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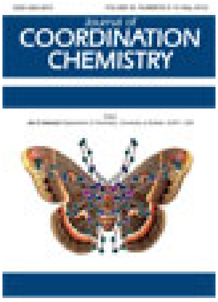

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Synthesis, crystal structures, and photoluminescence of two new zinc complexes based on 2,2′-thiodibenzoic acid

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Synthesis, crystal structures, and photoluminescence of two new zinc complexes based on 2,2′-thiodibenzoic acid

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$\{[Zn_2(tdba)_2(phen)_2(H_2O)_2]\cdot 2H_2O\cdot 2DMF\}_n$ (**1**) and $[Zn(tdba)(bpy)]_n$ (**2**) (H_2tdba = 2,2′-thiodibenzoic acid, phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine, DMF = dimethylformamide) were hydrothermally synthesized, and characterized by single-crystal X-ray diffraction analysis, FT-IR, and elemental analysis. The obtained complexes exhibit different structures. Compound **1** is 0-D with tdba connecting two Zn ions in a μ_1–η^1/μ_1–η^1 coordination forming a dinuclear molecule. Each molecule is further connected with neighbors *via* hydrogen-bonding and $\pi\cdots\pi$ interactions. Compound **2** displays a 1-D structure in which Zn^{2+} centers are connected *via* tdba anions into 1-D chains propagating along the *a*-axis; these chains are further packed *via* $\pi\cdots\pi$ interactions. In addition, photoluminescence for **1** and **2** has been investigated.

Keywords: 2,2′-Thiodibenzoic acid; Coordination polymer; Photoluminescence

1. Introduction

Metal–organic coordination polymers constructed with transition metals and organic ligands have attracted attention because of their intriguing architectures and applications as functional materials [1–8]. Among metal–organic coordination polymers, polycarboxylates, such as 1,3-benzenedicarboxylate, 1,3,5-benzenetricarboxylate, and 4,4′-biphenyldicarboxylate, have been employed extensively due to their variety of coordination modes and structural features [9–13]. Auxiliary N-containing ligands are usually introduced to carboxylate systems for the construction of polymeric frameworks, enhancing the stability of the ultimate frameworks and obtaining target products more easily [14, 15]. However, it remains a long-term challenge to rationally design and construct coordination polymers [16]. Hence, much work is required to extend the knowledge of relevant structural types and establish proper synthetic strategies leading to desirable architectures and useful properties.

In this article, 2,2′-thiodibenzoic acid (H_2tdba) was selected as the carboxylate ligand based on the following considerations: (1) H_2tdba possesses flexible –S– groups between the two phenyl rings and can adopt different conformations to meet the space

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requirement when coordinated to metal centers. (2) H_2tdba can also provide sites of hydrogen bonding and $\pi\cdots\pi$ stacking interactions to form complicated structures with higher dimensions.

Herein, we report the synthesis, crystal structure, and photoluminescence properties of $\{[Zn_2(tdba)_2(phen)_2(H_2O)_2]\cdot 2H_2O\cdot 2DMF\}_n$ (**1**) (phen = 1,10-phenanthroline, DMF = dimethylformamide) and $[Zn(tdba)(bpy)]_n$ (**2**) (bpy = 2,2′-bipyridine). The results indicate that the auxiliary ligands have a significant effect on the coordination of H_2tdba and the overall complexes.

2. Experimental

2.1. *General material and method*

All reagents and solvents were commercially available and used as received. C, H, and N analyses were performed on an Elementar Vario Micro Cube analyzer. Infrared (IR) spectra were recorded on a Thermo Nicolet IR200 FT-IR spectrometer as KBr pellets (4000–400 cm^{-1}). Fluorescent spectra were obtained on a Hitachi F-4600 spectrofluorometer.

2.2. *Preparation of compounds*

2.2.1. $\{[Zn_2(tdba)_2(phen)_2(H_2O)_2]\cdot 2H_2O\cdot 2DMF\}_n$ (1). To a mixture of H_2tdba (0.0304 g, 0.1 mmol), phen (0.0198 g, 0.1 mmol), and $Zn(NO_3)_2\cdot 6H_2O$ (0.030 g, 0.1 mmol) was added 3.0 mL DMF, 1.0 mL methanol, and 1.0 mL H_2O. The resulting mixture was thoroughly stirred in air at an ambient temperature for 30 min, then placed in a 16 mL Teflon-lined stainless steel vessel and heated to 130°C for 96 h to give colorless block crystals of **1**, which were collected by filtration. The colorless crystals obtained were washed with water and dried in air. Yield: 0.033 g (53% based on H_2tdba). Anal. Calcd for $C_{58}H_{54}N_6O_{14}S_2Zn_2$ (%): C, 55.51; H, 4.31; N, 6.69. Found (%): C, 55.43; H, 4.19; N, 6.75. IR (KBr pellet, cm^{-1}): 3420(s), 1667(s), 1588(s), 1572(s), 1548(s), 1516(s), 1378(s), 1227(m), 1103(m), 847(s), 728(s), 570(w).

2.2.2. $[Zn(tdba)(bpy)]_n$ (2). Compound **2** was prepared similar to that described for **1**, using bpy instead of phen as the secondary ligand. The colorless crystals obtained were washed with water and dried in air. Yield: 0.021 g (42% based on H_2tdba). Anal. Calcd for $C_{24}H_{16}N_2O_4SZn$ (%): C, 58.32; H, 3.24; N, 5.67. Found 9%): C, 58.27; H, 3.35; N, 5.59. IR (KBr pellet, cm^{-1}): 3416(s), 1663(s), 1573(s), 1437(m), 1378(s), 1151(w), 1101(w), 754(s), 651(m), 459(w).

2.3. *X-ray crystallography*

Single crystals of **1** and **2** suitable for the X-ray analysis were selected, mounted on glass fibers, and then the crystallographic data collections were carried out on a Bruker Smart ApexII CCD area-detector diffractometer with graphite-monochromated

Mo-Kα radiation ($\lambda = 0.71073$ Å) at 23°C using ω- and φ-scan techniques. The diffraction data were integrated using SAINT [17], which was also used for intensity corrections for Lorentz and polarization effects. Semiempirical absorption correction was applied using SADABS [18]. The crystal structures of **1** and **2** were solved by direct methods using the SIR97 program [19] and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on all F^2 data using SHELXL-97 [20]. The single suite WINGX was used as an integrated system for all crystallographic programs [21]. The hydrogen atoms of water in **1** were located from the Fourier map with the O–H distances being fixed at 0.85 Å. All other hydrogen atoms were added according to theoretical models, assigned isotropic displacement parameters and allowed to ride on their respective parent, $U_{iso}(H) = 1.2U_{eq}(C)$. Crystal data and a structure determination summary for **1** and **2** are listed in table 1; selected bond lengths and angles for **1** and **2** are listed in table 2.

3. Results and discussion

3.1. *Structure description*

3.1.1. $\{[Zn_2(tdba)_2(phen)_2(H_2O)_2]\cdot 2H_2O\cdot 2DMF\}_n$ (1). Single-crystal X-ray diffraction reveals that **1** crystallizes in the triclinic system, space group $P\bar{1}$. The asymmetric unit contains one Zn, one tdba, one phen, one coordinated water, one lattice water,

Table 1. Summary of crystallographic data for **1** and **2**.

Compounds	**1**	**2**
Empirical formula	$C_{58}H_{54}N_6O_{14}S_2Zn_2$	$C_{24}H_{16}N2O_4SZn$
Formula weight	1253.93	493.82
Temperature (K)	296(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	11.0784(6)	9.9918(5)
b	11.6186(6)	10.4472(6)
c	13.1828(7)	11.6000(6)
α	100.059(1)	71.971(1)
β	114.212(1)	66.543(1)
γ	108.385(1)	68.637(1)
Volume (Å^3), Z	1375(1), 1	1015(1), 2
Calculated density (g cm^{-3})	1.514	1.616
Absorption coefficient (mm^{-1})	1.022	1.349
$F(000)$	648	504
Reflections collected	7146	5289
Independent reflections	4771 [R(int) = 0.0135]	3536 [R(int) = 0.0135]
Parameters	370	289
Goodness-of-fit on F^2	1.028	1.037
Final $R^{a,b}$ indices [$I > 2\sigma(I)$]	$R_1 = 0.0309$, $wR_2 = 0.0806$	$R_1 = 0.0270$, $wR_2 = 0.0638$
R indices (all data)	$R_1 = 0.0355$, $wR_2 = 0.0829$	$R_1 = 0.0306$, $wR_2 = 0.0652$
Largest difference peak and hole (e Å^{-3})	0.412 and −0.385	0.347 and −0.132

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$.
[b] $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)]^{1/2}$.

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

1			
Zn(1)–N(1)	2.129(2)	Zn(1)–N(2)	2.160(2)
Zn(1)–O(2)	2.0370(18)	Zn(1)–O(1W)	2.0923(17)
Zn(1)–O(3)A	2.0340(17)		
O(3)A–Zn(1)–N(1)	107.13(8)	O(3)A–Zn(1)–N(2)	89.45(7)
O(3)A–Zn(1)–O(2)	102.62(8)	O(3)A–Zn(1)–O(1W)	93.64(7)
N(1)–Zn(1)–N(2)	77.39(8)	O(1W)–Zn(1)–N(1)	88.54(7)
O(2)–Zn(1)–N(2)	95.83(7)	O(2)–Zn(1)–O(1W)	96.92(7)
O(2)–Zn(1)–N(1)	149.34(7)	O(1W)–Zn(1)–N(2)	165.88(7)
2			
Zn(1)–O(1)	2.0003(16)	Zn(1)–N(1)	2.1647(19)
Zn(1)–N(2)	2.1232(19)	Zn(1)–O(3)A	1.9946(16)
Zn(1)–O(2)B	2.0874(18)		
O(1)–Zn(1)–N(1)	91.03(6)	O(1)–Zn(1)–N(2)	104.90(8)
O(1)–Zn(1)–O(3)A	100.50(7)	O(1)–Zn(1)–O(2)B	107.05(6)
N(1)–Zn(1)–N(2)	76.30(7)	N(1)–Zn(1)–O(3)A	94.13(7)
O(2)B–Zn(1)–N(2)	91.04(7)	O(2)B–Zn(1)–O(3)A	90.42(7)
N(1)–Zn(1)–O(2)B	160.23(7)	N(2)–Zn(1)–O(3)A	152.91(7)

[a] Symmetry codes for **1**: A: $-x+2,-y+2,-z+1$; for **2**: A: $-x+1,-y,-z+1$; B: $-x+2,-y,-z+1$.

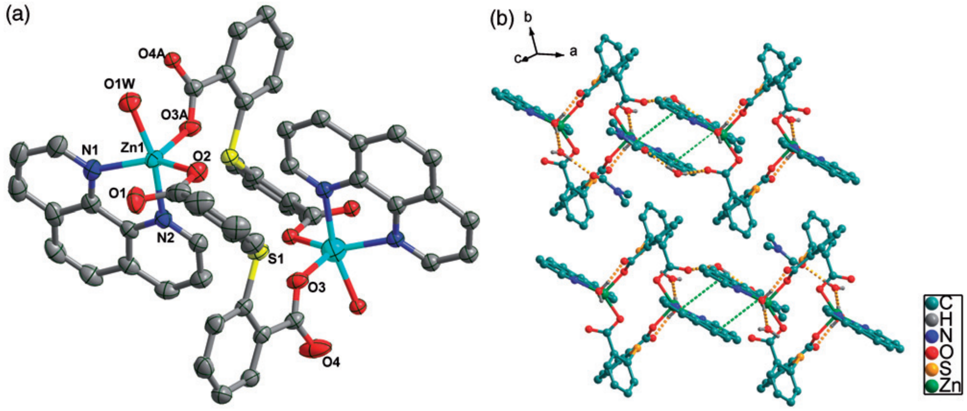
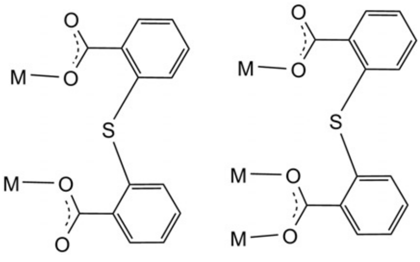


Figure 1. (a) Anisotropic displacement ellipsoid plot of **1** at the 50% probability level (symmetry code: (A) $-x+2,-y+2,-z+1$). (b) The packing diagram of **1** showing hydrogen bonding interactions (yellow dashed line involving water molecule) and $\pi\cdots\pi$ interactions (green dashed line between parallel phen rings). All hydrogen atoms except for the water molecules have been omitted for clarity.

and one lattice DMF. There is only one crystallographically unique Zn (figure 1a); Zn1 adopts a distorted trigonal bipyramid, coordinated by three oxygen atoms, two from tdba anions and one from water, and by two nitrogen atoms from one phen, though a sixth weak interaction between Zn1 and O1 (2.550 Å) is observed. Zn–O bond lengths range from 2.037(2) to 2.092(2) Å and Zn–N bond lengths are 2.129(2) Å and 2.160(2) Å. The tdba connects two Zn ions in a μ_1–η^1/μ_1–η^1 coordination (scheme 1a) to form a bimetallic molecule. The Zn$\cdots$Zn separation is 6.448(2) Å and the dihedral angle between two phenyl rings of tdba is 82.2°. The centroid distance between parallel phen rings of neighboring molecules is 4.103 Å, which means there are weak $\pi\cdots\pi$ interactions [22]. Therefore, the dinuclear molecules pack *via* weak $\pi\cdots\pi$



Scheme 1. Coordination modes of tdba in **1** and **2**.

Table 3. Hydrogen bonds for **1** (Å, °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1W)–H(11W)···O(4)A	0.85	1.80	2.624(3)	161.4
O(1W)–H(12W)···O(2W)B	0.86	1.80	2.649(3)	174.2
O(2W)–H(21W)···O(1)	0.82	2.02	2.832(3)	169.0
O(2W)–H(22W)···O(5)C	0.84	1.89	2.713(3)	167.5

Symmetry codes: A: $-x+2, -y+2, -z+1$; B: $-x+2, -y+2, -z+2$; C: $x, y+1, z+1$.

interactions and O–H···O hydrogen bonds involving tdba, water, and DMF (figure 1b, table 3).

3.1.2. [Zn(tdba)(bpy)]$_n$ (2). Compound **2** crystallizes in the triclinic system, space group $P\overline{1}$, and the asymmetric unit contains one Zn, one tdba, and one bpy. Zn1 is coordinated by two nitrogen atoms from bpy and three oxygen atoms from different tdba anions to form a square pyramid (figure 2a). The basal plane is composed of N1, N2, O2B, and O3A with mean deviation from the least-square plane of 0.073 Å; the apical coordination site is occupied by O1. Zn ions deviate about 0.398 Å from the basal plane. Zn–O bond lengths are 1.9946(16) to 2.0874(18) Å and the Zn–N bond lengths are 2.1232(19) and 2.1647(19) Å; these are similar to those observed in **1**.

The tdba shows μ_1–η^1/μ_2–$\eta^1:\eta^1$ coordination (scheme 1b), different from that observed in **1**. Zn1 and its symmetry-related counterpart are bridged by two tdba ligands to generate a dinuclear Zn unit. These dinuclear units are interlinked *via* tdba to form an infinite chain propagating along the *a*-axis and bpy are attached on both sides of the chain (figure 2b). Neighboring chains are further connected into the resulting 3-D supramolecular architecture *via* weak $\pi\cdots\pi$ interactions (figure 2c).

3.2. *Photoluminescence properties*

Photoluminescence of carboxylate containing systems with a d^{10} metal have been reported [23]. The solid-state luminescent emission spectra of **1**, **2**, and H$_2$tdba were studied at room temperature. As shown in figure 3, emission of H$_2$tdba shows a broad peak at 435 nm upon excitation at 350 nm, which is ascribed to $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electronic transitions. Compared with luminescence of ligand, emissions of **1**

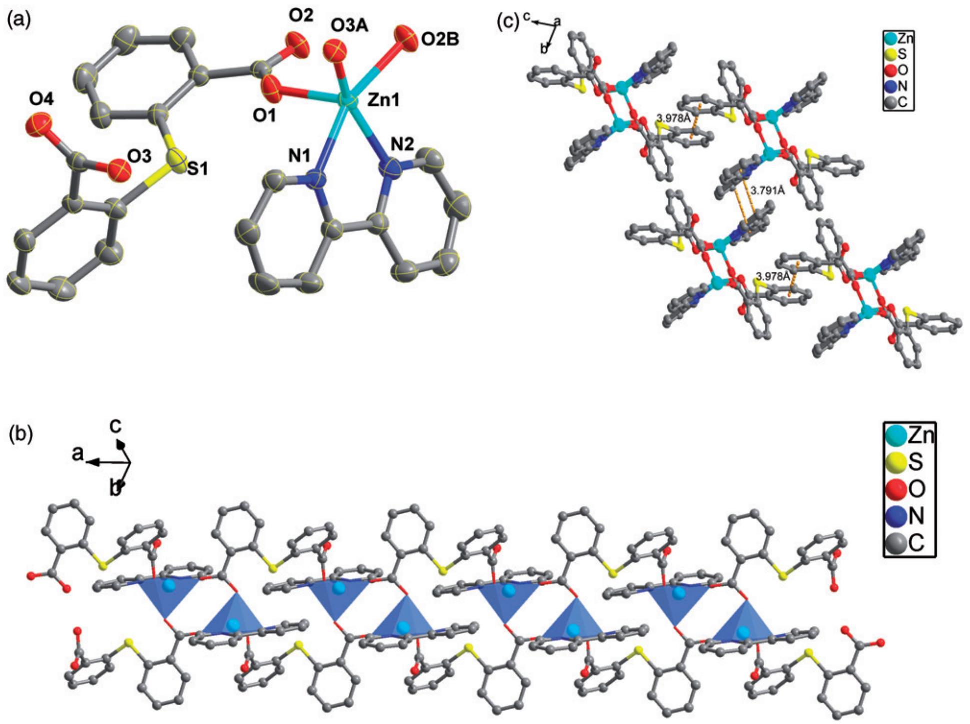


Figure 2. (a) The coordination environments of Zn^{2+} in **2** with 50% ellipsoid of probability (symmetry codes: (A) $-x+1,-y,-z+1$; (B) $-x+2,-y,-z+1$). (b) The 1-D chain structure of **2**. (c) Formation of supramolecular network by $\pi \cdots \pi$ interactions in **2**. All hydrogen atoms have been omitted for clarity.

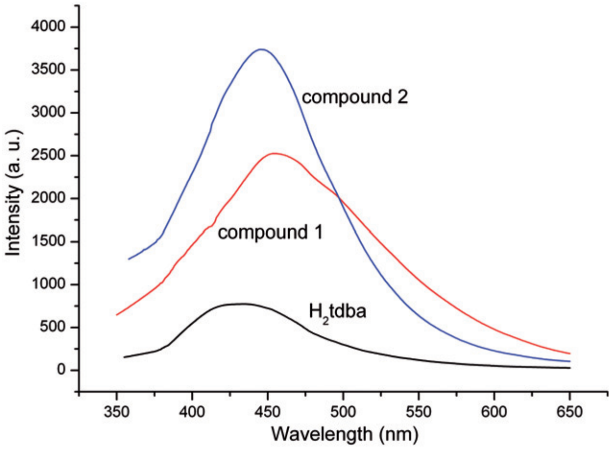


Figure 3. Photoluminescence of **1**, **2**, and H_2tdba in the solid state.

($\lambda_{em} = 455$ nm, $\lambda_{ex} = 380$ nm) and **2** ($\lambda_{em} = 445$ nm, $\lambda_{ex} = 380$ nm) are neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer since Zn^{2+} is difficult to oxidize or reduce due to its d^{10} configuration. Therefore, they can be assigned to intraligand ($\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$) fluorescent emission due to their resemblance with those of H_2tdba [24–27]. Emission spectra for **1** and **2** exhibit red-shifts with respect to free H_2tdba, ascribed to deprotonation of H_2tdba, and coordination of the ligands to Zn^{2+}. Difference of the emission peaks intensity for **1** and **2** is mainly derived from the differences of coordination of tdba, the coordination environments of the metal ions, and the rigidity of solid-state crystal packing.

4. Conclusions

We have synthesized two new coordination polymers with Zn^{2+} under hydrothermal conditions using flexible carboxylate contaning ligands and phen or bpy. Compound **1** shows a 0-D structure with tdba connecting two Zn^{2+} centers forming a dinuclear unit. Compound **2** shows a 1-D structure propagating along the *a*-axis. The different dimensionality of the two compounds mainly came from different N-chelating ligands because other synthetic parameters were intentionally held constant. Photoluminescence of **1** and **2** were also discussed.

Supplementary material

Crystallographic information of the two compounds has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC$\{[Zn_2(tdba)_2(phen)_2(H_2O)_2]\cdot 2H_2O\cdot 2DMF\}_n$ (853018) and CCDC $[Zn(tdba)(bpy)]_n$ (853019). Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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