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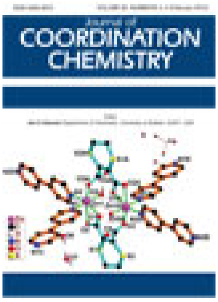

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Zinc(II) complexes with 5,6-dihydro-1,4-dithiin-2,3-dicarboxylic anhydrate and different N-donors: syntheses, crystal structures, and emission properties

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Zinc(II) complexes with 5,6-dihydro-1,4-dithiin-2,3-dicarboxylic anhydrate and different *N*-donors: syntheses, crystal structures, and emission properties

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Two new Zn^{II} complexes, $\{[Zn(\mathbf{L})(phen)(H_2O)] \cdot H_2O\}_\infty$ (**1**) and $\{[Zn(\mathbf{L})(4bpy)(H_2O)] \cdot H_2O\}_\infty$ (**2**) (**L** = 5,6-dihydro-1,4-dithiin-2,3-dicarboxylate, phen = 1,10-phenanthroline, and 4bpy = 4,4′-bipyridine), have been prepared by *in situ* reaction of $Zn(ClO_4)_2 \cdot 6H_2O$ with 5,6-dihydro-1,4-dithiin-2,3-dicarboxylic anhydrate in the presence of lithium hydroxide, together with incorporating chelating phen or bridging 4bpy as co-ligands. Their structures were determined by single-crystal X-ray diffraction. Complex **1** takes a 1-D helical structure that is further assembled into a 2-D network by O–H$\cdots$O, C–H$\cdots$O hydrogen bonds, and weak S$\cdots$S interactions, and then an overall 3-D supramolecular framework was formed by $\pi \cdots \pi$ stacking interactions. Complex **2** possesses a 2-D (4,4)-layered structure. The structural difference between **1** and **2** can be attributed to the different *N*-donor auxiliary co-ligands. Both **1** and **2** are photoluminescent materials whose emission properties are closely related to their intrinsic structure.

Keywords: Zinc(II) complexes; 5,6-Dihydro-1,4-dithiin-2,3-dicarboxylic anhydrate; Crystal structures; Luminescence

1. Introduction

Extensive experimental and theoretical efforts have focused on rational design and control of coordination polymers from pre-designed bridging ligands and metal ions due to their interesting structural topologies and potential applications [1–3]. Appropriate choice of well-designed organic building blocks and metal ions or clusters is an effective way to build such coordination polymers [4–7]. Utilizing suitable organic tectons with various functional groups that are capable of bridging metal centers to construct crystalline materials is an active area of multidisciplinary research, being connected with crystal engineering, coordination/supramolecular chemistry, and material science.

Multidentate ligands with various N and/or O donors have been widely utilized as building blocks in the construction of MOFs. The rigid/flexible dicarboxylic acids [8, 9],

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such as benzene- and cyclohexane-based 1,2-dicarboxylates, have been extensively used in the preparation of various metal–carboxylate complexes. However, investigation of dicarboxylates with heteroalicyclic skeleton, such as 5,6-dihydro-1,4-dithiin-2,3-dicarboxylate used here, has not been reported. Very recently, only one photoluminescent 3-D Ag^I coordination polymer was prepared by our group, exhibiting an unusual trinodal 6-connected $(4^{12} \cdot 6^3)_2(4^9 \cdot 6^6)$ topology [10]. In addition, mixed organic ligands, especially for various carboxylates with different ring skeletons and chelating/bridging *N*-donors, such as 1,10-phenanthroline (phen) and 4,4′-bipyridine (4bpy), are good candidates for the construction of coordination polymers with interesting architectures and potential properties [11–14].

Considering all the aspects mentioned above, we sequentially synthesized two new Zn^{II} coordination complexes in this research by *in situ* reaction of Zn^{II} with 5,6-dihydro-1,4-dithiin-2,3-dicarboxylic anhydrate in the presence of lithium hydroxide, together with incorporating phen or 4bpy as a co-ligand, a 1-D helical chain $\{[Zn(\mathbf{L})(phen)(H_2O)] \cdot H_2O\}_\infty$ (**1**), and a 2-D layer $\{[Zn(\mathbf{L})(4bpy)(H_2O)] \cdot H_2O\}_\infty$ (**2**) (**L** = 5,6-dihydro-1,4-dithiin-2,3-dicarboxylate, phen = 1,10-phenanthroline, and 4bpy = 4,4′-bipyridine). Herein, we report the syntheses, crystal structures, and luminescent properties of the complexes.

2. Experimental

2.1. *General methods*

All the starting reagents and solvents for the synthesis were commercially available and used as received. Elemental analyses (C, H, and N) were performed on a Vario EL III analyzer. The IR spectra were recorded from 4000 to 400 cm^{-1} on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. The X-ray powder diffraction (XRPD) was recorded on a Bruker D8 Advance diffractometer (Cu-Kα, $\lambda = 1.54056$ Å) at 40 kV and 30 mA, using a Cu-target tube and a graphite monochromator. The intensity data were recorded by continuous scan in a $2\theta/\theta$ mode from 3° to 80° with a step size of 0.02° and a scan speed of $2^\circ\ min^{-1}$. Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the *Mercury* (Hg) program available free of charge *via* the internet at http://www.iucr.org. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 900°C under nitrogen at a heating rate of $10^\circ C\ min^{-1}$. The solid-state emission/excitation spectra were recorded on an F-7000 (HITACHI) spectrophotometer at room temperature.

2.2. *Syntheses of 1 and 2*

Single crystals of **1** and **2** suitable for X-ray analysis were obtained by the similar method as described below for **1**.

2.2.1. $\{[Zn(L)(phen)(H_2O)] \cdot H_2O\}_\infty$ (1). A mixed solution of 5,6-dihydro-1,4-dithiin-2,3dicarboxylic anhydrate (0.05 mmol, 10.1 mg), phen (0.05 mmol, 9.01 mg), and

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lithium hydroxide (0.1 mmol, 2.39 mg) in distilled water (5 mL) was heated for *ca* 15 min with stirring magnetically. After cooling to room temperature, a solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol, 37.2 mg) in distilled water (5 mL) was added to the above solution and was stirred for *ca* 15 min. The resulting white solid was filtered off and the filtrate was kept at room temperature. Colorless single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent for 2 weeks. Yield: *ca* 40% based on **L**. Anal. Calcd for $C_{18}H_{16}ZnN_2O_6S_2$ (%): C, 44.46; H, 3.32; N, 5.76. Found (%): C, 44.33; H, 3.38; N, 5.89. IR (KBr pellet, cm^{-1}): 3423 m(br), 1613(s), 1567(s), 1518(m), 1428(m), 1397(m), 1351(s), 1291(m), 1223(w), 1146(w), 1087(w), 852(m), 782(w), 758(m), 727(m), 697(m), 643(w), 593(w), 475(w), 425(w).

2.2.2. $\{[Zn(L)(4bpy)(H_2O)] \cdot H_2O\}_\infty$ (2). The same procedure as that for **1** was used for this complex except for the introduction of bridging 4bpy (0.05 mmol, 7.8 mg) instead of chelating phen. Yellow block single crystals suitable for X-ray analysis were obtained at the beaker wall after approximately 2 weeks at room temperature. Yield: *ca* 30% based on **L**. Anal. Calcd for $C_{16}H_{16}ZnN_2O_6S_2$ (%): C, 41.57; H, 3.49; N, 6.06. Found (%): C, 41.79; H, 3.65; N, 6.15. IR (KBr pellet, cm^{-1}): 3456 m(br), 1610(s), 1567(s), 1538(m), 1492(w), 1416(m), 1359(s), 1284(w), 1217(w), 1125(w), 1071(m), 1046(w), 1015(w), 927(w), 870(w), 810(m), 749(m), 690(m), 640(m), 606(w), 569(w), 477(w).

Caution! Although we have met no problems in handling chlorate salt during this work, it should be treated cautiously owing to its potential explosive nature.

2.3. *Crystal structure determination*

X-ray single-crystal diffraction data for **1** was collected on an Xcalibur Gemini Eos CCD diffractometer and for **2** on a Bruker Smart 1000 CCD area-detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å), respctively. The program SAINT [15] was used for integration of the diffraction profiles. Semi-empirical absorption corrections were applied using SADABS [16]. Both structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares with SHELXL [17]. Zinc in each complex was located from the *E*-maps and the other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. Generally, C-bound hydrogen atoms were generated theoretically and refined with isotropic thermal parameters riding on the parent carbon. Hydrogen atoms of water were first located by difference Fourier *E*-maps and then treated isotropically as riding. Further crystallographic data and structural refinement details for **1** and **2** are summarized in table 1. Selected bond lengths and angles as well as hydrogen-bonding geometry for **1** and **2** are listed in tables 2–4, respectively.

3. Results and discussion

3.1. *Synthesis and general characterizations*

For investigating the coordination of **L**, we prepare two Zn^{II} complexes by changing co-ligands (phen for **1** and 4bpy for **2**) under ambient conditions. The presence of two

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Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{18}H_{16}N_2O_6S_2Zn$	$C_{16}H_{16}N_2O_6S_2Zn$
Formula weight	485.82	461.84
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	10.1189(3)	8.8691(16)
b	8.9923(2)	11.104(2)
c	21.2452(6)	11.616(2)
α	90	101.759(16)
β	90.163(2)	111.496(18)
γ	90	107.787(17)
Volume (Å^3), Z	1933.14(9), 4	946.9(3), 2
Calculated density (g cm^{-3})	1.669	1.620
Absorption coefficient (mm^{-1})	1.526	1.553
R_{int}	0.0351	0.0327
Goodness-of-fit on F^2	0.868	1.049
Temperature (K)	294(2)	294(2)
Final R indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0258$, $wR_2 = 0.0545$	$R_1 = 0.0424$, $wR_2 = 0.0897$
Largest difference peak and hole (e Å^{-3})	0.422 and −0.233	0.658 and −0.586

${}^{a}R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; ${}^{b}wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where F_o = observed and F_c = calculated structure factors, respectively.

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

Zn1–O4$^{\#1}$	1.9915(15)	Zn1–O5	2.1285(15)
Zn1–N2	2.1184(19)	Zn1–N1	2.149(2)
Zn1–O1	2.1218(17)	Zn1–O2	2.3805(18)
O4$^{\#1}$–Zn1–N2	103.16(7)	O1–Zn1–N1	91.29(7)
O4$^{\#1}$–Zn1–O1	106.60(6)	O5–Zn1–N1	162.44(7)
N2–Zn1–O1	150.11(7)	O4$^{\#1}$–Zn1–O2	162.11(6)
O4$^{\#1}$–Zn1–O5	89.83(6)	N2–Zn1–O2	92.98(7)
N2–Zn1–O5	90.85(7)	O1–Zn1–O2	58.03(6)
O1–Zn1–O5	92.00(6)	O5–Zn1–O2	82.19(6)
O4$^{\#1}$–Zn1–N1	105.73(7)	N1–Zn1–O2	84.96(7)
N2–Zn1–N1	77.89(8)		

Symmetry code #1: $-x+1/2$, $y+1/2$, $-z+3/2$.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Zn1–O3$^{\#1}$	2.015(3)	Zn1–O5	2.119(3)
Zn1–O1	2.046(3)	Zn1–N1	2.177(4)
Zn1–N2	2.090(3)	Zn1–O2	2.509(3)
O3$^{\#1}$–Zn1–O1	111.87(11)	N2–Zn1–N1	93.80(13)
O3$^{\#1}$–Zn1–N2	101.12(12)	O5–Zn1–N1	173.59(11)
O1–Zn1–N2	146.95(13)	O3$^{\#1}$–Zn1–O2	168.49(10)
O3$^{\#1}$–Zn1–O5	94.21(11)	O1–Zn1–O2	56.63(11)
O1–Zn1–O5	87.85(11)	N2–Zn1–O2	90.39(11)
N2–Zn1–O5	91.80(12)	O5–Zn1–O2	85.29(11)
O3$^{\#1}$–Zn1–N1	87.76(12)	N1–Zn1–O2	91.55(11)
O1–Zn1–N1	85.76(12)		

Symmetry code #1: $-x+2$, $-y+1$, $-z$.

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Table 4. Selected hydrogen–bonding geometry (Å, °) for **1** and **2**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	D–H···A
1				
C5–H5B···O1W[a]	0.97	2.53	3.363(4)	144
O5–H52···O1W	0.85	1.97	2.797(2)	166
O1W–H1W···O3	0.85	1.99	2.767(2)	151
O1W–H2W···O2[b]	0.85	1.99	2.841(2)	174
2				
O5–H1W···O2[a]	0.85	1.96	2.771(2)	160
O6–H4W···O7	0.85	2.06	2.878(2)	161
O7–H6W···O6	0.85	2.03	2.878(2)	174
O7–H5W···O4[b]	0.85	2.38	3.099(3)	143
C5–H5B···*Cg*1[b]	0.97	3.16	3.885(2)	133

Symmetry codes for **1**: a: $x+1$, y, z; b: $-x+1/2$, $y+1/2$, $-z+3/2$; for **2**: a: $-x+1$, $-y+1$, $-z$; b: $-x+2$, $-y+1$, $-z+1$. *Cg*1 is the centroid of the N1/C7–C11 pyridyl ring of bpy ligand.

carboxylates in **L** creates the possibility of various coordination modes, such as μ_1–$\eta^1:\eta^1$-chelating and μ_1–$\eta^1:\eta^0$-monodentate observed in this work. Use of lithium hydroxide is a key point for the formation of **1** and **2**, by adjusting the pH of the reaction system and also facilitating *in situ* hydrolyzation of 5,6-dihydro-1,4-dithiin-2,3-dicarboxylic anhydrate.

Both **1** and **2** are air stable with maintenance of their crystallinity for several months and are insoluble in common organic solvents and water, consistent with their polymeric nature. All general characterizations for **1** and **2** were carried out on single crystalline samples. In IR spectra of **1** and **2**, broad bands centered at *ca* 3400 cm^{-1} (3423 cm^{-1} for **1** and 3456 cm^{-1} for **2**) indicate O–H stretch of water. Characteristic bands of carboxylate in **1** and **2** appear in the usual region at 1613–1567 cm^{-1} for antisymmetric stretching vibrations and at 1351–1359 cm^{-1} for symmetric stretch. Furthermore, the $\Delta\nu$ values [$\Delta\nu = \nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)$] are 262 and 216 cm^{-1} for **1** as well as 251 and 208 cm^{-1} for **2**, in agreement with their structural features from crystal structures [18].

3.2. *Description of crystal structures*

3.2.1. $\{[\text{Zn(L)(phen)(H}_2\text{O)}]\cdot\text{H}_2\text{O}\}_\infty$ (1).

Single-crystal X-ray diffraction reveals that the structure of **1** consists of 1-D helical chains. Each asymmetric unit contains a Zn$^{\text{II}}$, one **L**, one chelating phen, one coordinated water, and one lattice water. In **1**, there is only one crystallographic-independent Zn$^{\text{II}}$ that is six-coordinate with three carboxylate oxygens from two different **L**, one phen, and one coordinated water molecule (figure 1a). All bond lengths [1.9915(15)–2.3805(18) Å] and angles [58.03(6)–162.44(7)°] around each Zn$^{\text{II}}$ (table 2) are comparable to those of similar carboxylato–Zn$^{\text{II}}$ complexes in the literature [19]. Two carboxylates of each **L** take two different coordination modes, μ_{1}–$\eta^1:\eta^1$-chelating for O1–C1–O2 carboxylate and μ_{1}–$\eta^1:\eta^0$-monodentate for the O3–C8–O4 carboxylate. Each **L** uses three oxygen atoms of two carboxylates to connect two Zn$^{\text{II}}$ ions, leading to the formation of two different left- and right-handed helical chains along the *b* axis with a period of 8.992 Å (figure 1b) [20]. The S1···S1 distance of 3.490 Å is shorter than the sum of the van der

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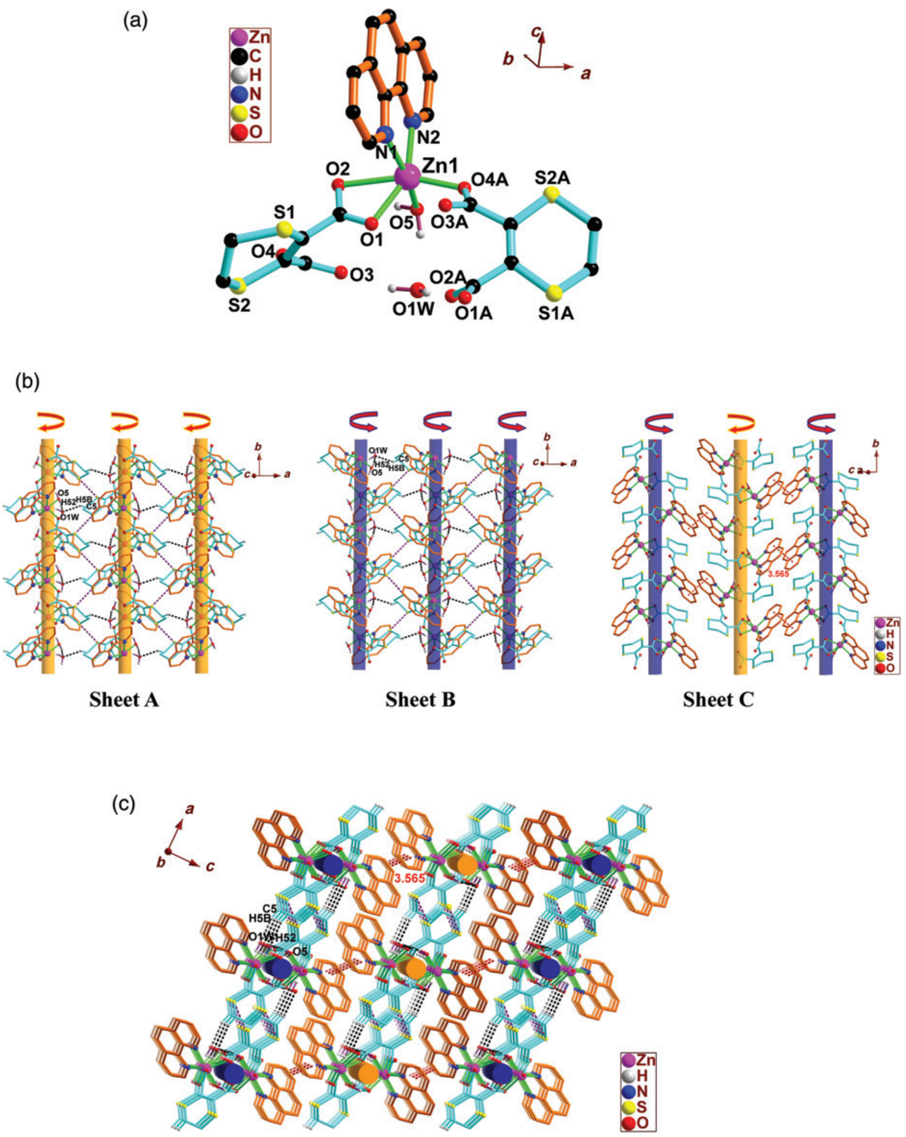

Figure 1. View of (a) the local coordination environment of Zn^{II} in **1**, (b) two different 2-D hydrogen-bonding sheets (Sheets A and B) through the inter-chain O–H ⋯ O (O5–H52 ⋯ O1W), C–H ⋯ O (C5–H5B ⋯ O1W) hydrogen-bonding (black dashed lines), and weak S ⋯ S interactions (purple dashed lines) as well as another 2-D sheet through $\pi \cdots \pi$ stacking interactions (red dashed lines) between neighboring left- and/or right-handed helical chains, and (c) the 3-D framework formed by interlayer O–H ⋯ O (O5–H52 ⋯ O1W), C–H ⋯ O (C5–H5B ⋯ O1W) hydrogen-bonding (black dashed lines), weak S ⋯ S interactions (purple dashed lines), and $\pi \cdots \pi$ stacking interactions (red dashed lines). Only hydrogen atoms involved in interactions are shown for clarity. The symmetry-related atoms labeled with the suffix A are generated by the symmetry operation $(-x+1/2,\ y+1/2,\ -z+3/2)$.

Waals radii of two sulfur atoms, indicating the existence of weak S ⋯ S interactions [21]. Adjacent left- or right-handed helical chains are linked uniformly together by inter-chain C–H ⋯ O (C5–H5B ⋯ O1W), O–H ⋯ O (O5–H52 ⋯ O1W) interactions, and weak S ⋯ S interactions (table 4 for detailed information) [22], running parallel to the

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ab plane, affording two different 2-D hydrogen-bonding sheets (denoted as Sheets A and B in figure 1b, left and middle). The left- and right-handed helical chains aforementioned can also be connected resulting in the formation of another 2-D sheet (Sheet C in figure 1b, right) running parallel to the *bc* plane, formed by inter-chain $\pi\cdots\pi$ stacking interactions between completely parallel phenanthroline rings of adjacent chains with centroid–centroid and interplanar separation of 3.565 Å, and then an overall 3-D framework (figure 1c). Finally, lattice water molecules were further fixed in the void space of the framework in **1** *via* O–H···O hydrogen-bonding interactions between themselves and oxygen of carboxylates of **L** (table 4). Some weak interactions, such as intra- and/or inter-molecular hydrogen-bonding, weak S···S, and $\pi\cdots\pi$ stacking supramolecular interactions, also affect the structures of coordination complexes, especially in the aspect of linking low-dimensional entities into higher-dimensional supramolecular network.

3.2.2. $\{[Zn(L)(4bpy)(H_2O)]\cdot H_2O\}_\infty$ (2). When 4bpy, a rigid linear spacer, was introduced into the reaction system instead of phen as a bridging co-ligand, a new 2-D layered network was isolated with dinuclear [Zn_2**L**$_2$] units as nodes (figure 2). Each asymmetric unit is composed of one Zn^{II}, one **L**, one 4bpy, one coordinated and one lattice water molecule. As shown in figure 2(a), each six-coordinate Zn^{II} is surrounded by three carboxylate oxygen atoms (Zn–O: 2.015(3)–2.509(3) Å) from two different **L**, two nitrogen atoms from two distinct 4bpy (Zn–N: 2.090(3)–2.177(4) Å), and one water molecule (Zn1–O5: 2.119(3) Å). In **2**, **L** adopts two different coordination modes, $\mu_{1-}\eta^1:\eta^1$-chelating for O1–C1–O2 carboxylate and $\mu_{1-}\eta^1:\eta^0$-monodentate for O3–C2–O4 carboxylate. Two **L** connect adjacent Zn^{II} ions to form the dinuclear [Zn_2**L**$_2$] units with a non-bonding Zn···Zn separation of 5.014 (3) Å (figure 2a); 4bpy is a linear spacer bridging adjacent [Zn_2**L**$_2$] units to generate a 2-D layer running parallel to the (100) plane (figure 2b). For network topology, the dinuclear [Zn_2**L**$_2$] can be considered as nodes and 4bpy as linkers in a simple (4,4) topology with 4-connected nodes. In addition, adjacent 2-D layers are further linked to form an overall 3-D network by the co-effects of inter-layer O–H···O hydrogen-bonds [O5–H1W···O2^a; symmetry code for $a=-x+1,\ -y+1,\ -z$; table 4] and C–H···π supramolecular interactions between **L** and 4bpy with an edge-to-face orientation ($d=3.16$ Å; $A=133°$). Free water molecules were included within the void space of the framework in **2** and formed a four-membered water cluster associated by O–H···O hydrogen-bonding interactions between themselves [O6–H4W···O7, O7–H6W···O6, O7–H5W···O4^b, symmetry codes for $b=-x+2,\ -y+1,\ -z+1$] (table 4).

Some rigid/flexible dicarboxylic acids, such as benzene- [23] and cyclohexane-based dicarboxylic acid [24], have been widely used to construct zinc metal–organic coordination architectures. For instance, incorporating phen as a chelating co-ligand, one 1-D zig-zag chain $\{Zn(\mathbf{L}_1)(phen)(H_2O)\}_n$, one 1-D ladder-like motif $\{[Zn(\mathbf{L}_2)(phen)]_2\}_n$, one 1-D helical chain $\{[Zn(\mathbf{L}_3)(phen)(H_2O)]\}_n$ [23a], and one dinuclear centrosymmetric complex $[Zn_2(\mathbf{L}_4)_2(phen)_2(H2O)_2]$ [24a] as well as one 2_1 helical chain $[Zn(\mathbf{L}_5)(phen)(H_2O)]_n$ [24b] ($\mathbf{L}_1$ = 1,4-benzenedicarboxylate, $\mathbf{L}_2$ = 1,3-benzenedicarboxylate, $\mathbf{L}_3$ = 1,2-benzenedicarboxylate, $\mathbf{L}_4$ = cyclohexane-1,3-dicarboxylate, and $\mathbf{L}_5$ = cyclohexane-1,4-dicarboxylate), have been reported. Employing 4bpy as a bridging co-ligand instead of phen, reaction with Zn^{II} under certain conditions, four complexes, pillared 2-D nets $[Zn_2(\mathbf{L}_1)_2(4bpy)]_n$ [23b], 2-D neutral layer $\{[Zn_2(\mathbf{L}_2)_2(4bpy)_2]\cdot DMF\}_n$

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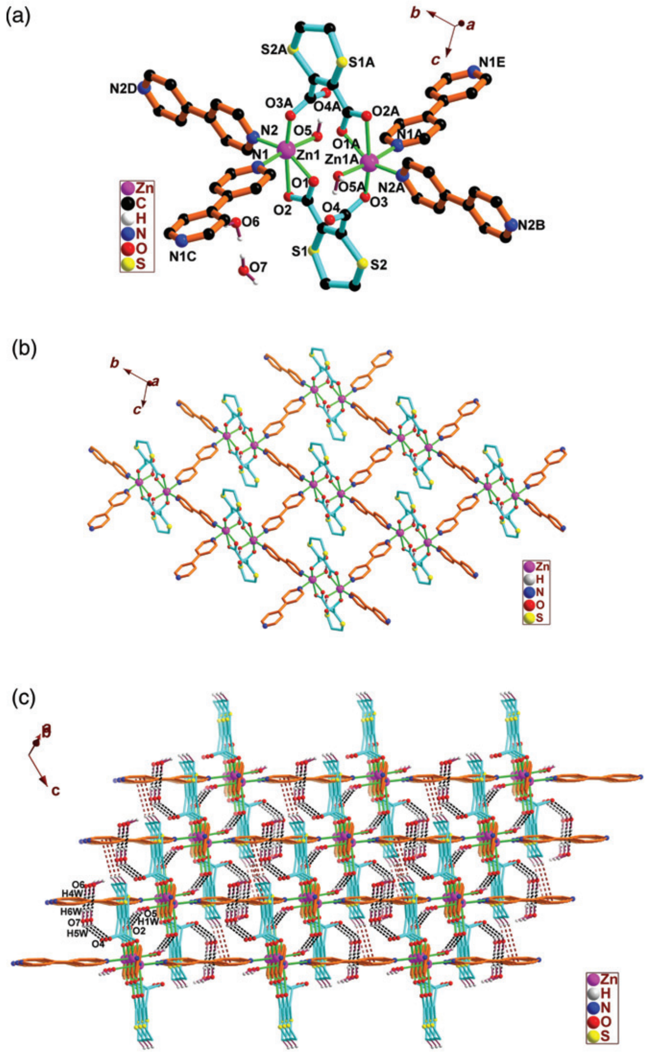

Figure 2. View of (a) the local coordination environment of Zn^{II} in **2**, (b) the 2-D layer running parallel to the (100) plane, and (c) the 3-D framework formed by inter-layer O–H$\cdots$O (O5–H1W$\cdots$O2) hydrogen-bonding interactions (black dashed lines). Only hydrogen atoms involved in interactions are shown for clarity. The symmetry-related atoms labeled with suffixes A, B, C, D, and E are generated by the symmetry operations $(-x+2, -y+1, -z)$, $(x+1, y-1, z)$, $(-x+3, -y+2, -z+1)$, $(-x+1, -y+2, -z)$, and $(x-1, y-1, z-1)$.

[23c], 1-D double-chain $[Zn(\mathbf{L}_3)_2(4bpy)_2]$ [23d], and 3-D coordination polymer $[Zn_2(\mathbf{L}_4)_2(4bpy)]_n$ [24c] as well as 2-D sheet $\{[Zn_2(\mathbf{L}_6)_2(4bpy)\cdot 3CH_3OH]\}_n$ ($\mathbf{L}_6 =$ *cis*-1,2-cyclohexanedicarboxylate) [24d] have been documented. In this work, involving mixed heteroalicyclic skeleton-based **L** and phen for **1** and 4bpy for **2** produced two new Zn^{II} complexes with 1-D helical chain and 2-D layer structures. Our result, from the viewpoint of ligand design, exhibits a new example of the coordination versatility of dicarboxylic acids with a heteroalicyclic skeleton.

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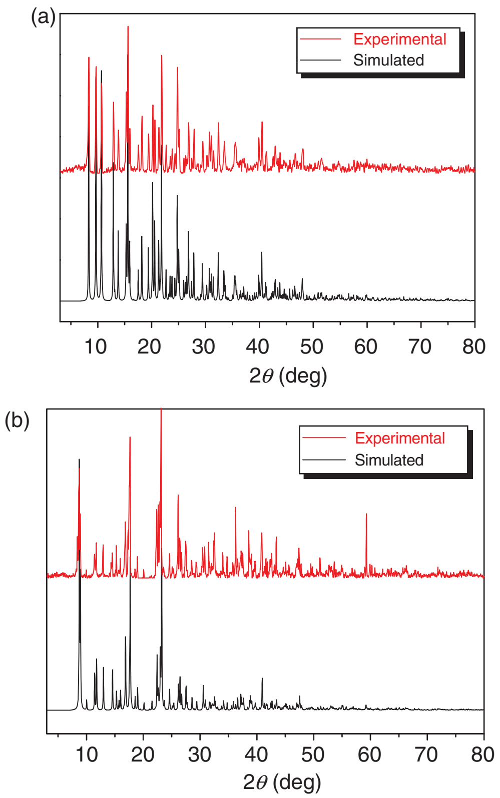

Figure 3. XRPD patterns of (a) **1** and (b) **2**.

3.3. *XRPD results*

To confirm whether the crystal structures are truly representative of the bulk materials, XRPD experiments were carried out for **1** and **2**. The XRPD experimental and computer-simulated patterns of the corresponding complexes are shown in figure 3. Although the experimental patterns have a few unindexed diffraction lines and some are slightly broadened in comparison with those simulated from the single crystal modes, it still can be considered favorably that the bulk synthesized materials and the as-grown crystals are homogeneous for **1** and **2**.

3.4. *Thermogravimetric analysis*

Thermogravimetric (TG) experiments of **1** and **2** were performed to explore their thermal stabilities (figure 4). Samples of the complexes were heated from room temperature to 900°C with a heating rate of $10^\circ\mathrm{C\,min^{-1}}$ under nitrogen. For **1**, one lattice and one coordinated water molecules are released before 100°C (peaking at 75°C), as revealed by a total weight loss of 7.58% (Calcd: 7.42%). Then the mass remained largely unchanged until the decomposition onset beyond 200°C. The critical weight losses 42.65% at 200–470°C (peaking at 264°C) can be attributed to the loss of **L** (Calcd: 42.04%), showing the collapse of the whole framework. The final residue is not

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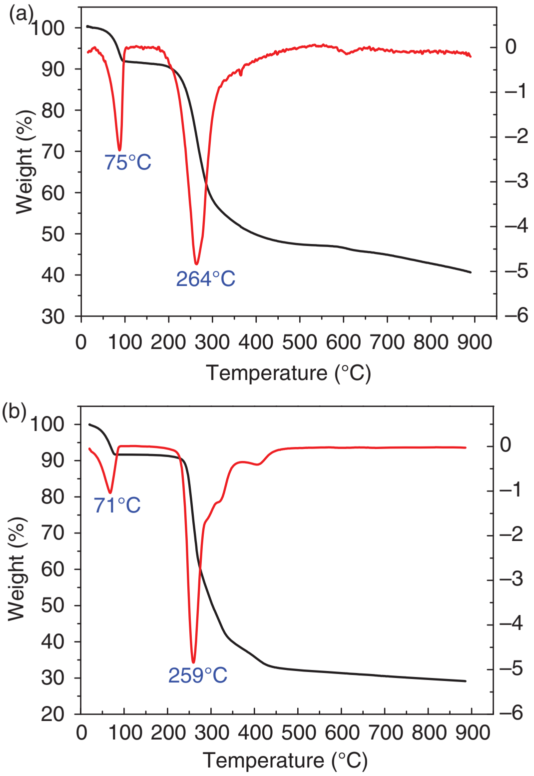

Figure 4. Thermogravimetric analysis (TGA) plots of (a) **1** and (b) **2**.

characterized because its weight loss does not stop until heating ends at 900°C. As for **2**, the first weight loss of 7.96% appeared before 80°C, corresponding to the removal of lattice and coordinated water molecules (Calcd: 7.80%). The remaining substance is stable to *ca* 230°C, where decomposition occurs with one sharp step of weight loss (peaking at 259°C). The weight loss of 45.29% between 230°C and 315°C is very close to the calculated value of 44.22%, for the removal of **L**. Upon further heating, the decomposition of framework continues. The remaining solid is thermally stable to 470°C. The final residues (32.54%) cannot be specifically identified and may be a mixture.

3.5. *Luminescent properties*

Photoluminescence of d^{10} coordination complexes have been extensively studied due to their potential applications as luminescent materials [19b, 25]. Thus, solid-state emission spectra of the as-synthesized Zn^{II} complexes **1** and **2** have been investigated at room temperature (figure 5). Excitation of the microcrystalline samples of **1** and **2** at 394 and 366 nm produces intense luminescence with peak maxima at 509 and 476 nm, respectively. Free **L** displays very weak luminescence in the solid state at ambient temperature [10]. To further analyze these emission bands, the photoluminescent

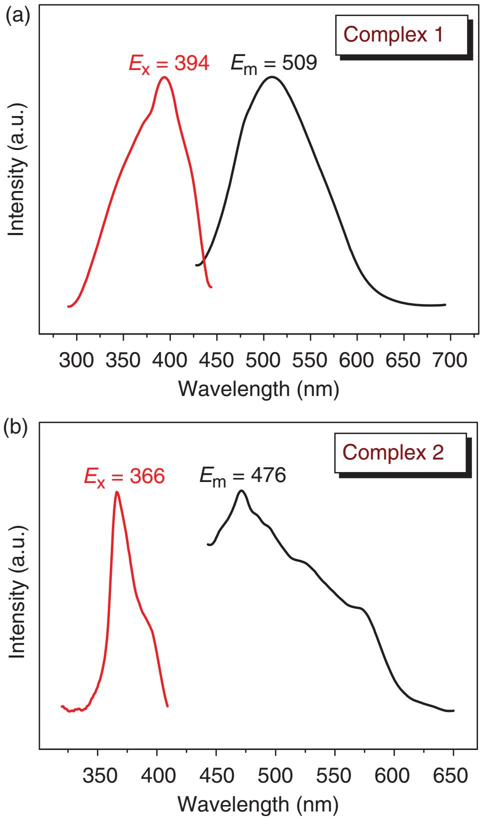

Figure 5. Excitation/emission spectra of (a) **1** and (b) **2** at room temperature.

properties of auxiliary co-ligands phen and 4bpy have also been investigated under the same experimental conditions. By comparing the locations and profiles of their excitation/emission peaks with those of **1** and **2**, we presume that these emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT), because the Zn^{II} is difficult to oxidize or to reduce [26], and should mainly be ascribed to the intraligand $\pi \rightarrow \pi^*$ transitions arising from phen for **1** and 4bpy for **2** [19b, 26a, 27], ligand-to-ligand charge transfer.

4. Conclusion

Two new Zn^{II} complexes with 1-D helical chain and 2-D layer structures have been synthesized by using *in situ* reaction of $Zn(ClO_4)_2 \cdot 6H_2O$ and 5,6-dihydro-1,4-dithiin-2,3-dicarboxylic anhydrate in the presence of lithium hydroxide, together with incorporating phen for **1** and 4bpy for **2**. Introduction of different auxiliary *N*-donors into the reaction systems involving carboxylic acids play an important role in the final structures. Isolation of **1** and **2** is new proof of the coordination versatility of

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dicarboxylates with semirigid ring skeleton, which might be generally used to react with different non-d^{10} transition metal ions, such as Cu^{II}, Co^{II}, and Mn^{II}, for constructing other coordination complexes with fascinating structures and properties.

Supplementary material

Crystallographic data (excluding structure factors) for the crystal structures reported in this article have been deposited with the Cambridge Crystallographic Data Center and allocated the deposition numbers: CCDC 807835 and 807836. The materials can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: t44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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