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Hydrothermal Synthesis, Crystal Structure, and Properties of Two Novel Binuclear Complexes Based on Zaltoprofen and 2,2'-Bipyridine Ligands[1]

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Abstract—Two novel binuclear metal-organic coordination complexes [M_2(Zaltoprofen)$_2$(Bipy)$_2$] [M = Cd (**I**), Zn (**II**); Zaltoprofen = 5-(1-carboxyethyl)-2-(phenylthio)phenylacetic acid, Bipy = 2,2'-bipyridine) have been synthesized under hydrothermal conditions and characterized by single crystal X-ray diffraction, elemental analysis, IR and electronic spectroscopy, powder X-ray diffraction, and fluorescent properties. Complexes **I**, **II** crystallize isomorphously in the monoclinic space group $P2_1/c$. Structural analysis shows that the M(II) atom of **I** and **II** is coordinated with four oxygen atoms from the carboxyl group of the Zaltoprofen together with two nitrogen atoms from the Bipy. The 3D structures of the complexes are stabilized by π–π stacking interactions.

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INTRODUCTION

During the past decade, the design of new metal-organic supramolecular solids has attracted ever-increasing focus in the elds of coordination chemistry and crystal engineering, for the sake of developing desired crystalline materials with potential functionality [1–3]. Generally, extended higher-dimensional supramolecular architectures can be obtained by the assembly of lower-dimensional structures via coordinative force and other weak non-covalent interactions. Aromatic ring stacking is one important type of intramolecular non-covalent interactions, which play vital roles in highly efficient and specific biological reactions and are essential for molecular recognition and self-organization [4, 5].

Zaltoprofen is one of non-steroidal anti-inflammatory drugs that exhibit favorable anti-inflammatory, anal-genesic and antipyretic properties. But to our knowledge, using Zaltoprofen to construct metal-organic frameworks has not been reported. As a multifunctional ligand, Zaltoprofen has attracted our attention on the basis of the following considerations. The carboxyl is always deprotonated to compensate the charge of the metal ions, and it may allow for diversity in the coordination mode. The ligand has larger conjugated π-systems, therefore π–π stacking interactions and/or C–H···π interactions may play important roles in the formation of higher-dimensional supramolecular frameworks. Chelating bipyridine-like ligands, such as 1,10-phenanthroline and 2,2'-bipyridine (Bipy) may provide supramolecular recognition sites for π–π stacking interactions to form interesting supramolecular structures [6, 7]. The chemistry of metal-organic molecular architectures of Bipy-like and carboxylate ligands has been reviewed [8].

As a continuation of our research, we report synthesis, crystal structure, elemental analyses, IR spectrum, powder X-ray diffraction (XRD) and fluorescent properties of two novel supramolecular complexes [M_2(Zaltoprofen)$_2$(Bipy)$_2$], which is formed by π–π stacking interactions. Electronic spectra (UV-vis) and photoluminescence properties of complexes in the solid state have also been investigated below in detail.

EXPERIMENTAL

Materials and physical measurements. All chemicals were commercial materials of analytical grade and used without purification. Elemental analysis for C, H, and N was carried out on a PerkinElmer 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} region, using KBr pellets. XRD patterns were obtained using a pinhole camera (Anton Paar) operating with a point focused Ni-filtered CuK_α radiation in the 2θ range from 5° to 50° with a scan rate of 0.08° per second. The optical properties were analyzed by the UV-vis diffuse reflectance spectroscopy (DRS) using a UV-vis spectrophotometer (Cary-500, Varian Co.), in which $BaSO_4$ was used as the internal standard.

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Synthesis of $[Cd_2(Zaltoprofen)_2(Bipy)_2]$ (I). $3CdSO_4 \cdot 8H_2O$ (0.2565 g, 0.33 mmol), Zaltoprofen (0.1582 g, 0.5 mmol), NaOH (0.04 g, 1 mmol), Bipy (0.0783 g, 0.5 mmol) were added into 15 mL mixed solvent of DMF–EtOH–H_2O (volume ratio 1 : 1 : 1) and then stirred. The resulting mixture was sealed in a 25 mL Teon-lined stainless reactor, kept under autogenous pressure at 130°C for 72 h and then slowly cooled to room temperature at a rate of 5°C per hour. The colorless block crystals suitable for X-ray diffraction were isolated directly. The yeld was 78% based on Cd.

For $C_{54}H_{44}N_4O_8S_2Cd_2$

anal. calcd., %:	C, 55.63;	H, 3.80;	N, 4.81.
Found: %:	C, 55.67;	H, 3.76;	N, 4.83.

IR data (KBr; ν, cm^{-1}): 3070 w, 2963 w, 1564 v.s, 1475 m, 1439 m, 1385 s, 1318 w, 1264 w, 1169 w, 1067 m, 948 w, 880 w, 770 m, 736 m, 690 w, 648 w.

Synthesis of $[Zn_2(Zaltoprofen)_2(Bipy)_2]$ (II). The reagents of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2975 g, 1 mmol), Zaltoprofen (0.1582 g, 0.5 mmol), Bipy (0.0783 g, 0.5 mmol), five drop of pyridine and 15 mL mixed solvent of DMF–H_2O (volume ratio 1 : 2) were sealed in a 25 mL Teon-lined stainless reactor and the mixture was stirred for 0.5 h, then kept under autogenous pressure at 145°C for 72 h. The resulting reaction mixture was slowly cooled to room temperature at a rate of 5°C per hour. The colorless block crystals suitable for X-ray diffraction were isolated directly. The yield was 63% based on Zn.

For $C_{54}H_{44}N_4O_8S_2Zn_2$

anal. calcd., %:	C, 60.51;	H, 4.14;	N, 5.23.
Found: %:	C, 60.38;	H, 4.05;	N, 5.35.

IR data (KBr; ν, cm^{-1}): 3070 w, 1598 v.s, 1520 w, 1490 w, 1476 w, 1383 s, 1319 w, 1269 w, 1251 w, 1179 w, 1066 m, 1025 m, 880 w, 832 w, 801 m, 774 m, 736 m, 690 w.

X-ray structure determination. Single crystal of the complex was mounted on glass fibers and measured on a Bruker SMART CCD area detector at 298 K using graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the SADABS program [9]. The complexes were solved by the direct method and PATT method, respectively. And refined by full-matrix least squares on F^2 using the SHELXTL program [10]. All non-hydrogen atoms were refined anisotronically. A summary of the crystallographic data and structure refinement is shown in Table 1, selected bond lengths and angles of the complexes are listed in Table 2.

Further information about the Crystallographic analysis is deposited in the Cambridge Crystallographic Data Centre (nos. 882954 (**I**) and 902638 (**II**); www.ccdc.cam.ac.uk/data_request/cif or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Single-crystal X-ray diffraction on **I**, **II** reveals that they are extremely similar in structure with the formula $[M_2(Zaltoprofen)_2(Bipy)_2]$ (M = Cd (**I**), Zn (**II**)). The crystal lattice of the complexes belong to the monoclinic system with a space group $P2_1/c$. The coordination environments of M^{2+} ion in the two binuclear complexes are shown in Fig. 1. The coordination environment around the M(II) center is best portrayed as a distorted $[MN_2O_4]$ octahedral geometry, ligated by four oxygen atoms from one Zaltoprofen ligand, two nitrogen atoms from one chelate Bipy. The 1D chains are linked by π–π stacking interaction (Fig. 2). Two adjacent Bipy molecules are connected by π–π stacking between pyridine rings with a distance of 3.737 Å in complex **I** and 3.709 Å in complex **II**. These weak interactions (C–H···O nonclassical hydrogen bonds) play a vital role in determining the crystal packing and construction of the extended 3D supramolecular network.

Dried samples of complexes **I** and **II** were characterized by IR spectroscopy. The IR spectrum of free ligand shows strong bands of the carboxylate groups at 1697 cm^{-1}, which can be assigned as the ν(C=O) antisymmetric stretching vibrations. In complex **I**, the corresponding bands shifted by 133 to 1564 cm^{-1}. In **II**, the corresponding bands shifted by 99 to 1598 cm^{-1}. The shift to the lower position suggests that the relevant oxygen of the ligand coordinates to metal. The bands attributed to the ν(C=C) and ν(C=N) stretching vibrations of the N,N'-donors in the region 1600–1400 cm^{-1} are sensitive to chelation and shift to higher frequencies upon coordination [11]. Other characteristic vibrations of the N,N'-donors are the C–H out-of-plane deformations which appear at ~800 cm^{-1}; these bands shift to lower frequencies upon coordination [12].

Simulated and experimental PXRD patterns are demonstrated on complex **I**. 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. The differencein reflection intensity between the simulated and experimental patterns is due to acertain degree of preferred orientation of the powder samples during data collection.

The spectroscopic behavior of Cd(II) complex **I** containing Zaltoprofen as a ligand is discussed in various spectroscopic transitions including ligand-centered and metal-ligand charge transfer. The bands in the UV region were attributed to the intraligand transition mainly centered in Zaltoprofen ligands. The intraligand bands are sufficiently intense to mask a MLCT band involving $d\pi$Cd(II)–π*(Zaltoprofen)

Table 1. Crystallographic data and refinement details for structures **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	1165.89	1071.79
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions:		
a, Å	13.602(3)	13.2873(14)
b, Å	11.658(3)	11.9309(19)
c, Å	15.667(3)	15.267(2)
β, deg	92.552(1)	93.0760(10)
Volume, Å^3	2481.9(10)	2416.8(6)
Z	2	2
$\rho_{calcd,}$ mg m^{-3}	1.560	1.473
Absorption coefficient, mm^{-1}	1.000	1.140
F(000)	1176	1104
Crystal size	0.32 × 0.31 × 0.29	0.16 × 0.15 × 0.13
θ Range for data collection, deg	1.50–25.00	2.17–25.00
Reflections collected	12653	12869
Unique reflections (R_{int})	4323 (0.0733)	4248 (0.0575)
Completeness to θ = 25.00, %	98.9	99.8
Absorption correction	Semiempirical	Semiempirical
Max and min transmission	0.748 and 0.733	0.862 and 0.833
Data/restraints/parameters	4323/0/317	4248/19/236
Goodness-of-fit on F^2	1.011	0.956
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0432$, $wR_2 = 0.0911$	$R_1 = 0.0485$, $wR_2 = 0.1132$
R indices (all data)	$R_1 = 0.0988$, $wR_2 = 0.1203$	$R_1 = 0.1010$, $wR_2 = 0.1363$
Largest diff. peak and hole, e Å^{-3}	0.958 and –0.458	0.673 and –0.444

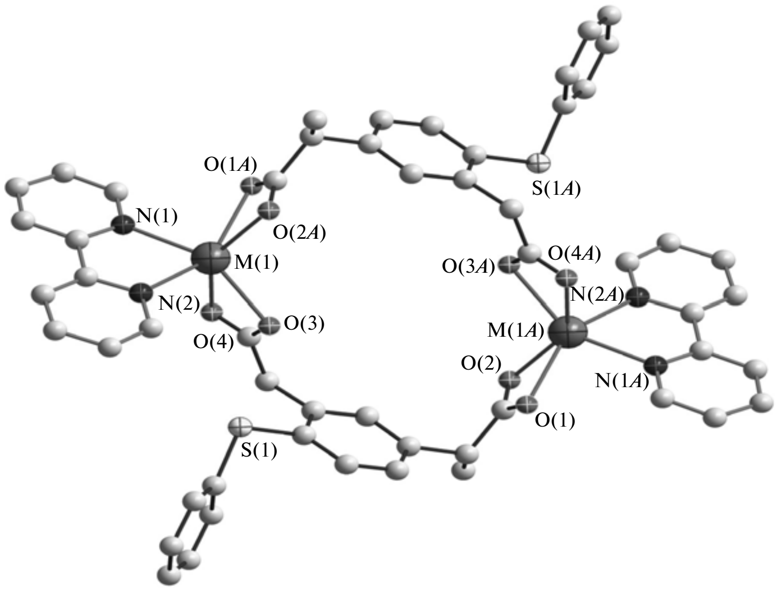

Fig. 1. The coordination environment of M^{2+} ion of the complexes.

Table 2. The selected bond lengths (Å) and angles (deg) for structure **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
I			
Cd(1)–O(2)	2.288(4)	Cd(1)–O(1)	2.417(4)
Cd(1)–O(3)$^{\#1}$	2.350(3)	Cd(1)–O(4)$^{\#1}$	2.327(4)
Cd(1)–N(1)	2.335(4)	Cd(1)–N(2)	2.313(4)
II			
Zn(1)–O(2)	2.008(6)	Zn(1)–O(3)$^{\#1}$	2.040(6)
Zn(1)–N(2)	2.067(6)	Zn(1)–N(1)	2.090(7)
Zn(1)–O(1)	2.372(0)	Zn(1)–O(4)$^{\#1}$	2.417(9)
Angle	ω, deg	Angle	ω, deg
I			
O(2)Cd(1)N(2)	111.85(15)	O(3)$^{\#1}$Cd(1)O(1)	116.82(14)
O(2)Cd(1)O(4)$^{\#1}$	142.23(15)	N(1)Cd(1)O(1)	85.56(16)
N(2)Cd(1)O(4)$^{\#1}$	98.97(14)	O(4)$^{\#1}$Cd(1)O(1)	107.46(14)
O(2)Cd(1)N(1)	113.92(15)	N(2)Cd(1)O(1)	146.48(14)
N(2)Cd(1)N(1)	71.31(16)	O(2)Cd(1)O(1)	55.60(15)
O(4)$^{\#1}$Cd(1)N(1)	95.92(15)	N(1)Cd(1)O(3)$^{\#1}$	147.27(15)
O(2)Cd(1)O(3)$^{\#1}$	98.71(15)	O(4)$^{\#1}$Cd(1)O(3)$^{\#1}$	56.01(13)
N(2)Cd(1)O(3)$^{\#1}$	94.89(14)		
II			
O(2)Zn(1)O(3)$^{\#1}$	139.6(5)	O(2)Zn(1)N(2)	104.0(0)
O(3)$^{\#1}$Zn(1)N(2)	105.2(9)	O(2)Zn(1)N(1)	98.2(7)
O(3)$^{\#1}$Zn(1)N(1)	114.3(7)	N(2)Zn(1)N(1)	78.2(9)
O(2)Zn(1)O(1)	58.6(0)	O(3)$^{\#1}$Zn(1)O(1)	92.3(1)
N(2)Zn(1)O(1)	93.6(6)	N(1)Zn(1)O(1)	153.2(6)
O(2)Zn(1)O(4)$^{\#1}$	104.3(5)	O(3)$^{\#1}$Zn(1)O(4)$^{\#1}$	56.9(0)
N(2)Zn(1)O(4)$^{\#1}$	149.7(1)	N(1)Zn(1)O(4)$^{\#1}$	87.2(9)
O(1)Zn(1)O(4)$^{\#1}$	110.1(4)		

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, -y, -z + 1$ (**I**); $^{\#1}$ $-x + 1, -y + 1, -z + 1$ (**II**).

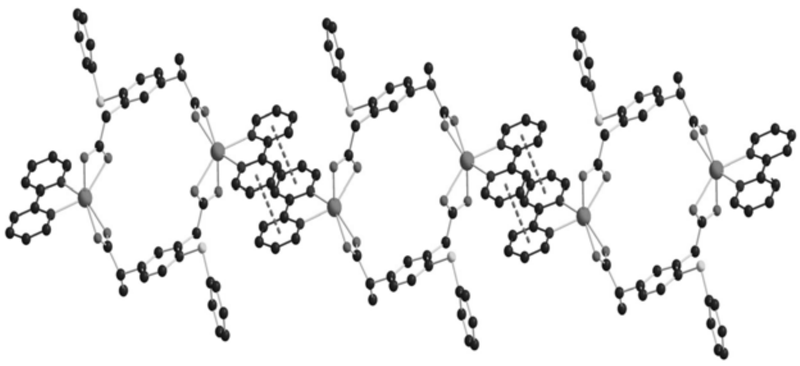

Fig. 2. A perspective view of the π–π stacking interaction. All the hydrogen atoms are omitted for clarity.

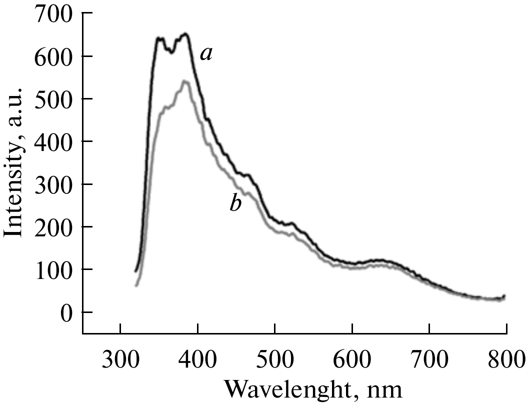

Fig. 3. Solid state emission spectra of the complexes **I** (*a*) and **II** (*b*) recorded at room temperature.

which are observed in the 313 nm region as assigned in a UV-vis spectrum of [Cd_2(Zaltoprofen)$_2$(Bipy)$_2$].

Inorganic-organic hybrid coordination polymers, especially those with d^{10} metal centers, have been investigated for photoluminescent properties. Previous studies have shown that coordination polymers containing cadmium(II) and zinc(II) exhibit photoluminescent properties [13–18]. The fluorescence properties of the M(II) complexes were studied in the solid state at room temperature (298 K) (Fig. 3). In the solid state, strong photoluminescence emission bands at 386 nm ($\lambda_{ex} = 272$ nm), 385 nm ($\lambda_{ex} = 263$ nm) are observed for complex **I**, **II**, respectively. For excitation wavelength between 320 and 480 nm, there is no obvious emission observed for free Zaltoprofen under the same experimental conditions, while free Bipy ligands present weak photoluminescence emission. Therefore, the fluorescent emissions in the coordination polymers may be proposed to originate from the coordination of Zaltoprofen^{2-} to the M(II) atoms. It is proved by the similar fluorescent emission bands of **I** and **II**.

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