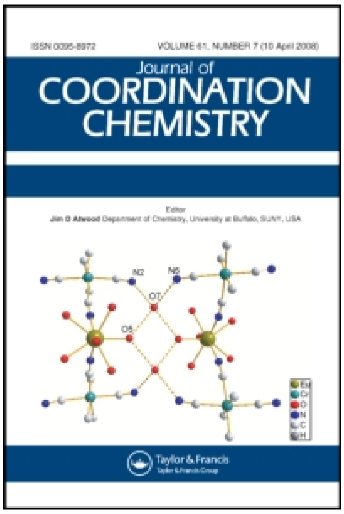

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Synthesis, crystal structure and characterization of a 1D chain coordination polymer of zinc(II) with aroylamide, $[Zn(H_2bpb)Cl_2]_{<b><i>n</i>}$ · CH_3OH, (H_2bpb = 1,2-<i>bis</i>(3-pyridylcarboxamide)benzene)

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Synthesis, crystal structure and characterization of a 1D chain coordination polymer of zinc(II) with aroylamide, $[Zn(H_2bpb)Cl_2]_n \cdot CH_3OH$, ($H_2bpb$ = 1,2-*bis*(3-pyridylcarboxamide)benzene)

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A four-coordinate zinc(II) coordination polymer, $[ZnCl_2(H_2bpb)]_n \cdot CH_3OH$ ($H_2bpb = 1,2$-*bis*(3-pyridylcarboxylamide)benzene), has been prepared and the crystal structure determined by X-ray diffraction. It crystallizes in the triclinic system, space group $P\bar{1}$ with $a = 7.898(3)$ Å, $b = 11.792(4)$ Å, $c = 11.911(4)$ Å, $\alpha = 76.051(4)^\circ$, $\beta = 89.919(4)^\circ$, $\gamma = 78.267(4)^\circ$, $V = 1052.9(7)$ Å, $Z = 2$. The crystal structure consists of chains of complex zig-zaging along the b lattice translation. Fluorescent and thermal properties of the complex were also investigated.

Keywords: Zinc(II) complex; Crystal structure; Coordination polymer; Fluorescent property; Thermal property

1. Introduction

Novel and fascinating types of entanglements of individual motifs are exhibited in coordination network polymers [1]. Transition metal ion directed self-assembly of coordination polymers plays an important part in functional solid materials [2], host-guest chemistry, ion exchange, catalysis, optical devices, magnetism, electrical conductivity, separation, biology and topology [3]. Many coordination polymers have been synthesized by self-assembly. The complexities of self-assembled systems are controlled by the geometric preference of the metal ion for a particular geometry, and the number and design of the ligand is the key to new self-assembly processes where the variety and unpredictability of self-assembly arises [4].

The carboxamide [–C(O)NH–] group, ubiquitous throughout nature in the primary structure of proteins, is an important ligand construction unit for coordination chemists [5]. Many pyridine carboxamide ligands have been prepared [6] and are extending to potential applications as diverse as azo dye [7] and telomerase inhibitors [8]. Zinc has been a popular choice in the preparation of coordination networks, is a relatively abundant element in biological organisms and plays

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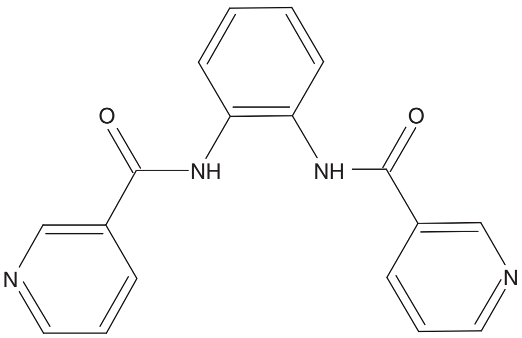

Scheme 1. Molecular structure of H_2bpb.

an essential role in a large number of enzymatic reactions [9]. A large number of zigzag chain coordination polymers have been reported [10–14]. The first example of Zn(II) and 1,2-*bis*(3-pyridinecarboxamide)benzene (H_2bpb)-bridged coordination polymer with general formula $[ZnH_2bpb)Cl_2]_n \cdot CH_3OH$ of 1D zigzag chain has been synthesized and characterized. The structure of H_2bpb is shown in (scheme 1). We found that π–π stacking interaction and weak hydrogen bonding formed between these one-dimensional chains promote the polymer into three-dimensional supramolecular structures. Herein we report synthesis, the crystal structure, fluorescent and thermal properties of tetra-coordinated Zn(II) coordination polymer $[ZnH_2bpb)Cl_2]_n \cdot CH_3OH$.

2. Experimental

2.1. *Materials and methods*

Nicotinic acid was analytical pure grade from Alfa Aesar, *o*-phenylenediamine and other reagents were also analytically pure grade, purchased from TianJin Reagent Factory and used without further purification. The 1,2-*bis*(3-pyridinecarboxamide)benzene (H_2bpb) was synthesized following a procedure reported previously [15] with a yield of 70%. Thionyl chloride and pyridine were redistilled. Melting points were taken on a XT-5 microscope melting point apparatus. IR spectra were recorded on a Nicolet IR-470 spectrometer from KBr pellets in the range 4000–400 cm^{-1}. Crystallographic data was measured on a Bruker APEX-II area-detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073'$). Thermal analysis curve was scanned in the range 35–600°C with air on a STA 409 PC thermal analyzer. The fluorescence spectra were determined in the solid state at room temperature on HITRCHI F-4500 fluorophotometer.

2.2. *Synthesis of* $[ZnH_2bpbCl_2)]_n \cdot CH_3OH$

At room temperature, a clear DMF solution (5 mL) of H_2bpb (63.7 mg, 0.2 mmol) was slowly added to a methanol solution (10 mL) of $ZnCl_2$ (27.3 mg, 0.2 mmol) with continuous stirring for 30 min, then was filtered. The filtrate was left undisturbed for evaporation at ambient temperature; colorless block crystals suitable for X-ray single crystal diffraction analysis were collected one week later by filtration and washed with methanol and acetone. Yield: 30%. IR (KBr, υ cm^{-1}): 3279 m, 1670 s, 1606 s, 1523 s, 1321 s, 1273 s, 1201s, 1127 s, 1056 m, 759 m, 695 m.

2.3. *X-ray structure determination*

Crystallographic data for the title compound were collected at 291(2) K on a Bruker APEX-II area detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073'$). Absorption corrections were applied by using SADABS. The structure was solved with direct methods and refined with full-matrix least-squares techniques on F^2 using the SHELXTL program package [16]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restrains. Crystal data are summarized in table 1. Selected bond lengths and bond angles are in table 2.

Table 1. Crystallographic data and structure refinement for the complex.

Structural parameter	
Empirical formula	$C_{18.50}H_{16}Cl_2N_4O_{2.50}Zn$
M	472.64
Crystal group	Triclinic
Space group	$P\bar{1}$
a (Å)	7.898(3)
b (Å)	11.792(4)
c (Å)	11.911(4)
α (°)	76.051(4)
β (°)	89.919(4)
γ (°)	78.267(4)
V (Å^3)	1052.9(7)
D_c (g cm^{-3})	1.491
Z	2
μ (mm^{-1})	1.444
Crystal size (mm^3)	0.49 × 0.30 × 0.17
Reflns collected/unique	7797/3838
R_1, ωR_2 [$I > 2\sigma(I)$]	0.0694[a], 0.1980[b]

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; [b] $\omega R_2 = [\Sigma(\|F_o| - |F_c\|)^2/\Sigma\omega|F_o|^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for the zinc(II) complex.

Zn(1)–N(1)	2.044(5)
Zn(1)–N(4)#1	2.071(5)
Zn(1)–Cl(2)	2.2328(17)
Zn(1)–Cl(1)	2.2377(17)
N(1)–Zn(1)–N(4)#1	105.7(2)
N(1)–Zn(1)–Cl(2)	110.24(14)
N(4)#1–Zn(1)–Cl(2)	108.06(14)
N(1)–Zn(1)–Cl(1)	103.45(14)
N(4)#1–Zn(1)–Cl(1)	104.63(14)

3. Results and discussion

3.1. *IR spectra*

In IR spectra of the ligand υ(N–H), υ(C=O) and υ(C=N) appeared at 3282, 1665 and 1470 cm^{-1}, respectively, indicating that the free ligand exists in keto-form. In the IR spectrum of the zinc(II) complex, the υ(N–H) and υ(C=O) shift trivially to 3279 and 1670 cm^{-1}, suggesting that the complex is still in the keto-form and is not coordinated. Differences between the IR spectra of H$_2$bpb and its zinc(II) complex are noticeable in the regions of δ (py) vibration. The υ(C=N) bands of the complex shift to a lower frequency 1448 cm^{-1} suggesting nitrogen of pyridyl coordinating Zn(II), consistent with the N$_{py}$ mode of coordination established by X-ray crystallography. Further, the υ(N–H) absorption bands of the complex are broader than those of the ligand, indicating inter- and/or intra-molecular hydrogen bonding [17].

3.2. *Crystal structure of complex*

Figure 1 shows an ORTEP drawing of the Zn(II) complex with the labelling scheme of the wave-like coordination polymer. The crystal structural unit of the Zn(II) complex is one Zn(II), one molecular H$_2$bpb, two chlorines, and one methanol. Zn(II) has a coordination geometry that approximates to distorted tetrahedral with two nitrogen atoms (N(1) and N(4)) from H$_2$bpb and two chlorine atoms (Cl(1) and Cl(2)) at the corners of the tetrahedron and Zn(II) in the center; methanol does not coordinate. Mean value (2.055(8) Å) of Zn–N (H$_2$bpb) bond lengths is shorter than literature value (2.043(3) Å) [18] and the lengths (2.235(3) and 2.238(3) Å) of Zn–Cl bond are longer than Zn–N (H$_2$bpb). The N–Zn–N bond angle is ca 105.6° and the N–Zn–Cl bond angle is 110.2°, close to normal tetrahedral angles.

H$_2$bpb is a hexadentate ligand containing two imines, two carbonyls and two pyridyls; here it only participates in coordination by two nitrogen atoms from two pyridyls which bridge adjoining Zn atoms to form a novel one-dimensional

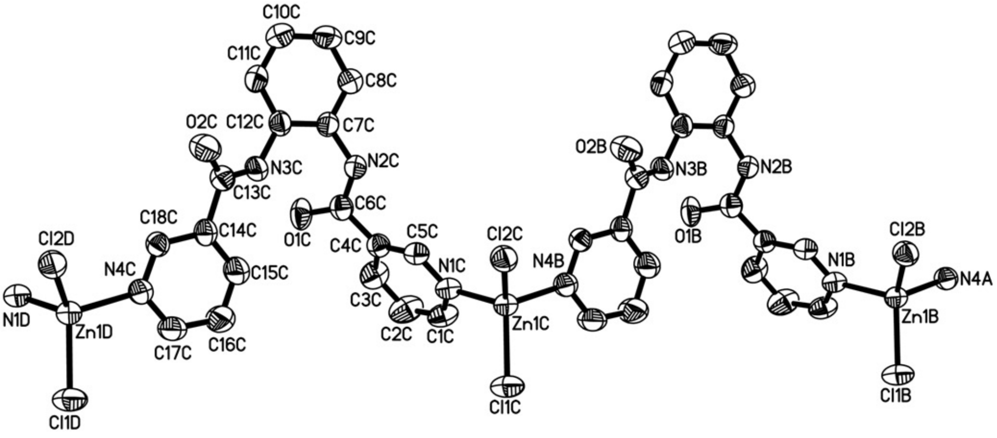

Figure 1. Molecular structure and atomic labelling scheme of the wave-like coordination polymer with solvent molecules omitted for clarity.

zigzag-like chain. The intra chain Zn···Zn separation is 11.792 Å. In the crystal structure unit, one benzene ring and two pyridine rings of H_2bpb do not position on the same plane, the dihedral angle between planes (1) (C(7C), C(8C), C(9C), C(10C), C(11C), C(12C) and (2) (C(1C), C(2C), C(3C), C(4C), C(5C), N(1C)) is 105.6°; between planes (2) and (3) (C(14C), C(15C), C(16C),C(17C), C(18C), N(4C)) is 104.8°; and between planes (1) and (3) is 4.8°, respectively.

As shown in figure 2, the complex contains hydrogen bonds, one, N(2)–H(2N)···O(1) = 2.701(11) Å, formed from imine group and carbonyl group; another is O(3)–H(3)···O(2)#1 = 3.09(5) Å, formed between lattice methanol and carbonyl group; the other is weak hydrogen bond, O(3)–H(3)···C(11) = 3.655 Å, formed between lattice methanol and benzene ring in the same structural unit; also there is a weak hydrogen bond, N(2)–H(2N)···Cl(2)#3 = 3.401(8) Å, formed from chlorine atom and imine group of neighboring chain.

Each structural unit has one lattice methanol molecule, two close methanol molecules (C(19)···C(19A) = 3.248 Å) of neighboring chains arrange to form a coupled pair. The neighboring chains are parallel and unsymmetrically arranged by hydrogen bonding coupled methanol pairs. There is $\pi\cdots\pi$ stacking interaction between the neighboring phenyl ring and pyridyl ring on both sides, between which the shortest distance is 3.704 and 3.828 Å, respectively, and the dihedral angle is 4.8°. The polymer

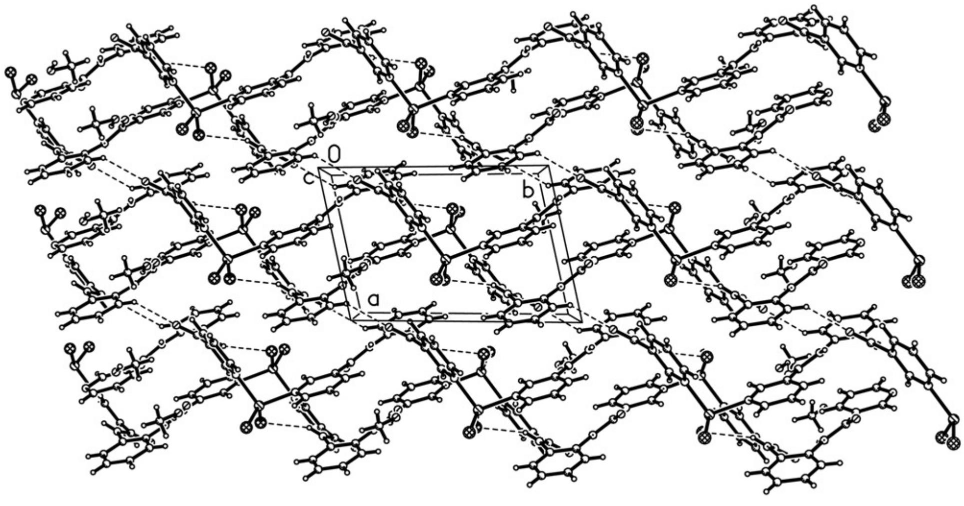

Figure 2. Packing diagram for the complex with hydrogen bonding shown as dotted lines with solvent molecules omitted for clarity.

Table 3. Hydrogen bonds for L (Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	(DHA)
O(3)–H(3)···O(2)#1	0.82	2.48	3.09(5)	132.7
N(2)–H(2N)···Cl(2)#3	0.86	2.60	3.401(8)	154.6
N(3)–H(3N)···O(1)	0.86	1.94	2.701(11)	147.2
C–H···O	0.93	2.556	3.282	135.19

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

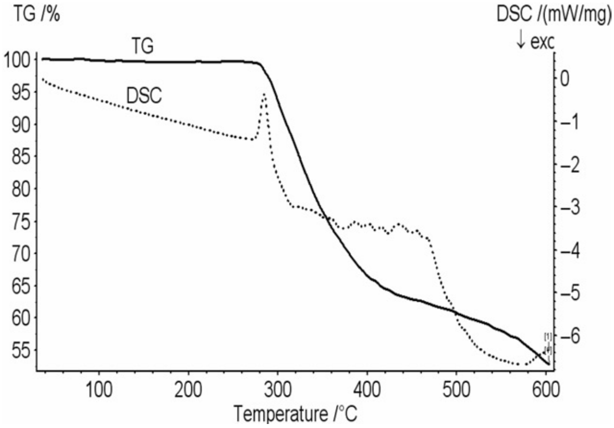

Figure 3. The DSC-TG curve of the coordination polymer.

chains expand into a supramolecular coordination polymer by $\pi\cdots\pi$ stacking interaction and intermolecular hydrogen bonds (as shown in figure 2).

3.3. *Thermo-gravimetric analysis (TGA)*

The DSC-TG curve of the coordination polymer (shown in figure 3) was scanned in the range 35–600°C with air atmosphere on a STA 409 PC thermal analyzer. It is seen from figure 3 that at 275°C the coordination polymer begins to decompose and the DSC curve shows an endothermic peak. Up to 408°C weight loss is 34.1%, corresponding to loss of one methanol, two chlorine atoms and two carbonyl groups (Calcd 32.65%). At 408°C the remnants of the complex have a calorific effect of strong decomposition, the DSC curve shows an exothermic peak. To 603.5°C weight loss in all is 52.74% and decomposition still occurs in corresponding part remains. In crucible the remains, 47.26%, may be organic remnants and ZnO.

3.4. *Photoluminescent properties*

The fluorescence spectra of the ligand H_2bpb and the complex are determined in the solid state at room temperature on a HITRCHI F-4500 fluorophotometer. The fluorescence emission and excitation spectra of H_2bpb and the complex are shown in figures 4 and 5, respectively. Emission spectra of H_2bpb ($\lambda_{max} = 390$ nm) and the complex ($\lambda_{max} = 388$ nm) are observed upon excitation at 244 nm. Excitation at 244 nm leads to broad, violet-fluorescent emission bands at 390 nm for the complex which are near the maximum emission at 388 nm for H_2bpb under the same conditions. Compared with the free H_2bpb, the fluorescent intensity of the complex is slightly enhanced. The enhancement of the complex fluorescence intensity is probably due to coordination increasing conformational rigidity and expanding conjugation of the complex, thereby reducing energy of the complex excited state [19]. Therefore, the emissions observed in the complex are neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) and can be assumed as intraligand fluorescent emission [20].

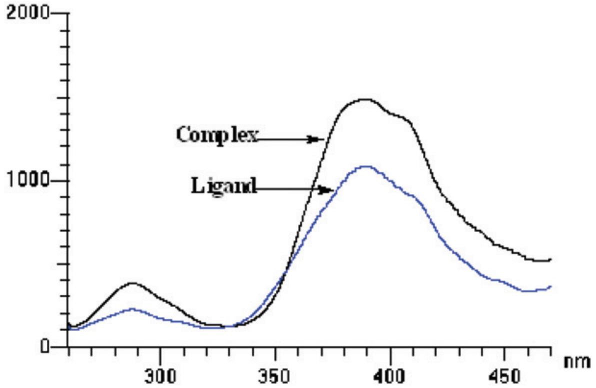

Figure 4. The fluorescence emission spectra of ligand and the complex in solid state.

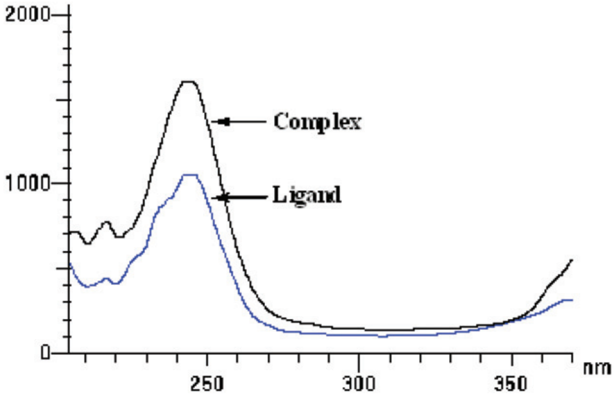

Figure 5. The fluorescence excitation spectra of ligand and the complex in solid state.

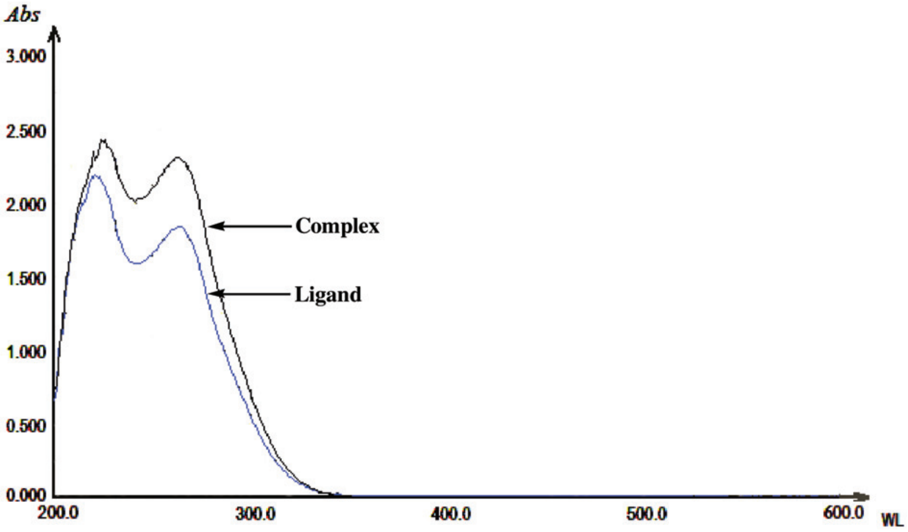

Figure 6. Uv spectra of the complex and the ligand (H_2bpb).

3.5. *UV spectra*

UV spectra of the complex and the ligand are shown in figure 6, where π–π^* (C=C and C=N) and π–π^* (C=O) absorption bands of the ligand appear near 221 and 263 nm, respectively. UV spectrum of the complex is similar to that of the ligand, corresponding absorption bands appear near 225 and 264 nm, respectively, with little bathochromic shift resulting from the ligand coordinating to Zn(II) increasing conjugation.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos 609197 for the complex. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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