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Jin-Niu Tang^a, Zhong-Jing Huang^a, Dai-Yin Wang^a, Tian-Tian Ren^a, Long Li^a & Gang-Hong Pan^a

^a College of Chemistry and Chemical Engineering, Guangxi University for Nationalities, Nanning 530006, P.R. China

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Synthesis, crystal structures, and properties of two Cd(II) complexes based on Zaltoprofen

JIN-NIU TANG*, ZHONG-JING HUANG, DAI-YIN WANG, TIAN-TIAN REN,
LONG LI and GANG-HONG PAN

College of Chemistry and Chemical Engineering, Guangxi University for Nationalities,
Nanning, P.R. China

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Two metal–organic coordination complexes, $[\text{Cd}(\text{Zaltoprofen})(\text{phen})]_n$ (**1**) and $[\text{Cd}(\text{Zaltoprofen})(\text{btz})]_n$ (**2**) (where Zaltoprofen = 5-(1-carboxyethyl)-2-(phenylthio)phenylacetic acid, phen = 1,10-phenanthroline, btz = thiabendazole), have been synthesized by reaction of $\text{Cd}(\text{NO}_3)_2$ with Zaltoprofen, 1,10-phenanthroline or thiabendazole under hydrothermal conditions and characterized by single-crystal X-ray diffraction (XRD), IR spectra, elemental analyzes, powder XRD, electronic spectra (UV–vis), and fluorescent properties. Compound **1** crystallizes in the monoclinic $P21/c$ space group and **2** in the monoclinic system with space group $P21/n$. $[\text{Cd}(\text{Zaltoprofen})(\text{phen})]_n$ (**1**) features a 1-D zigzag chain. The zigzag chains are linked to form a 2-D layer through π – π stacking interactions. $[\text{Cd}(\text{Zaltoprofen})(\text{btz})]_n$ (**2**) displays a 2-D net with alternately arranged left- and right-handed helical chains.

Keywords: X-ray crystal diffraction; XRD; Electronic spectra; Fluorescent properties; Helical chains; Zaltoprofen

1. Introduction

Low-dimensional coordination polymers have received attention owing to their intriguing structural features and potential as functional materials different from those of 3-D coordination polymers [1]. A particularly interesting and challenging area is the synthesis of helical coordination polymers and exploration of their potential utility in asymmetric catalysis and non-linear optics [2,3]. Metal–organic helical structures containing single-, double-, and multi-stranded helices [4–6] have been constructed; the chemistry of coordination polymers with helical structures has been reviewed [7].

The influence of ligand spacers of flexible bridging ligands on framework formation of coordination polymers has widely been documented [8]. Zaltoprofen is a non-steroidal anti-inflammatory drug that exhibits favorable anti-inflammatory, analgesic, 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 non-steroidal anti-inflammatory drugs such as ibuprofen and fenoprofen

*Corresponding author. Email: tangjinniu@126.com

[9]. But to our knowledge, using Zaltoprofen to construct metal–organic frameworks has not been reported. The flexible Zaltoprofen building blocks as V-shaped dicarboxylates may generate zigzag and helical chains. Chelating bipyridine-like ligands such as 1,10-phenanthroline and btz are important in maintaining the one dimensionality of the coordination polymers and may provide supramolecular recognition sites for π – π aromatic stacking interactions to form interesting supramolecular structures, such as double-stranded helices and molecular zippers [10]. Many helical architectures based on bipy-like and carboxylate ligands have been reported [11].

Herein we report two new coordination polymers, $[\text{Cd}(\text{Zaltoprofen})(\text{phen})]_n$ (**1**) and $[\text{Cd}(\text{Zaltoprofen})(\text{btz})]_n$ (**2**), which were constructed by cadmium(II) salts with Zaltoprofen and N-donor ligands. Electronic spectra (UV–vis) and photoluminescence properties in the solid state have also been investigated.

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 from 4000 to 400 cm^{-1} using KBr pellets. Powder X-ray diffraction (XRD) patterns were obtained using a pinhole camera (Anton Paar) operating with a point focused Ni-filtered Cu $K\alpha$ radiation in the 2θ range from 5° to 50° with a scan rate of 0.08° per second. The optical properties were analyzed by UV–vis diffuse reflectance spectroscopy using a UV–vis spectrophotometer (Cary-500, Varian Co.), in

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

Complexes	1	2
Empirical formula	$\text{C}_{29}\text{H}_{22}\text{CdN}_2\text{O}_4\text{S}$	$\text{C}_{27}\text{H}_{21}\text{CdN}_3\text{O}_4\text{S}_2$
Formula weight	606.95	627.99
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, $P2(1)/c$	Monoclinic, $P2(1)/n$
<i>Unit cell dimensions</i>		
a (Å)	9.386(3)	14.254(3)
b (Å)	24.029(3)	10.179(4)
c (Å)	11.343(3)	18.630(2)
β ($^\circ$)	99.3820(10)	109.3420(10)
Volume (Å ³)	2524.0(11)	2550.5(11)
Z	4	4
$D_{\text{calc.}}$ ($\text{Mg}\cdot\text{m}^{-3}$)	1.597	1.635
Absorption coefficient (mm^{-1})	0.987	1.060
$F(000)$	1224	1264
Crystal size	$0.30 \times 0.29 \times 0.27$	$0.26 \times 0.25 \times 0.23$
θ range for data collection ($^\circ$)	1.69–25.00	1.57–25.00
Reflections collected	13,448	13,393
Unique reflections	4443 [$R(\text{int}) = 0.0247$]	4464 [$R(\text{int}) = 0.008$]
Completeness to $\theta = 25.00$	100%	99.6%
Absorption correction	Semi-empirical	Semi-empirical
Max. and min. transmission	0.766 and 0.751	0.784 and 0.767
Data/restraints/parameters	4443/1/335	4464/0/335
Goodness-of-fit on F^2	1.069	1.015
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0370$, $wR_2 = 0.0975$	$R_1 = 0.0583$, $wR_2 = 0.1200$
R indices (all data)	$R_1 = 0.0423$, $wR_2 = 0.1006$	$R_1 = 0.1126$, $wR_2 = 0.1437$
Largest diff. peak and hole ($e \text{ \AA}^{-3}$)	0.722 and -0.495	0.697 and -0.806

which BaSO₄ was used as the internal standard. Fluorescence spectra were recorded with a F-2500 FL Spectrophotometer analyzer.

2.1. Preparation of [Cd(Zaltopfen)(phen)]_n (1)

Cd(NO₃)₂·7H₂O (0.1542 g, 0.5 mmol), Zaltopfen (0.1582 g, 0.5 mmol) and phen (0.0991 g, 0.5 mmol) were dissolved in 15 mL of DMF/EtOH/H₂O (volume ratio 1 : 1 : 1) and adjusted to pH 6 with NH₃·H₂O and then stirred 0.5 h. The resulting mixture was sealed in a 25 mL Teflon-lined stainless container, heated at 130 °C for 72 h, and then slowly cooled to room temperature at a rate of 5 °C per hour. Colorless block crystals suitable for XRD were isolated directly in 82% yield based on Cd. Anal. Calcd for C₂₉H₂₂CdN₂O₄S (%): C, 57.38; H, 3.65; N, 4.62. Found: C, 57.57; H, 3.76; N, 4.53. IR data (KBr pellets, cm⁻¹): 2949 (w), 1565 (vs), 1478 (m), 1423 (s), 1406 (s), 1338 (m), 1145 (m), 1016 (m), 908 (w), 869 (w), 837 (s), 763 (m), 727 (s), 635 (w).

2.2. Preparation of [Cd(Zaltopfen)(btz)]_n (2)

Cd(NO₃)₂·7H₂O (0.1542 g, 0.5 mmol), Zaltopfen (0.1582 g, 0.5 mmol) and btz (0.105 g, 0.5 mmol) were dissolved in 15 mL of DMF/EtOH/H₂O (volume ratio 1 : 1 : 1), adjusted to

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

Complex 1			
Cd(1)–O(1)#1	2.305(3)	O(3)–Cd(1)–N(2)	130.57(11)
Cd(1)–O(3)	2.310(3)	N(1)–Cd(1)–N(2)	70.65(12)
Cd(1)–N(1)	2.348(3)	O(1)#2–Cd(1)–N(2)	80.20(11)
Cd(1)–O(1)#2	2.374(3)	O(1)#1–Cd(1)–O(4)	85.10(11)
Cd(1)–N(2)	2.375(3)	O(3)–Cd(1)–O(4)	53.00(11)
Cd(1)–O(4)	2.488(3)	N(1)–Cd(1)–O(4)	90.11(12)
Cd(1)–O(2)#1	2.570(3)	O(1)#2–Cd(1)–O(4)	117.81(11)
O(1)#1–Cd(1)–O(3)	109.15(12)	N(2)–Cd(1)–O(4)	160.76(12)
O(1)#1–Cd(1)–N(1)	132.64(10)	O(1)#1–Cd(1)–O(2)#1	52.70(9)
O(3)–Cd(1)–N(1)	104.90(13)	O(3)–Cd(1)–O(2)#1	136.19(11)
O(1)#1–Cd(1)–O(1)#2	73.69(10)	N(1)–Cd(1)–O(2)#1	79.94(10)
O(3)–Cd(1)–O(1)#2	79.92(12)	O(1)#2–Cd(1)–O(2)#1	120.69(9)
N(1)–Cd(1)–O(1)#2	145.30(11)	N(2)–Cd(1)–O(2)#1	92.58(11)
O(1)#1–Cd(1)–N(2)	107.82(11)	O(4)–Cd(1)–O(2)#1	83.93(11)
Complex 2			
Cd(1)–N(1)	2.289(6)	O(1)#1–Cd(1)–O(4)	120.4(2)
Cd(1)–O(1)#1	2.342(5)	O(2)#1–Cd(1)–O(4)	85.81(18)
Cd(1)–O(2)#1	2.361(5)	O(4)#2–Cd(1)–O(4)	72.74(19)
Cd(1)–O(4)#2	2.367(5)	N(1)–Cd(1)–N(2)	71.0(2)
Cd(1)–O(4)	2.398(5)	O(1)#1–Cd(1)–N(2)	88.6(2)
Cd(1)–N(2)	2.438(6)	O(2)#1–Cd(1)–N(2)	82.0(2)
Cd(1)–O(3)	2.477(5)	O(4)#2–Cd(1)–N(2)	153.2(2)
N(1)–Cd(1)–O(1)#1	114.4(2)	O(4)–Cd(1)–N(2)	132.39(18)
N(1)–Cd(1)–O(2)#1	151.7(2)	N(1)–Cd(1)–O(3)	89.02(18)
O(1)#1–Cd(1)–O(2)#1	54.90(19)	O(1)#1–Cd(1)–O(3)	151.05(19)
N(1)–Cd(1)–O(4)#2	89.02(19)	O(2)#1–Cd(1)–O(3)	96.39(19)
O(1)#1–Cd(1)–O(4)#2	83.44(18)	O(4)#2–Cd(1)–O(3)	115.21(16)
O(2)#1–Cd(1)–O(4)#2	113.23(19)	O(4)–Cd(1)–O(3)	52.75(16)
N(1)–Cd(1)–O(4)	118.74(18)	N(2)–Cd(1)–O(3)	83.13(18)

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

pH 6 with $\text{NH}_3 \cdot \text{H}_2\text{O}$ and then stirred 0.5 h. The resulting mixture was sealed in a 25 mL Teflon-lined stainless container, heated at 130 °C for 72 h, and then slowly cooled to room temperature at a rate of 5 °C per hour. Colorless block crystals suitable for XRD were isolated directly in 76% yield based on Cd. Anal. Calcd for $\text{C}_{27}\text{H}_{21}\text{CdN}_3\text{O}_4\text{S}_2$ (%): C, 51.64; H, 3.37; N, 6.69. Found: C, 51.75; H, 3.48; N, 6.56. IR data (KBr pellets, cm^{-1}): 3422 (s), 3097 (m), 2966 (m), 2763 (w), 2682 (w), 1546 (vs), 1475 (m), 1423 (s), 1406 (s), 1316 (m), 1289 (m), 1267 (m), 1236 (m), 1175 (w), 1017 (m), 991 (m), 942 (w), 923 (m), 871 (m), 823 (s), 773 (m), 751 (s), 724 (w), 698 (m), 635 (m), 604 (w), 573 (w), 502 (w), 481 (w), 434 (m).

2.3. X-ray data collection and structure refinement

A high-quality crystal was selected and mounted on a glass fiber. The data were collected on a Bruker SMART CCD diffractometer at 296(2) K using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS [12]. All structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL package [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens attached to carbon were placed in geometrically idealized positions and refined using a riding model. The crystallographic data as well as details of the data collection and refinement are listed in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. Crystal structure descriptions

Complex **1** crystallizes in the monoclinic space group $P21/c$. Each Cd(II) is seven-coordinate by two nitrogens (N1, N2) from one phen and five oxygens (O1A, O1B, O2B, O3 and O4) of the carboxylates from three Zaltoprofen²⁻ (figure 1(a)). The Cd–O bond distances vary from 2.305(3) to 2.570(3) Å, while Cd–N bond lengths are 2.348(3) and 2.375(3) Å. One carboxylate is $\mu^1\text{-}\eta^2\text{:}\eta^1$ chelating to one Cd(II) atom while the other carboxylate is a $\mu^2\text{-}\eta^2\text{:}\eta^1$ bridge linking two Cd(II) ions. As shown in figure 2, carboxylates of Zaltoprofen²⁻ connect Cd1 and Cd1A to form infinite 1-D zigzag chains with Cd1...Cd1A distances of 3.744 Å; the chains are stabilized by $\pi\text{-}\pi$ stacking interactions between the phenyl ring of Zaltoprofen and phen at 3.711 Å (figure 2). Face-to-face $\pi\text{-}\pi$ stacking between two phen molecules from two adjacent chains cause a 2-D supramolecular network [14]. The interchain $\pi\text{-}\pi$ interactions between the two phen of two adjacent zigzag chains have a distance of 3.7544 Å (figure 3). These weak interactions (C–H...O non-classical hydrogen bonding) play a vital role in determining the crystal packing and construction of the extended 3-D supramolecular network.

Single-crystal XRD analysis reveals that **2** crystallizes in the monoclinic system, space group $P21/n$. The asymmetric unit contains one Cd(II), one btz and one completely deprotonated Zaltoprofen²⁻. Cd(II) is bound by five oxygen donors (O1B, O2B, O3, O4, O4A) of three Zaltoprofen²⁻ and N1 and N2 from one btz, forming a $[\text{CdN}_2\text{O}_5]$ coordination sphere. The Cd–N bond lengths are 2.289(6) and 2.438(6) Å, while Cd–O bond lengths are 2.342(5) to 2.477(5) Å, in the normal range [15]. In **2**, two carboxylates of Zaltoprofen²⁻ adopt different coordination, one bidentate chelating and the other $\mu^2\text{-}\eta^1\text{:}\eta^2$ -bridging mode. Zaltoprofen²⁻ is a μ^5 -bridge linking Cd(II) ions to produce a 2-D net with

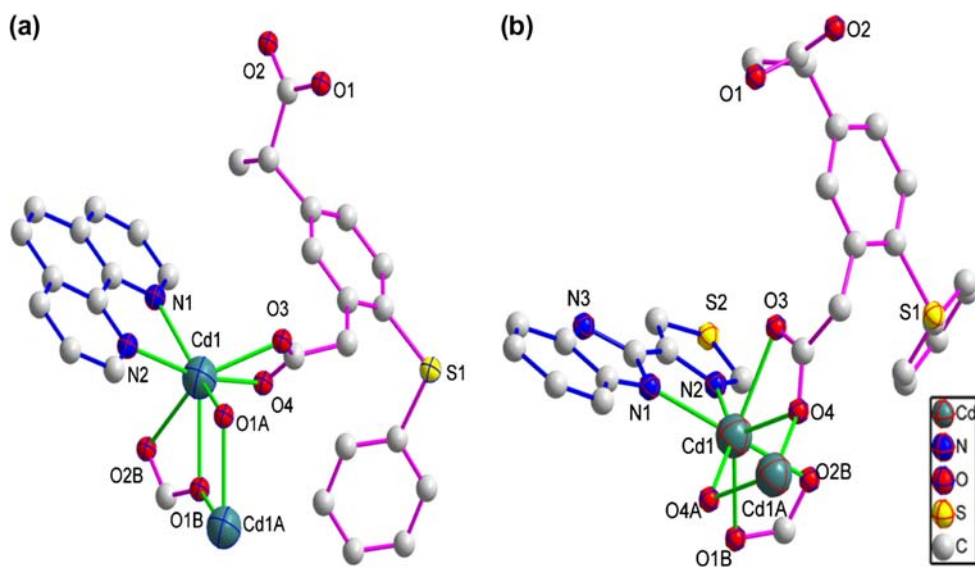


Figure 1. Coordination environment of Cd(II) in **1** and **2** with hydrogens omitted for clarity.

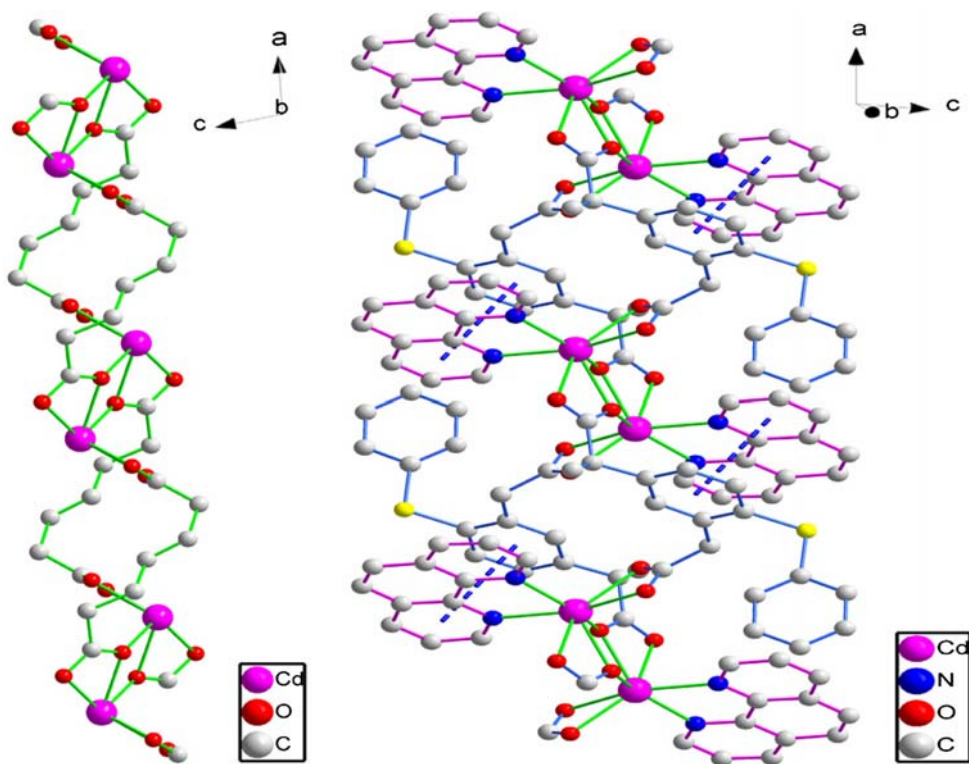


Figure 2. View of the 1-D zigzag chain and π - π stacking interactions of **1**. Unnecessary atoms are omitted for clarity.

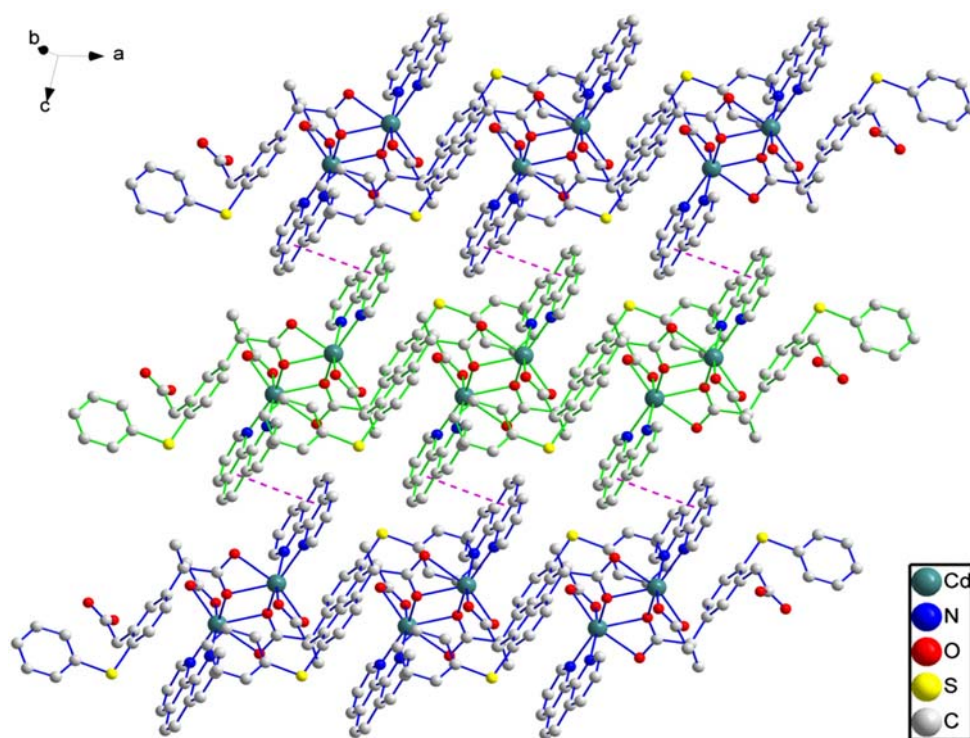


Figure 3. View of the π - π intramolecular stacking interaction in **1**. All hydrogens are omitted for clarity.

alternately arranged left- and right-handed helical chains (figure 4). Each pair of Cd(II) ions is bridged by two Zaltoprofen²⁻ anions to generate a planar rhombus with a Cd...Cd separation of 3.837 Å, markedly longer than observed complexes with this mode (3.4–3.7 Å) [16]. Two adjacent btz molecules are connected by π - π stacking interactions with a distance of 3.8766 Å. The hydrogen-bonding (N3–H3...O3 = 1.960(5) Å) and π - π interactions play important roles in stabilizing the 2-D net (figure 5).

3.2. Spectroscopic properties

IR spectra of **1** and **2** are similar, indicating similar structures. In **2**, the band at 3422 cm⁻¹ is attributed to ν (N–H). The IR spectrum of free ligand shows strong bands of carboxylate at 1697 cm⁻¹, assigned as ν (C=O) antisymmetric stretch. In **1**, the band shifted by 132 cm⁻¹ for ν (C=O) and 151 cm⁻¹ in **2**. The shift suggests that oxygen of the ligand coordinates to metal.

3.3. XRD Patterns

In order to confirm the phase purity of these polymers, PXRD patterns were recorded for **1** and **2** and compared to the corresponding simulated ones calculated from the single-crystal diffraction data (Supplementary material), indicating a pure phase of each bulk sample.

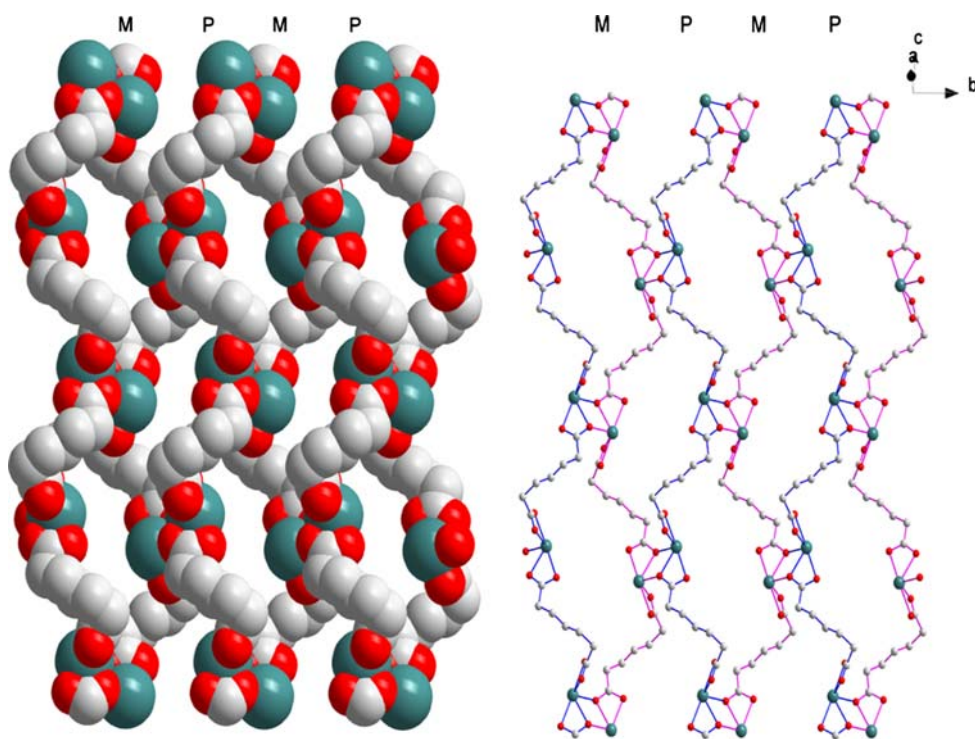


Figure 4. View of the 2-D Cd(II)/Zaltoprofen²⁻ net constructed by alternately left- and right-handed helical chains of **2**. Unnecessary atoms are omitted for clarity.

The difference in reflection intensity between the simulated and experimental patterns is due to preferred orientation of the powder samples during data collection.

3.4. Electronic spectra

UV-vis spectra of $[\text{Cd}(\text{Zaltoprofen})(\text{phen})]_n$ and $[\text{Cd}(\text{Zaltoprofen})(\text{btz})]_n$ complexes have similar bands in the UV-vis-near-IR region (Supplementary material). The spectroscopic behavior of Cd(II) complexes containing Zaltoprofen have various spectroscopic transitions including ligand-centered and metal-ligand charge transfer. Bands in the UV region were attributed to the intraligand transition mainly centered in Zaltoprofen. The intraligand bands are sufficiently intense to mask a MLCT band involving $d\pi\text{Cd(II)}-\pi^*(\text{Zaltoprofen})$ observed at 303 nm as assigned in a UV-vis spectrum of $[\text{Cd}(\text{Zaltoprofen})(\text{phen})]_n$ (**1**) as well as 322 nm for $[\text{Cd}(\text{Zaltoprofen})(\text{btz})]_n$ (**2**).

3.5. Fluorescence properties

Coordination polymers with d^{10} metal centers and conjugated organic linkers are promising photoactive materials with potential applications such as chemical sensors and photochemistry [17]. Hence, solid-state photoluminescence properties of **1** and **2** were investigated at room temperature (Supplementary material) under the same experimental conditions. In the

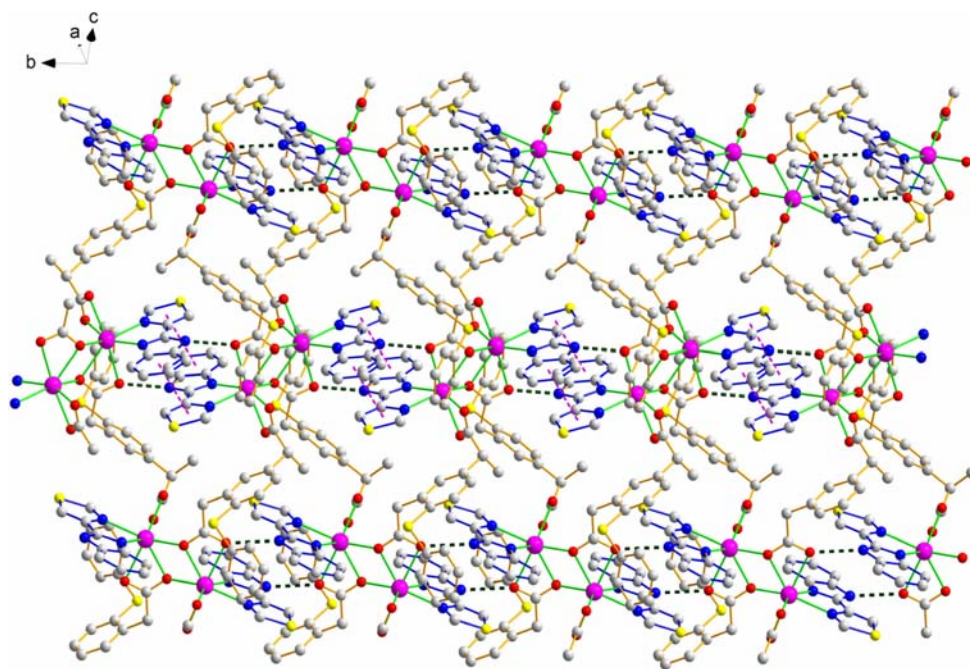


Figure 5. View of the π - π intramolecular stacking interaction and N3-H3...O3 hydrogen bonds in **2**. All hydrogens are omitted for clarity.

solid state, strong photoluminescence emission bands at 386 nm ($\lambda_{\text{ex}}=325$ nm) and 384 nm ($\lambda_{\text{ex}}=280$ nm) are observed for **1** and **2**. 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 and btz ligands present weak photoluminescence emission. Therefore, the fluorescent emissions in the coordination polymers may be proposed to originate from the coordination of Zaltoprofen²⁻ to cadmium(II), confirmed by similar fluorescent emission bands of **1** and **2**.

4. Conclusions

Selecting Cd(II), Zaltoprofen²⁻, and N-donors as building blocks, two new coordination polymers have been isolated under hydrothermal conditions. Complex **1** is an infinite 1-D zigzag chain, while **2** is a 2-D net with alternately arranged left- and right-handed helical chains. The presence of chelating 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 dicarboxylates as connectors, especially 1-D chains, and the employment of a V-shaped dicarboxylate may generate zigzag and helical chains. Theoretically, the flexible Zaltoprofen building blocks can be considered as V-shaped connectors. The two Cd(II) polymers exhibit intense emissions, which appear to be potential hybrid inorganic-organic photoactive materials. Subsequent studies will focus on the biological activity of the metal complexes, the structures and properties of a series of coordination polymers constructed by Zaltoprofen with more N-donor ligands and other metal ions.

Supplementary material

CCDC 882963 and 882954 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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