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Article

A New 1D Chained Coordination Polymer: Synthesis, Crystal Structure, Antitumor Activity and Luminescent Property

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Abstract: A new 1D chained coordination polymer of Zn(II), $\{[Zn(L)_2(4,4'\text{-bipy})]\cdot(H_2O)\}_n$(**1**) (HL = *N*-acetyl-L-phenylalanine; 4,4′-bipy = 4,4′-bipyridine) has been synthesized and characterized by elemental analysis, IR and X-ray single crystal diffraction analysis. Theresults show that each asymmetric unit of Zn(II) complex belongs to monoclinic, space group $P2_1$ with a = 11.421(2) Å, b = 9.2213(17) Å, c = 15.188(3) Å,β = 106.112(3)°, V = 1536.7(5) Å^3, Z = 2, Dc = 1.444 g·cm^{-3}, μ = 0.857 mm^{-1}, F(000) = 696, and final R_1 = 0.0439, ωR_2 = 0.1013. The molecules form one-dimensional chained structure by its the bridging 4,4′-bipyridine ligands. The antitumor activities and luminescent properties of Zn(II) coordination polymer have also been investigated.

Keywords: *N*-acetyl-L-phenylalanine; Zn(II) coordination polymer; 1D chained structure; antitumor activity; luminescent property

1. Introduction

Coordination polymer materials have attracted more research interest because of their versatile applications in luminescent probe, catalysis, gas absorption, antitumor activity, and so on [1–13]. Over the past decade, A variety of Zn(II) coordination polymer derivatives, such as prophyrins [14], imidazole [15], phosphonate [16], carboxylate [17], amide [18], monoterpenes [19], tetra-(4-pyridyl)-butane [20], and

bipyridyl [21] complexes have been reported. Among them, carboxylate ligands are the most frequently used to construct coordination polymer because of their multiple coordination modes [22–27]. In addition, 4,4′-bipyridine ligand was frequently selected to study the effect on the structure of metal complex [28–30].

Based on the above investigation, in this paper, a new 1D chained coordination polymer of Zn(II), $\{[Zn(L)_2(4,4'\text{-bipy})]\cdot(H_2O)\}_n$, has been synthesized using *N*-acetyl-L-phenylalanine and 4,4′-bipyridine as ligands. The Zn(II) complex was characterized by elemental analysis, infrared spectroscopy, single-crystal X-ray crystallography and thermogravimetric analyses. The antitumor activities and luminescent properties of Zn(II) coordination polymer have also been investigated.

2. Results and Discussion

2.1. Structural Description of $\{[Zn(L)_2(4,4'\text{-bipy})]\cdot(H_2O)\}_n$ (1)

The result of X-ray diffraction reveals that the complex **1** crystallizes in monoclinic $P2_1$ space group. The coordination environment of Zn(II) ion of **1** is shown in Figure 1. The molecular packing arrangement is shown in Figure 2. The asymmetrical unit contains one Zn(II) ion, two *N*-acetyl-L-phenylalanine ligand, one 4,4′-bipy ligand, two coordinated H_2O molecules and one lattice H_2O molecule. Zn is six-coordinated and resides in a distorted octahedral environment defined by two oxygen atoms (O1, O5)from two *N*-acetyl-L-phenylalanine anions, two nitrogen atoms (N3, N4) from two different 4,4′-bipy,and two oxygen atoms (O6, O7) from two coordinated H_2O molecules. The molecules form one-dimensional chained structure by its the bridging 4,4′-bipyridine ligands (Figure 3). The one-dimensional chains form 3D framework structure by the interaction of π-π stacking and hydrogen bonds (Figure 4). The uncoordinated water molecule exists in the crystal through hydrogen bonds and enhances thestructure stability. The Zn-O lengths are in the range of 2.072(3)–2.254(3) Å (Zn1-O1 = 2.135(3) Å, Zn1-O5 = 2.072(3) Å, Zn1-O7 = 2.100(4) Å, Zn1-O6 = 2.254(3) Å), and the Zn-N lengths are in the range of 2.150(3)–2.166(3) Å (Zn1-N3 = 2.166(3) Å, Zn1-N4 = 2.150(3) Å), respectively. The carboxylate groups of *N*-acetyl-L-phenylalanine in **1** adopt monodentate chelating mode.

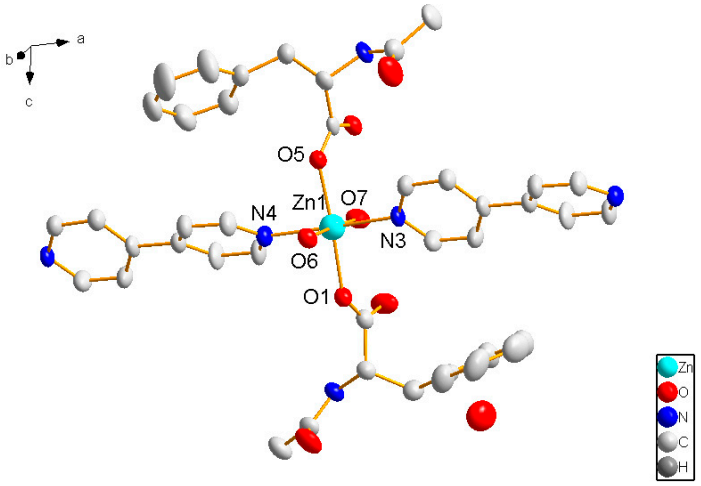

Figure 1. The coordination environment of Zn(II) in **1**.

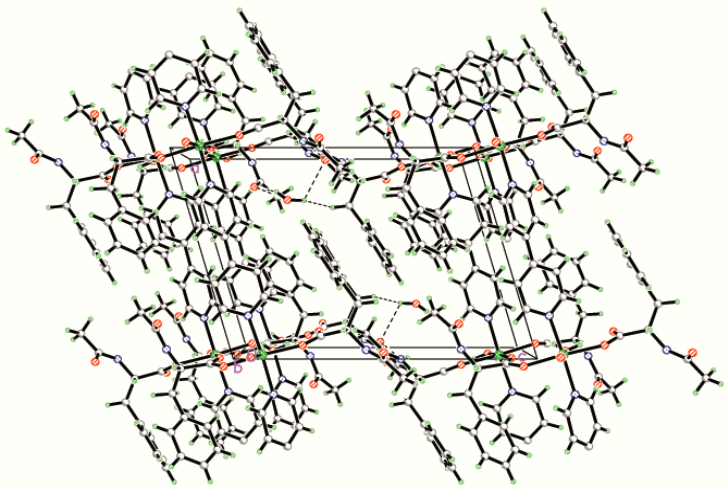

Figure 2. Crystal packing of **1**.

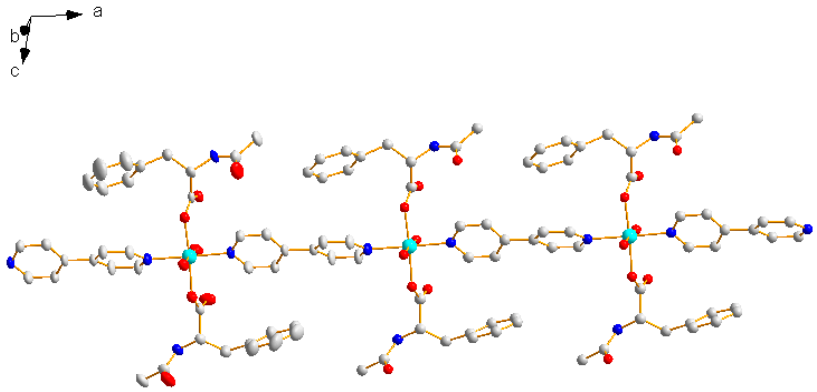

Figure 3. The 1D chained structure of **1**.

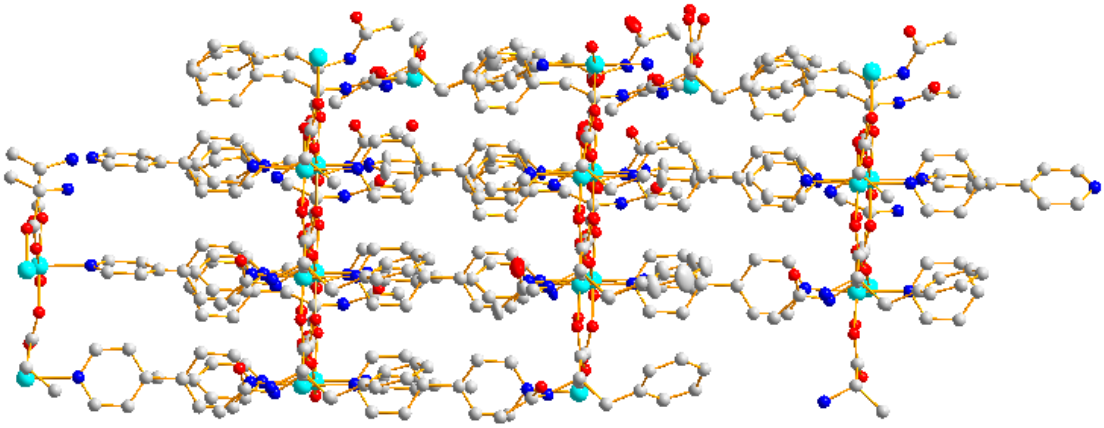

Figure 4. The 3D structure of **1**.

2.2. IR Spectra

The IR spectra of *N*-acetyl-L-phenylalanine ligand and complex **1**are shown in Figure 5. As shown in Figure 5, the free *N*-acetyl-L-phenylalanine ligand exhibits two sharp bands at 1695 $cm^{-1}$and 1552 cm^{-1}, and in complex **1**, they appear at 1602 $cm^{-1}$and 1433 cm^{-1}, respectively. This shows that the O atoms of $COO^{-}$are coordinated to Zn(II) ion [31].

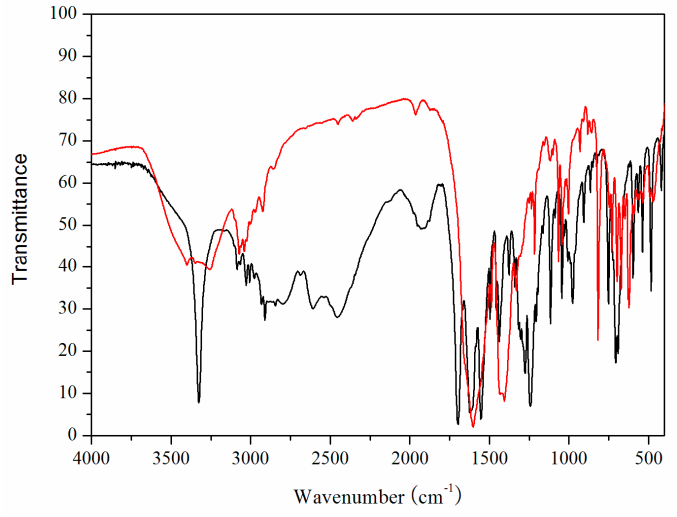

Figure 5. The IR spectra of *N*-acetyl-L-phenylalanine (black) and complex **1**(red).

2.3. AntitumorActivity

The antitumor activities of *N*-acetyl-L-phenylalanine ligand and complex **1** were tested against human hepatoma *SMMC-7721* cells, human lung adenocarcinoma *A549* cells and human colon carcinoma*WiDr*cells based on MTT method according to the literature procedure [32]. The results of antitumor activities of *N*-acetyl-L-phenylalanine ligand and complex **1** are given in Table 1. It can be seen that complex **1**exerted cytotoxic effect against human hepatoma *SMMC-7721* cells and human colon carcinoma *WiDr*cells, and *N*-acetyl-L-phenylalanine ligand exerted cytotoxic effect against human lung adenocarcinoma *A549* cells and human colon carcinoma *WiDr* cells. The antitumor effect against human hepatoma *SMMC-7721* of complex **1** is better than that of *N*-acetyl-L-phenylalanine ligand, and the antitumor effect against human colon carcinoma *WiDr* cells of *N*-acetyl-L-phenylalanine ligand is better than that of complex **1**.

Table 1. Antitumor activities of complex 1 and *N*-acetyl-L-phenylalanine ligand.

Compound	**IC_{50} (μg/mL)**		
	SMMC-7721	***WiDr***	***A549***
N-acetyl-L-phenylalanine	--	18 ± 0.3	28 ± 0.1
Complex **1**	12 ± 0.2	25 ± 0.9	--

--: no antitumor activity.

2.4. Luminescent Property

The luminescent spectrum of complex **1** was investigated in the solid state at room temperature. As shown in Figure 6, the ligand displays emission peak at 439 nm with excitation at 349 nm, which may be attributed to the π*-π or π-n transition. However, the *N*-acetyl-L-phenylalanine ligand does not display any emissions with excitation from 200 to 400 nm.

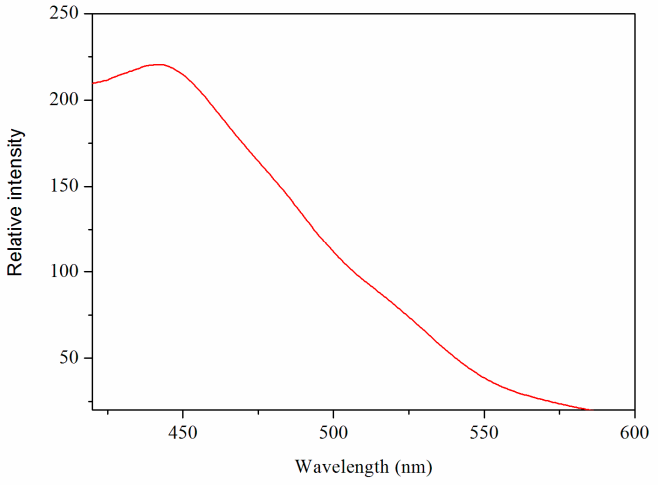

Figure 6. Luminescent spectrum of complex **1**.

3. Experimental Section

3.1. Materials and Instrumentation

N-acetyl-L-phenylalanine, 4,4′-bipyridine, $Zn(OAc)_2 \cdot 2H_2O$, NaOH and solvents were purchased commercially and used without further purification. Elemental analyses for C, H and N were carried out on a Elementar Vario III EL elemental analyzer. The FT-IR spectra were recorded in the range 4000–400 cm^{-1} on a Nicolet AVATAR 360 FTIR Spectrophotometer (Nicolet Instrument Inc., Madison, WI, USA). Luminescence spectra were measured on a PE LS-55 fluorescent spectrophotometer (PerkinElmer, Billerica, MA, USA). Single crystal data of $\{[Zn(L)_2(4,4'\text{-bipy})] \cdot (H_2O)\}_n$ were collected by a Bruker smart CCD diffractometer(Bruker, Billerica, MA, USA).

*3.2. Synthesis of $\{[Zn(L)_2(4,4'\text{-bipy})] \cdot (H_2O)\}_n$(**1**)*

A mixture of *N*-acetyl-L-phenylalanine (207 mg, 1.0 mmol), 4,4′-bipyridine (156 mg, 1.0 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (109 mg, 0.5 mmol), and NaOH (40 mg, 1.0 mmol) were dissolved in 15 mL mixed solvents of H_2O:CH_3OH (v:v = 1:2). The mixture was stirred for 6 h at 60 °C, and then colorless crystals were collected and dried in the air. Yield: 52%. Anal. Calcd. (%) for $C_{32}H_{34}N_4O_8Zn$: C, 57.49; H, 5.09; N, 8.38. Found (%): C, 57.22; H, 5.48; N, 8.67. IR data (KBr, cm^{-1}): 3257 (m), 3072 (w), 1602 (s), 1433 (s), 1066 (m), 818 (s), 731 (m), 698 (m), 673 (m), 622 (m), 474 (w).

3.3. Data Collection, Structural Determination,and Refinement

A colorless single crystal of the complex 1 with dimensions of 0.32 mm × 0.26 mm × 0.22 mm was selected and mounted on a glass fiber for data collection. The X-ray diffraction data were measured at 293(2) K on a Bruker smart CCD diffractometer with a graphite-monochromatized Mo*K*α (λ = 0.71073 Å) radiation. The structure was solved by direct methods with SHELXL-97 [33] and refined on F^2 by full-matrix least-squares procedures with SHELXTL-97 [33]. The non-hydrogen atoms were located refined anisotropically, and hydrogen atoms were added according to theoretical models. The crystal data of 1 are given in Table 2.

Table 2. Summary of crystalresult for Mg(II) complex.

Empirical Formula	**$C_{32}H_{34}N_4O_8Zn$**
Formula weight	668.00
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	11.421(2)
b/Å	9.2213(17)
c/Å	15.188(3)
β/°	106.112(3)
Volume/Å^3	1536.7(5)
Z	2
ρ_{calc}mg/mm^3	1.444
μ/mm^{-1}	0.857
S	1.005
F(000)	696
Index ranges	$-15 \le h \le 13$
	$-9 \le k \le 12$
	$-18 \le l \le 20$
Reflections collected	8997
Reflections with $I > 2\sigma(I)$	4217
Absolute structure parameter	0.026(16)
Independent reflections	5465 [R(int) = 0.0362]
Data/restraints/parameters	5465/1/411
Goodness-of-fit on F^2	1.005
Final *R* indexes [$\geq 2\sigma$ (*I*)]	*R*1 = 0.0439, *wR*2 = 0.1013
Final *R* indexes [all data]	*R*1 = 0.0711, *wR*2 = 0.1156
Largest diff. peak/hole/e Å^{-3}	0.87/−0.88

4. Conclusions

In summary, we have synthesized and characterized a new 1D chained coordination polymer of Zn(II). The results show that the molecules form one-dimensional chained structure by its the bridging 4,4′-bipyridine ligands. The antitumor activities and luminescent properties of Zn(II) coordinationpolymer have also been investigated. Based on the above results, more and more coordination polymers containing *N*-acetyl-L-phenylalanine and 4,4′-bipyridine ligands will be synthesized to study their novel structures and properties.

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Author Contributions

Xi-Shi Tai designed the method and wrote the manuscript. Hai-YingYou analyzed the crystal data for the Zn(II) coordination polymer. All authors have read and approved the final manuscript.

Conflicts of Interest

The authors confirm that this article content has no conflict of interest.

Appendix

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1055436. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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