 1591 (vs), 1514 (s), 1426(s), 1383 (m), 1346 (s), 1142 (w), 1100 (w), 847 (m), 727 (s), 669 (w), 532 (w), 470 (w), 451 (w).

Synthesis of Complex $[Zn(3 - NPA)(phen)(H_2O)]_n$ (2)

A solution of 3-NPAH_2 (0.106 g, 0.500 mmol) and phen (0.0991 g, 0.500 mmol) in 3 mL DMF was added dropwise with stirring at room temperature to a solution of $ZnCl_2$ (0.136 g, 1.00 mmol) in the mixture of 10 mL water and 5 mL ethanol. Then an aqueous solution of sodium hydroxide was added dropwise with stirring to adjust the pH value of the solution being 6. The resulting mixture was sealed in a 30 mL Teflon-lined stainless reactor, kept under autogenous pressure at 150 °C for 72 h, and then slowly cooled to room temperature at a rate of 5 °C per hour. The block crystals suitable for X-ray diffraction were

Table 1. Experimental data for complex **1** and **2**

Complexes	**1**	**2**
Empirical formula	$C_{112}H_{74}Cd_4N_{18}O_{16}$	$C_{20}H_{13}N_3O_7Zn$
Formula weight	2377.49	472.70
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, *P*–1	Monoclinic, *P2(1)/c*
a (Å)	14.290(10)	22.929(8)
b (Å)	14.534(10)	9.229(2)
c (Å)	14.812(10)	19.646(5)
α (°)	90.445(10)	90
β (°)	110.470(10)	115.332(3)
γ (°)	103.744(10)	90
Volume (Å^3)	2785(3)	3757.5(18)
Z	1	8
$D_{\text{calc.}}$ (Mg·m^{-3})	1.417	1.671
Absorption coefficient (mm^{-1})	0.823	1.359
$F(000)$	1192	1920
Crystal size	0.23 × 0.22 × 0.21	0.23 × 0.22 × 0.22
θ range for data collection (°)	1.45 to 25.00	0.98 to 25.00
Reflections collected	9709	19,265
Unique reflections	9709 [R(int) = 0.0000]	6579 [R(int) = 0.0613]
Completeness to $\theta = 25.00$	98.9%	99.7%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8461 and 0.8333	0.7541 and 0.7451
Data/restraints/parameters	9709/577/646	6579/18/559
Goodness-of-fit on F^2	1.055	1.197
R indices [$I > 2\sigma(I)$]	R1 = 0.0855, wR2 = 0.2560	R1 = 0.1379, wR2 = 0.3310
R indices (all data)	R1 = 0.1142, wR2 = 0.2797	R1 = 0.1489, wR2 = 0.3364
Largest diff. peak and hole (e.Å^{-3})	3.525 and −1.379	2.595 and −1.363

isolated directly, washed with ethanol and dried in air (Yield: 65%, based on Zn). Anal. Calcd for $C_{20}H_{13}ZnN_3O_7$(%): C, 50.82; H, 2.77; N, 8.89. Found: C, 50.69; H, 2.69; N, 9.04. IR data (KBr pellets, cm^{-1}): 3406 (w), 3077 (w), 1622 (s), 1581 (s), 1519 (m), 1458 (m), 1369 (s), 1148 (m), 1032 (m), 930 (w), 853 (w), 783 (w), 728 (w), 682 (w), 550 (w), 533 (w), 516 (w), 500 (w), 401 (w).

Crystal Structure Determination

Suitable single crystal with approximate dimensions were mounted on a glass fiber and used for X-ray diffraction analyses. Data were collected at 293(2) K on a Bruker Apex CCD diffractometer using the ω scan technique with Mo Kα radiation ($\lambda = 0.71069$ Å).

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**

Complex **1**			
Cd(1)-O(8)	2.211(7)	Cd(2)-O(1)	2.259(7)
Cd(1)-O(4)	2.240(7)	Cd(2)-O(7)	2.327(11)
Cd(1)-N(5)	2.320(8)	Cd(2)-N(4)	2.327(7)
Cd(1)-N(6)	2.353(8)	Cd(2)-N(2)	2.378(6)
Cd(1)-N(7)	2.371(8)	Cd(2)-N(1)	2.426(6)
Cd(1)-N(8)	2.494(8)	Cd(2)-N(3)	2.436(8)
O(8)-Cd(1)-O(4)	104.9(3)	O(4)-Cd(1)-N(8)	155.0(3)
O(8)-Cd(1)-N(5)	92.7(3)	N(5)-Cd(1)-N(8)	84.0(3)
O(4)-Cd(1)-N(5)	120.8(3)	N(6)-Cd(1)-N(8)	89.1(3)
O(8)-Cd(1)-N(6)	158.4(3)	N(7)-Cd(1)-N(8)	68.0(3)
O(4)-Cd(1)-N(6)	95.6(3)	O(1)-Cd(2)-O(7)	88.8(4)
N(5)-Cd(1)-N(6)	70.6(3)	O(1)-Cd(2)-N(4)	95.5(3)
O(8)-Cd(1)-N(7)	96.2(3)	O(7)-Cd(2)-N(4)	86.8(3)
O(4)-Cd(1)-N(7)	87.3(3)	O(1)-Cd(2)-N(2)	98.5(2)
N(5)-Cd(1)-N(7)	147.2(3)	O(7)-Cd(2)-N(2)	154.1(3)
N(6)-Cd(1)-N(7)	91.5(3)	N(4)-Cd(2)-N(2)	117.0(2)
O(8)-Cd(1)-N(8)	75.3(3)	O(1)-Cd(2)-N(1)	110.7(2)
O(7)-Cd(2)-N(1)	87.6(4)	N(4)-Cd(2)-N(1)	153.1(2)
N(2)-Cd(2)-N(1)	66.48(12)	O(1)-Cd(2)-N(3)	165.6(3)
O(7)-Cd(2)-N(3)	88.7(4)	N(4)-Cd(2)-N(3)	70.2(3)
N(2)-Cd(2)-N(3)	89.9(2)	N(1)-Cd(2)-N(3)	83.4(2)
Complex **2**			
Zn(1)-O(5)#1	2.063(4)	Zn(2)-O(11)#2	2.045(4)
Zn(1)-O(3)	2.069(5)	Zn(2)-O(8)	2.068(4)
Zn(1)-N(1)	2.159(5)	Zn(2)-N(5)	2.120(6)
Zn(1)-N(2)	2.181(5)	Zn(2)-N(4)	2.149(4)
Zn(1)-O(2)	2.185(4)	Zn(2)-O(9)	2.209(5)
Zn(1)-O(1)	2.280(4)	Zn(2)-O(10)	2.242(5)
O(5)-Zn(1)#3	2.063(4)	O(11)-Zn(2)#4	2.045(4)
O(5)#1-Zn(1)-O(3)	89.51(19)	O(5)#1-Zn(1)-N(1)	92.95(19)
O(3)-Zn(1)-N(1)	172.77(18)	O(5)#1-Zn(1)-N(2)	98.09(18)
O(3)-Zn(1)-N(2)	95.5(2)	N(1)-Zn(1)-N(2)	77.4(2)
O(5)#1-Zn(1)-O(2)	150.63(16)	O(3)-Zn(1)-O(2)	85.75(18)
N(1)-Zn(1)-O(2)	95.35(18)	N(2)-Zn(1)-O(2)	111.21(18)
O(5)#1-Zn(1)-O(1)	93.52(16)	O(3)-Zn(1)-O(1)	95.09(18)
N(1)-Zn(1)-O(1)	91.55(18)	N(2)-Zn(1)-O(1)	164.3(2)
O(2)-Zn(1)-O(1)	58.19(17)	O(11)#2-Zn(2)-O(8)	90.21(16)
O(11)#2-Zn(2)-N(5)	97.19(19)	O(8)-Zn(2)-N(5)	95.61(19)
O(11)#2-Zn(2)-N(4)	93.78(16)	O(8)-Zn(2)-N(4)	172.90(19)
N(5)-Zn(2)-N(4)	78.07(19)	O(11)#2-Zn(2)-O(9)	154.68(18)
O(8)-Zn(2)-O(9)	85.63(17)	N(5)-Zn(2)-O(9)	108.06(18)
N(4)-Zn(2)-O(9)	93.20(16)	O(11)#2-Zn(2)-O(10)	97.35(17)
O(8)-Zn(2)-O(10)	94.30(19)	N(5)-Zn(2)-O(10)	162.34(16)
N(4)-Zn(2)-O(10)	91.02(18)	O(9)-Zn(2)-O(10)	58.21(17)

Note: Symmetry transformations used to generate equivalent atoms for **2**: #1 $-x+1$, $y-1/2$, $-z+3/2$; #2 $-x$, $y-1/2$, $-z+3/2$; #3 $-x+1$, $y+1/2$, $-z+3/2$; #4 $-x$, $y+1/2$, $-z+3/2$.

Table 3. Hydrogen-bond geometry (Å) and angles (°) for complexes

D-H···A	Symmetry code	D-H	H···A	D···A	D-H···A
	Complex **1**				
O(7)-H(7A)···O(8)	$-x+1, -y, -z+2$	0.85	1.17	2.008(14)	170
C(12)-H(12)···O(2)		0.93	2.42	2.938(9)	115
C(14)-H(14)···O(5)		0.93	2.52	3.359(14)	151
C(22)-H(22)···O(3)		0.93	2.36	3.062(12)	132
C(30)-H(30)···O(2)		0.93	2.53	3.128(14)	122
C(46)-H(46)···O(4)		0.93	2.58	3.175(15)	122
	Complex **2**				
O(3)-H(3A)···O(1)	$-x+1, y+1/2, -z+3/2$	0.85	1.89	2.731(7)	169
O(3)-H(3B)···O(4)	$-x+1, y-1/2, -z+3/2$	0.85	1.82	2.656(7)	169
O(8)-H(8A)···O(10)	$-x, y+1/2, -z+3/2$	0.85	1.95	2.707(7)	170
O(8)-H(8B)···O(12)	$-x, y-1/2, -z+3/2$	0.85	1.82	2.656(7)	170
O(8)-H(8B)···O(11)	$-x, y-1/2, -z+3/2$	0.85	2.50	2.913	111
C(1)-H(1)···O(14)		0.93	2.53	3.000(10)	111
C(3)-H(3)···O(5)		0.93	2.59	3.415(8)	148
C(6)-H(6)···O(2)		0.93	2.59	3.216(8)	125
C(23)-H(23)···O(11)		0.93	2.59	3.410(9)	148

Absorption corrections were applied using the multi-scan technique [23]. The structures were solved by the Direct Method and refined by full-matrix least-square techniques on F^2 using SHELXL-97 [24]. All non-hydrogen atoms were refined anisotropically. The crystal data and structure refinement details for two complexes are shown in Table 1. Selected bond lengths and angles of the complexes are listed in Table 2, and possible hydrogen bond geometries are given in Table 3.

Results and Discussion

Description of the Structure

The single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the triclinic system, space group of *P–1*. The asymmetric unit of **1** consists of two Cd(II) ions lying on a mirror plane, one 3-NPA^{2-}, four phen, and two coordinated water molecules. As depicted in Fig. 1, the Cd1 ion is in a distorted octahedral geometry environment, coordinated by one oxygen atoms (O4) from one 3-NPA^{2-} and three nitrogen atoms (N5, N7, N8) from two phen composing the equatorial plane, and one oxygen atom (O8) from one water molecule at the apical position. The Cd1–O bond lengths are 2.211(7) and 2.240(7) Å, while the Cd1–N bond distances vary from 2.320(8) to 2.494(8) Å. The Cd2 also adopts a distorted octahedral geometry, and its coordination environment is similar to Cd1. In **1**, each fully deprotonated 3-NPA^{2-} ligand coordinates to two Cd atoms, with two carboxylate groups adopting $\mu 1$-$\eta 1$:$\eta 0$ mode. The structure is stabilized by intermolecular O–H···O and C–H···O hydrogen bonds (Table 3). The crystal structure is further connected through face-to-face π–π stacking between two adjacent phen. Two adjacent

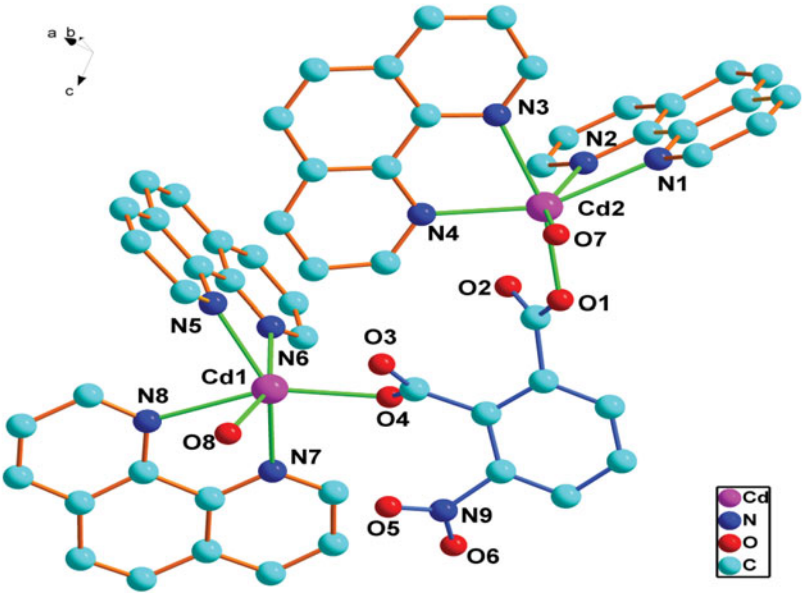

Figure 1. The coordination environment of Cd(II) ion of the complex **1**. All the hydrogen atoms are omitted for clarity.

phen molecules are completely parallel with a interplanar separation of ca. 3.4875(18), 3.6574(23), and 4.0698(27) Å. In the crystal, complex **1** is connected to a regular 2D structure in the *bc* plane via face-to-face π–π stacking interactions, O–H···O and C–H···O hydrogen bonds (Fig. 2). It can be seen that the *ac* plane is also a regular 2D web structure (Fig. 3). Therefore, the complex **1** packed into a 3D supramolecular structure via π–π stacking interactions and hydrogen bonds.

Single-crystal X-ray diffraction analysis reveals that complex **2** possesses a 1D infinite structure and its building unit is [Zn(3-NPA)(phen)(H_2O)] (Fig. 4). The Zn(II) ion is six-coordinate with an N_2O_4 donor set in the distorted octahedron environment. Three oxygen atoms (O1, O2, O5) from two 3-NPA^{2-}, nitrogen atoms (N1, N2) are from one phen and one oxygen atom (O3) from one water molecule (Fig. 4). The equatorial plane is defined by the O1, O2, O5, and N2 atoms with the O3 and N1 atoms occupying the apical positions. The bond lengths of Zn1–O range from 2.063(4) to 2.280(4) Å, the bond lengths of Zn1–N are 2.159(5) and 2.181(5) Å. The Zn2 also adopts a distorted octahedral geometry, and its coordination environment is similar to Zn1. Each fully deprotonated 3-NPA^{2-} ligand coordinates to two Zn atoms, with two carboxylate groups adopting μ1-η1: η0 and μ1-η1: η1 modes. In the crystal, the carboxylate group plays a bridging role. The cadmium(II) centers are bridged by multidentate 3-NPAH$_2$ ligand to form a 1D chain structure (Fig. 5), And the crystal structure is further stacked with face-to-face π–π stacking between two adjacent phen and O–H···O as well as C–H···O hydrogen bonds, resulting in a 2D layer framework (Fig. 6). The resulting 2D structure is cross-linked by hydrogen-bond interactions between C–H groups from phen and carboxylate oxygen atoms, thus leading to the formation of a 3D supramolecular architecture (Fig. 7).

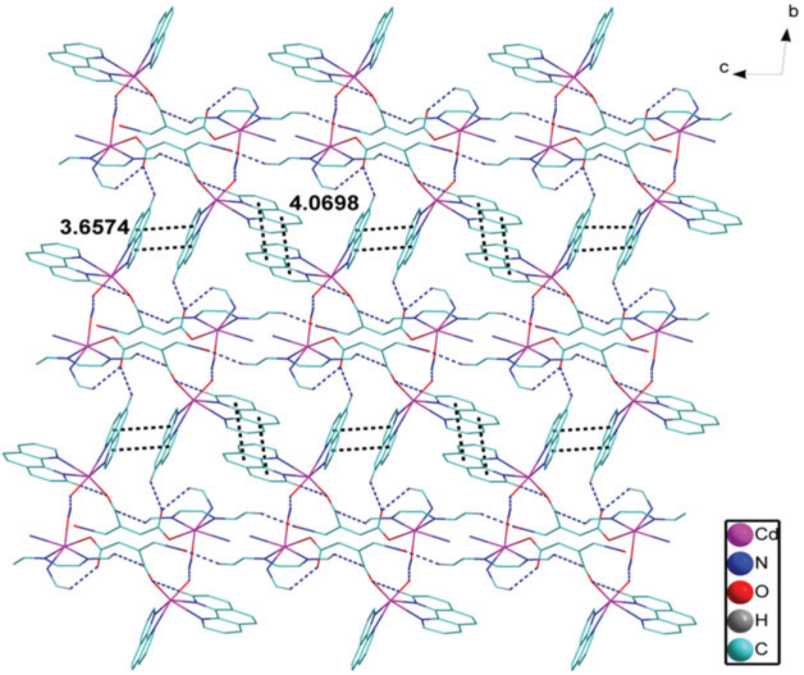

Figure 2. The 2D structure of the *bc* plane in complex **1**. Unnecessary atoms are omitted for clarity.

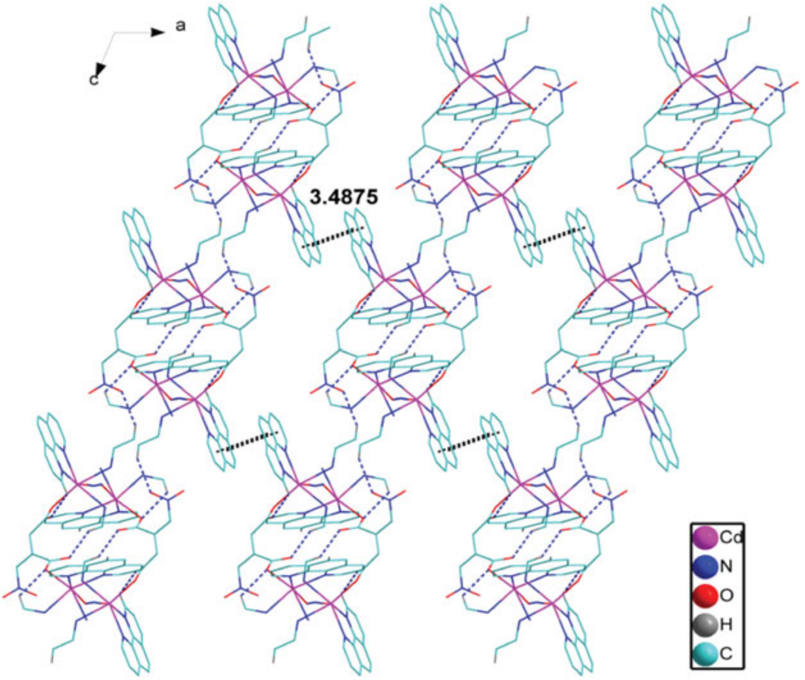

Figure 3. The 2D structure of the *ac* plane in complex **1.** Unnecessary atoms are omitted for clarity.

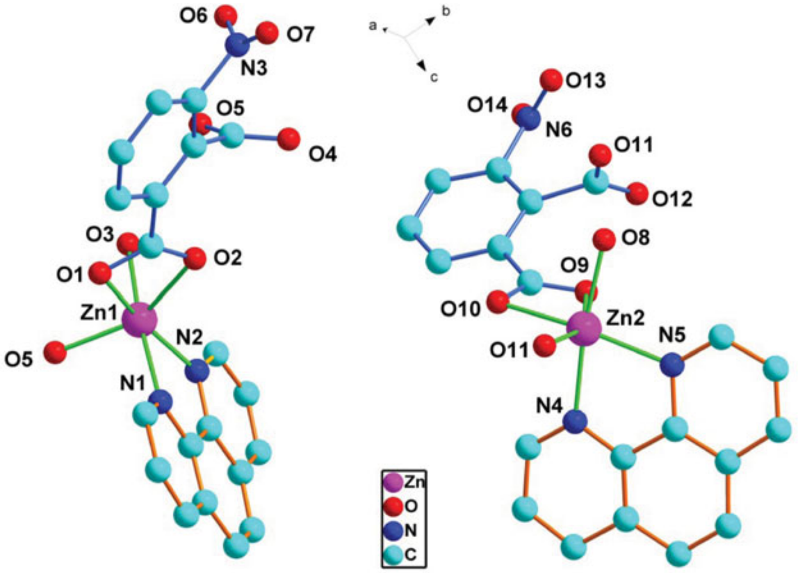

Figure 4. The coordination environment of Zn(II) ion of the complex **2**. All the hydrogen atoms are omitted for clarity.

IR Spectrum

In the IR spectra of two complexes, the strong and broad bands (O–H stretching vibration) in the 3500–3000 cm^{-1} region indicate the presence of coordinated water molecule. υ_{as}COO appears strong peak at 1591 cm^{-1} in complex **1**, 1622 cm^{-1} in **2.** υ_{s}COO appears medium intensity peak at 1383 cm^{-1} in **1**, 1458 in **2**. For complex **1**, the strong peak at 1514 cm^{-1} are attributed for $\upsilon_{\mathrm{as}}NO_2$, additional peaks at 1346 and 1426 cm^{-1} are attributed for $\upsilon_{\mathrm{s}}NO_2$ and C=N, respectively. In addition, for complex **2**, the strong peak at 1581 cm^{-1} are attributed for $\upsilon_{\mathrm{as}}NO_2$, additional peaks at 1369 and 1519 cm^{-1} are consistent with $\upsilon_{\mathrm{s}}NO_2$ and C=N, respectively.

XRD Patterns

In order to confirm the phase purity of the complexes, simulated and experimental powder X-ray diffraction (PXRD) patterns of **1**–**2** are shown in Figure S1. All the peaks in the recorded curves approximately match those in the simulated curves generated from single-crystal diffraction data, which confirms the phase purity of the as-prepared products.

Fluorescence Properties

Recently, the coordination complexes with their metal cations adopting d^{10} configuration have been intensively investigated for attractive fluorescence properties and potential applications as new luminescent materials [25]. For example, some zinc complexes have been used as organic light-emitting diodes (OLEDs) [26]. Hence, the solid state photoluminescence properties of 3-NPAH$_2$ ligand and complexes **1**–**2** were investigated at room temperature (Fig. 8) under the same experimental conditions. In the solid state, the strongest emission peak for the free ligand 3-NPAH$_2$ is at 438 nm with the excitation peak at 233 nm,

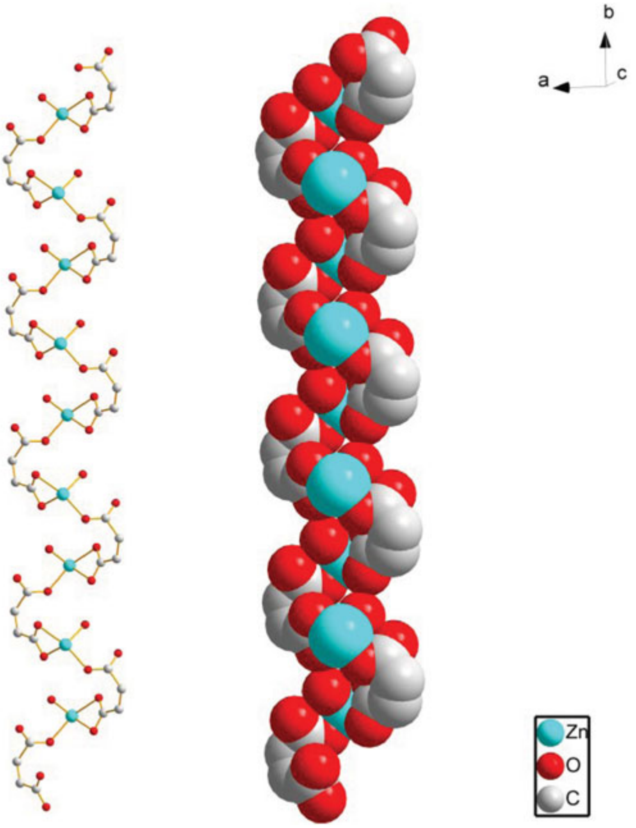

Figure 5. View of the 1D chain structure of **2**. Unnecessary atoms are omitted for clarity.

which is attributed to the π^*–n transitions [27]. The strongest excitation peaks for **1**–**2** are at 231 and 244 nm, emission spectra mainly show strong peaks at 445 and 440 nm, respectively. The ligand chelation to the metal center may effectively increase the rigidity of the ligand and reduce the loss of energy by radiationless decay, thus causing the red shift in **1** and **2**. Therefore, the luminescence behavior of complexes is caused by metal ligand charge transfer (MLCT) [28].

Thermogravimetric(TG) Analyses

In order to study the framework stability of the title complexes, the thermogravimetric (TG) analysis was performed in N_2 atmosphere on polycrystalline samples of complexes **1**–**2**, and the TG curves are shown in Fig. 9. The TG curve of **1** shows the first loss of 3.69% in the temperature range of 33–150°C, which indicates the exclusion of coordinated water molecules (calcd, 3.03%); The second stage occurs between 170 and 327°C, the anhydrous complex loses 17.17% of total weight, which is due to the decomposition of one 3-NPA^{2-} (calcd, 17.56%). The final weight loss of 59.09% (calcd, 60.53%) corresponds to the loss of four phen in the temperature range of 329–960°C.

For **2**, the weight loss attributed to the gradual release of watermolecules is observed in the range of 107–182°C (obsd, 4.02%; calcd, 3.81%). When the temperature holds on

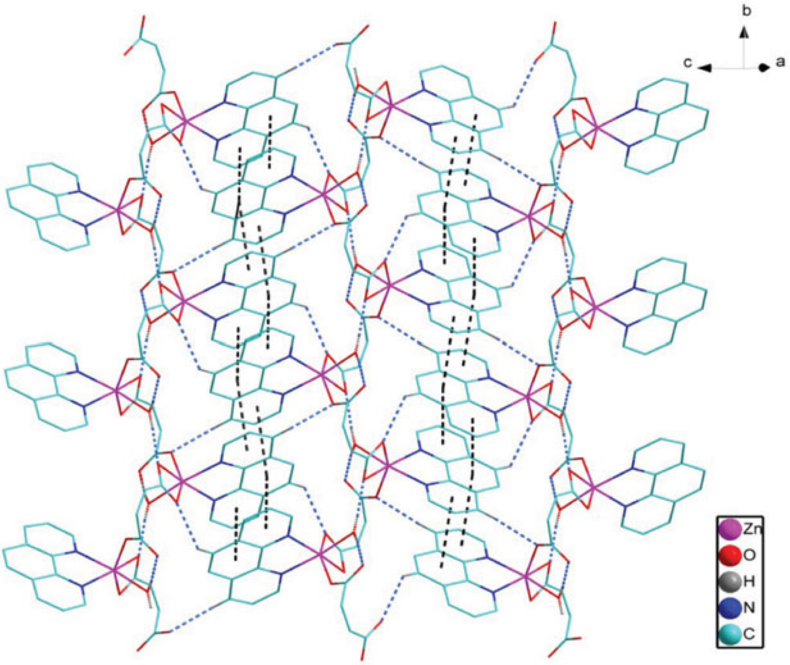

Figure 6. View of π–π stacking interactions and H-bonding of complex **2**. Unnecessary atoms are omitted for clarity.

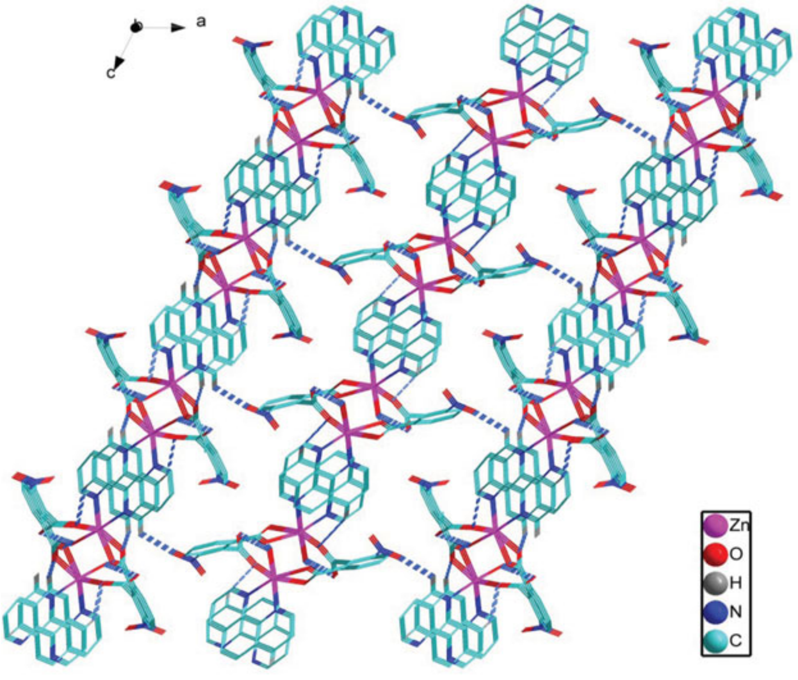

Figure 7. View of the overall 3D supramolecular framework of complex **2**.

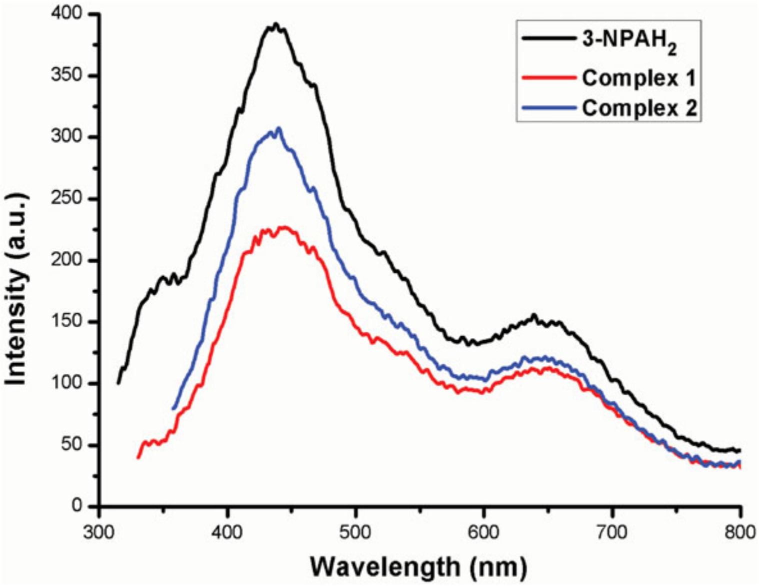

Figure 8. Solid-state fluorescent emission spectra of 3-NPAH$_2$ (black), complex **1** (red), and complex **2** (blue) at room temperature.

rising, the product lost 44.12% of the total weight in the temperature range of 189 to 702°C, which is related to the loss of 3-NPA^{2-} (calcd, 44.24%). Beyond 704°C, one phen processes with a total weight loss of 36.10% (calcd. 38.12%) was observed. The residual percentage weight at the end of the decomposition of the complex is observed 15.77%.

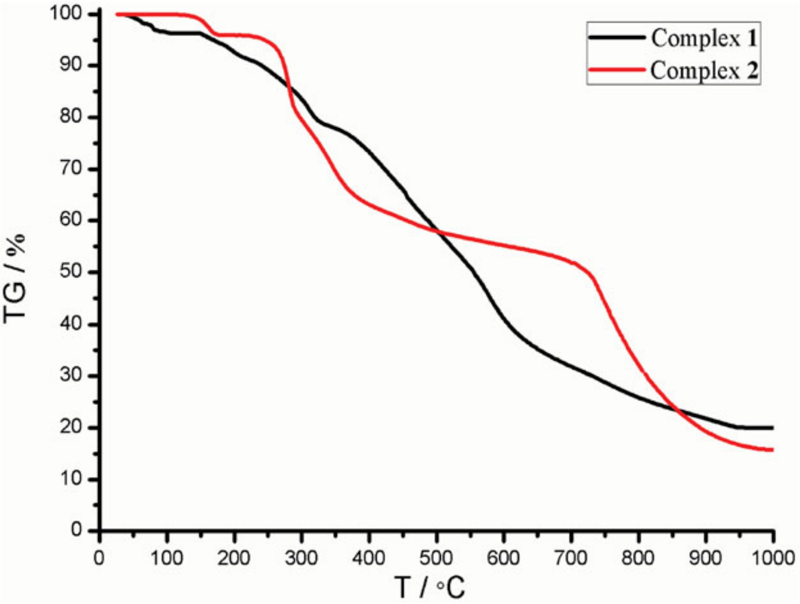

Figure 9. The TG curves of two complexes.

Conclusion

In summary, this paper reports two new d^{10} transition metal coordination complexes, $[Cd_2(3\text{-NPA})(phen)_4(H_2O)_2]_2$ (**1**) and $[Zn(3\text{-NPA})(phen)(H_2O)]_n$ (**2**) under hydrothermal condition. The two new complexes were characterized by single crystal X-ray diffraction, IR spectroscopy, TGA, and luminescent spectra. Complex **1** possesses a 0D dinuclear structure which is arranged to form a 3D supramolecular framework through hydrogen bonds and π–π stacking interactions. Compound **2** features a 1D infinite chain structure through phen and 3-NPA^{2-} ligands, and the chain are further held together through hydrogen bonds and π–π stacking interactions. In addition, the luminescence measurements reveal that two complexes exhibit good fluorescent emissions in the solid state at room temperature. Also, the thermal analyses of two complexes were investigated in detail.

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Supplementary Material

Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-947707 (**1**), No. CCDC-947708 (**2**)). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk.

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