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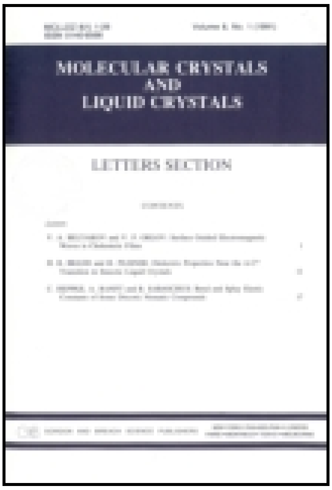

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Xia Yin[a], Jin-Niu Tang[b], Gang-Hong Pan[b], Wei-Man Tian[a], Wen-Jia Xu[b] & Zhong-Jing Huang[b]
[a] The NO. 2 Middle School of Dongkou Hunan, Dongkou, P.R. China
[b] College of Chemistry and Chemical Engineering, Guangxi University for Nationalities, Nanning, P.R. China
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A Novel Supramolecular Complex Based on Zaltoprofen Ligand: Synthesis, Crystal Structure, and Properties

XIA YIN,[1],* JIN-NIU TANG,[2] GANG-HONG PAN,[2] WEI-MAN TIAN,[1] WEN-JIA XU,[2] AND ZHONG-JING HUANG[2]

[1]The NO. 2 Middle School of Dongkou Hunan, Dongkou, P.R. China
[2]College of Chemistry and Chemical Engineering, Guangxi University for Nationalities, Nanning, P.R. China

A novel metal-organic supramolecular complex [Zn_2 (Zaltoprofen)$_2$(phen)$_2$] (where Zaltoprofen = 5-(1-carboxyethyl)-2-(phenylthio)phenylacetic acid, phen = 1,10-phenanthroline) has been synthesized under hydrothermal condition and characterized by single crystal X-ray diffraction, elemental analysis, spectral method (IR), powder X-ray diffraction (XRD), electronic Spectra (UV-vis), and fluorescent properties. The compound crystallizes in the monoclinic P2(1)/c space group. [Zn_2(Zaltoprofen)$_2$(phen)$_2$] features 0-D structural, the π–π stacking interactions and C—H···O hydrogen-bonds play a vital role in determining the crystal packing and construction of the extended 3-D supramolecular network.

Keywords Crystal structure; photoluminescence properties; zaltoprofen; π–π stacking

Introduction

In recent years, the low-dimensional coordination polymers have received much attention owing to their intriguing structural features and potential as functional materials different from those of 3-D coordination polymers [1–4]. Against this background, spectacular examples of supramolecular architectures organized by means of covalent bonds, hydrogen bonds, π–π interactions, or their combination in different ways have been reported [5–14]. π–π interactions and hydrogen-bonding play important roles in the fabrication of the supramolecular architectures.

In this respect, the influence of ligand spacers of flexible bridging ligands on framework formation of their coordination polymers has widely been documented [15–18]. Zaltoprofen is one of nonsteroidal anti-inflammatory drugs that exhibit favorable anti-inflammatory, anal-gesic, and antipyretic properties. Most anti-inflammatory drugs are carboxylic acids in which carboxylate is available for metal–ligand interaction. Much work has focused on interactions of transition metal ions with nonsteroidal anti-inflammatory drugs such as ibuprofen, fenoprofen [19–21]. But to our knowledge, using Zaltoprofen to construct metal–organic frameworks has not been reported. As a multi-functional ligand, Zaltoprofen has attracted our attention on the basis of the following considerations. The

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*Address correspondence to X. Yin, The NO. 2 Middle School of Dongkou Hunan, Dongkou, P.R. China. E-mail: 342662554@qq.com multi-carboxylates are capable of functioning as hydrogen bond donors and/or acceptors. The carboxyl is always deprotonated to compensate the charge of the metal ions, and it may allow for diversity in the coordination mode. The flexible Zaltoprofen building blocks considered as V-shaped dicarboxylate may generate helical chains.

As a continuation of our research, we report synthesis, crystal structure, elemental analyses, IR spectrum, powder XRD, and electronic Spectra (UV-vis) properties of a novel complex $[Zn_2(Zaltoprofen)_2(phen)_2]$, which is constructed and stabilized the framework via π–π stacking interactions and hydrogen bonding. Photoluminescence properties of complex in the solid state have also been investigated below in detail.

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. Powder X-ray diffraction 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. 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. Fluorescence spectra were recorded with F-2500 FL Spectrophotometer analyzer.

Synthesis of $[Zn_2(Zaltoprofen)_2(phen)_2]$

The reagents of $ZnCl_2$ (0.1363 g, 1 mmol), phen (0.0991 g, 0.5 mmol), Zaltoprofen (0.1582 g, 0.5 mmol), two 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 hr, then kept under autogenous pressure at 135°C for 72 hr. 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, Yield: 57%, based on Zn. Anal. Calcd. for $C_{58}H_{44}Zn_2N_4O_8S_2$ (%): C, 62.20; H, 3.96; N, 5.00. Found: C, 62.34; H, 3.83; N, 5.21. IR data (KBr pellets, cm-1): 3053 (w), 1613 (vs), 1514 (vs), 1474 (m), 1426 (m), 1380 (s), 1256 (m), 1222 (w), 1105 (w), 1065 (m), 1022 (w), 855 (s), 728 (s), 691 (m), and 648 (m).

Crystal 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 Mo Ka radiation (λ = 0.71073 Å). Empirical absorption corrections were applied using the SADABS program [22]. The complexes were solved by Patterson method and direct method, respectively. And refined by full-matrix least squares on F^2 using the SHELXTL program [23]. All nonhydrogen 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 complex are listed in Table 2.

Table 1. Experimental data for complex

Empirical formula	$C_{58}H_{44}N_4O_8S_2Zn_2$
Formula weight	1119.83
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *P2(1)/c*
a (Å)	13.528(2)
b (Å)	11.739(3)
c (Å)	16.081(2)
β (°)	95.0970(10)
Volume (Å^3)	2543.5(8)
Z	2
$D_{calc.}$ (Mg·m^{-3})	1.462
Absorption coefficient (mm^{-1})	1.086
F(000)	1152
Crystal size	0.26 × 0.24 × 0.23
θ range for data collection (°)	1.51 to 24.99
Reflections collected	13405
Unique reflections	4448 [*R*(int) = 0.0213]
Completeness to $\theta = 25.00$	99.7%
Absorption correction	Semi-empirical
Max. and min. transmission	0.779 and 0.762
Data/restraints/parameters	4448/6/335
Goodness-of-fit on F^2	1.071
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0392, wR_2 = 0.1012$
R indices (all data)	$R_1 = 0.0511, wR_2 = 0.1088$
Largest diff. peak and hole (e.Å^{-3})	0.666 and −0.330

Results and Discussion

Description of the Structure

The single-crystal X-ray diffraction analysis reveals that polymer crystallizes in the monoclinic system, space group $P2_1/c$. The asymmetric unit contains one Zn(II) ion, one phen and one completely deprotonated Zaltoprofen^{2-}. As showed in Fig. 1, the coordination

Table 2. The selected bond lengths (Å) and angles (°)

Zn(1)-O(3)#1	1.941(2)	Zn(1)-O(1)	1.983(2)
Zn(1)-N(1)	2.087(2)	Zn(1)-N(2)	2.095(2)
O(3)#1-Zn(1)-O(1)	128.50(9)	N(1)-Zn(1)-N(2)	80.09(10)
O(3)#1-Zn(1)-N(1)	106.60(9)	O(1)-Zn(1)-N(2)	109.67(9)
O(1)-Zn(1)-N(1)	109.24(10)	O(3)#1-Zn(1)-N(2)	111.94(9)

Symmetry transformations used to generate equivalent atoms: for Complex**:** #1 $-x+1, -y+1, -z+1$.

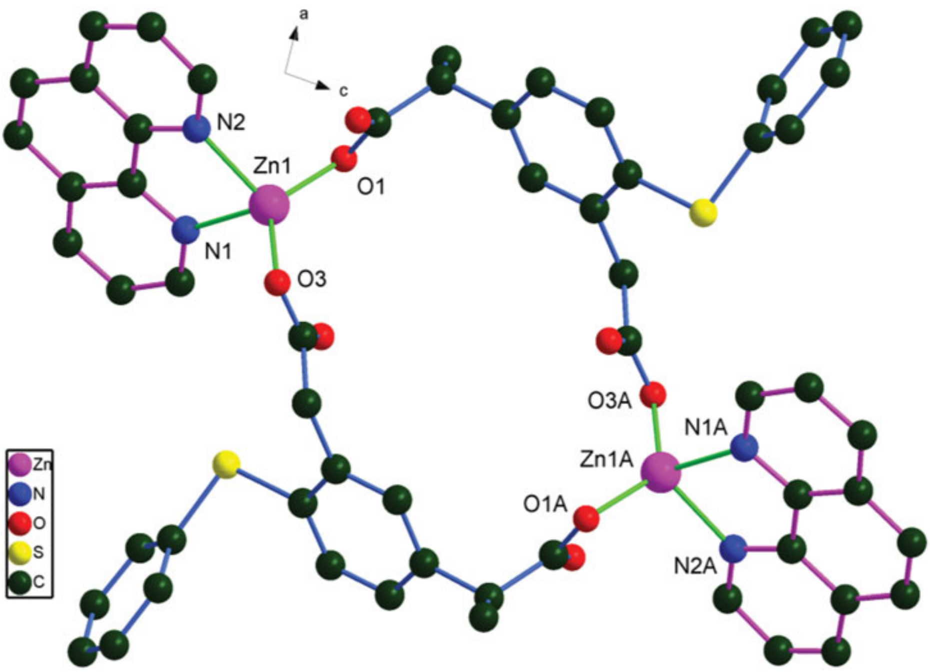

Figure 1. The coordination environment of Zn(II) ion of complex. All the hydrogen atoms are omitted for clarity.

environment around the Zn(II) center is best portrayed as a distorted [ZnO2N2] tetrahedron geometry, ligated by two oxygen donors (O1, O3) belonging to two Zaltoprofen^{2-} ligands and two nitrogen donors (N1, N2) from one phen molecule. The Zn—O bond lengths vary from 1.941(2) to 1.983(2) Å, while the Zn-N bond lengths are from 2.087(2) to 2.095(2) Å. In complex, two carboxylate groups of the V-shape ligand Zaltoprofen^{2-} adopt μ^1-η^1:η^0 coordination mode to connect two Zn(II) ions. Two adjacent phen molecules are connected by π–π stacking interactions with a distance of 3.914 Å. The π–π stacking interactions and C—H···O hydrogen bonding (Fig. 2) play important roles in determining the crystal packing and construction of the extended 3-D supramolecular network.

IR Spectra

Dried samples of complex 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 addition, in the complex the corresponding bands of the coordinated carboxyl group at 1613 cm^{-1} shifted by 84 cm^{-1}. The shift to the lower position suggests that the relevant oxygen of the ligand coordinates to metal.

XRD Patterns

Simulated and experimental powder X-ray diffraction (PXRD) patterns of complex 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

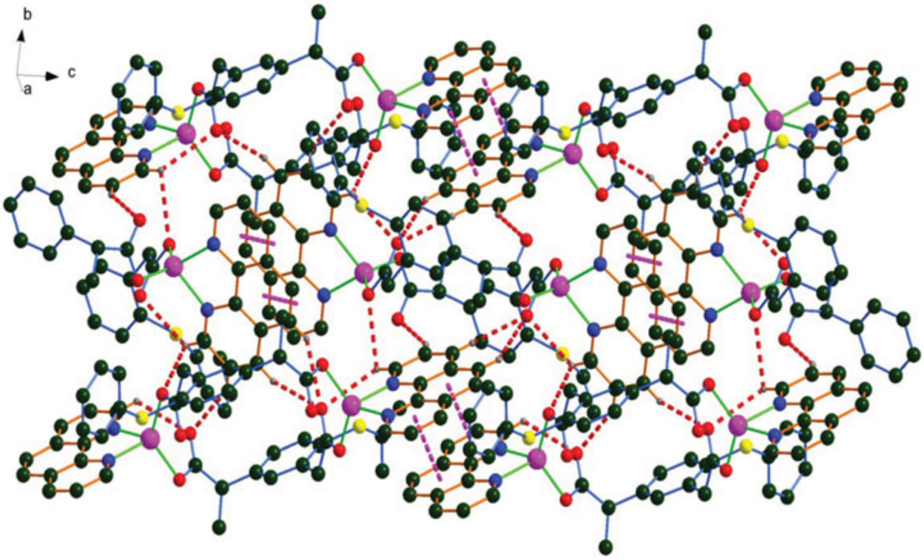

Figure 2. A perspective view of the π–π stacking interaction, C–H···O hydrogen bonds for complex. The hydrogen atoms are omitted for clarity.

phase purity of the as-prepared products. The difference in reflection intensity between the simulated and experimental patterns is due to a certain degree of preferred orientation of the powder samples during data collection.

Electronic Spectra

Figure 3 shows the Uv-vis spectra of the complex. The spectroscopic behavior of Zn(II) complex containing Zaltoprofen as a ligand is discussed in various spectroscopic transitions including ligand-centered and metal-ligand charge transfer. The band in the UV region was attributed to the intraligand transition mainly centered in Zaltoprofen ligand. The intraligand band is sufficiently intense to mask a MLCT band involving dπZn(II)–π^*(Zaltoprofen) which is observed in the 269 nm region as assigned in a UV-vis spectrum of [Zn_2(Zaltoprofen)$_2$(phen)$_2$].

Fluorescence Properties

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 [24–29]. The solid state photoluminescence properties of Zn(II) polymer was investigated at room temperature (Fig. 4). In the solid state, strong photoluminescence emission bands at 385 nm (λex = 276 nm) is observed for complex. For excitation wavelength between 280 and 480 nm, there is no obvious emission observed for free Zaltoprofen under the same experimental conditions, while free phen ligand 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 Zinc(II) ion.

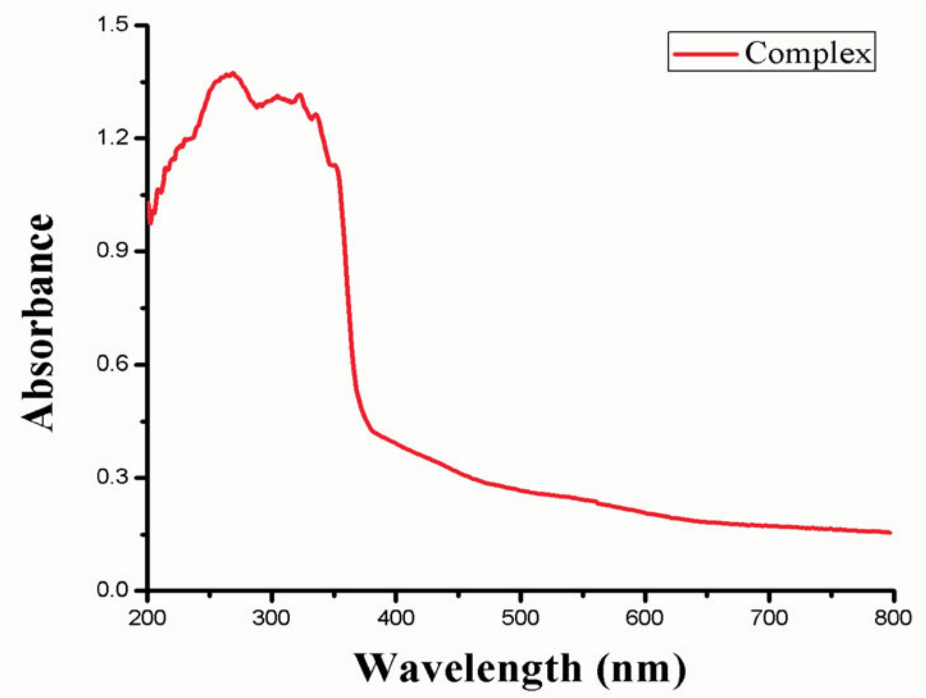

Figure 3. Diffuse reflectance UV-vis spectra of complex.

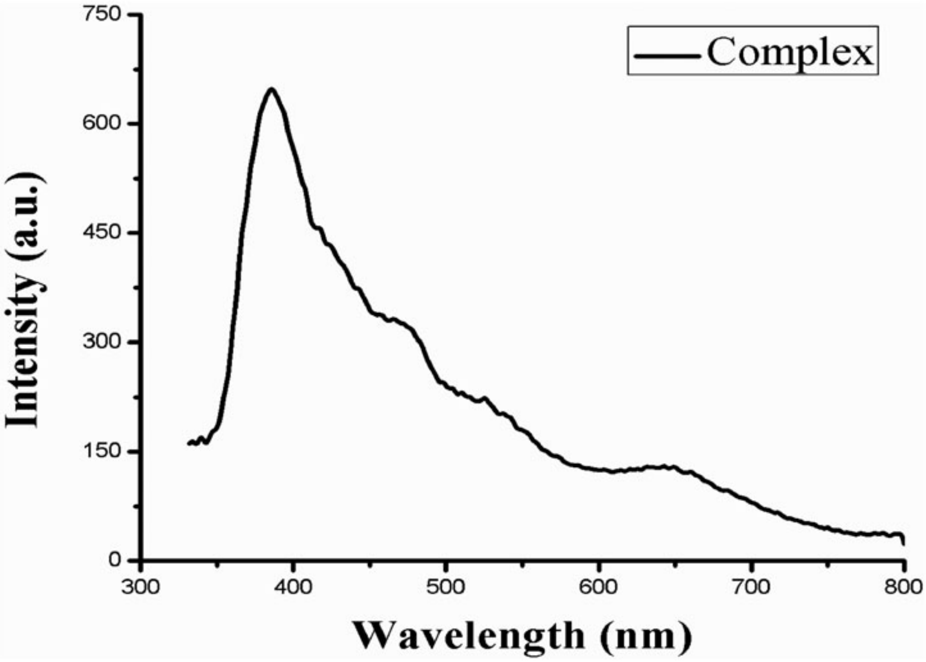

Figure 4. Solid-state fluorescence emissions recorded at room temperature for complex.

Conclusion

On this work, we report the synthesis and characterization of one complex [Zn_2(Zaltoprofen)$_2$(phen)$_2$] by X-ray diffraction analysis, elemental analysis, IR spectrum, powder X-ray diffraction, and fluorescence Properties. The successful preparation of the complex manifest that the conformations and functions of π–π stacking interactions and hydrogen-bonding are important factors in influencing the nal architecture of Zaltoprofen coordination polymers. The presence of chelate ligands in transition metal dicarboxylate systems usually results in the formation of low-dimensional coordination polymers with the metal ions acting as nodes and the dicarboxylate ligands as connectors. The Zn(II) polymer exhibits intense emission, which appear to be potential hybrid inorganic-organic photoactive materials. Subsequent studies will be focused on the structures and properties of a series of coordination polymers constructed by Zaltoprofen with more organic ligands and other metal ions.

Supplementary Material

CCDC 955440 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conflict of Interest

No conflict of interest exists in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the manuscript that is enclosed.

Acknowledgments

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