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Synthesis, Crystal Structure, and Fluorescent Property of a Zn(II) Complex with *N*-Nicotinoylglycine Ligand

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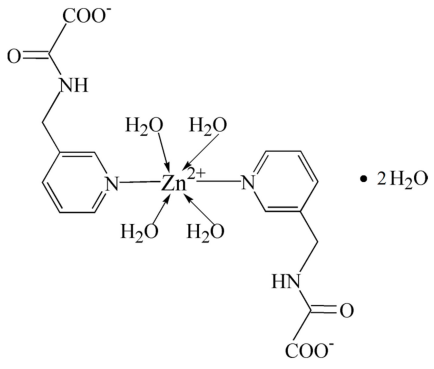
Abstract: A new Zn(II) complex, $[ZnL_2(H_2O)_4]\cdot 2H_2O$ (**1**) (HL = *N*-nicotinoylglycine), was synthesized by $Zn(OAc)_2\cdot 2H_2O$ with *N*-nicotinoylglycine in 95% ethanol solution. Its structure has been determined by single-crystal X-ray diffraction, elemental analysis, and infrared spectrum. The crystal analysis show that complex **1** crystallizes in triclinic, space group $P\bar{1}$. The Zn(II) ion, located on an inversion center, is coordinated by two N-nicotinoylglycine ligands through pyridine nitrogen and four water molecules. The crystal packing indicates 1D polymeric chains which expand into a 3D network structure by hydrogen bonds and $\pi\cdots\pi$ stacking. The luminescent properties of Zn(II) complex in solid state and in ethanol have also been investigated.

Keywords: Zn(II) complex; luminescence; carboxylic ligand; synthesis; crystal structure

1. Introduction

Nitrogen heterocyclic compounds have received much attention, because they have exhibited intriguing structures and potential practical applications in fluorescence [1–5], catalysis [6–8], electrochemistry [9], antitumor and antibacterial [10–13], gas adsorption [14], and chemical sensor [15,16]. Among ligands, nitrogen heterocyclic molecules and carboxylate ligands have been used widely to synthesize metal complexes because of their various coordination models [17–20]. Aiming to investigate the structure and fluorescent properties, a new Zn(II) complex, $[ZnL_2(H_2O)_4]\cdot 2H_2O$ (**1**) (HL = *N*-nicotinoylglycine), has been synthesized by $Zn(OAc)_2\cdot 2H_2O$ with *N*-nicotinoylglycine in 95% ethanol solution. Its structure has been determined by single-crystal X-ray diffraction, elemental analysis, and infrared spectrum. The fluorescent behaviors of Zn(II) complex in solid state and in ethanol solution have been investigated. The Zn(II) complex showed blue fluorescence both in solid state and in ethanol. The scheme depicting a chemical diagram of the Zn(II) complex is shown in Scheme 1.



Scheme 1. Chemical diagram of the Zn(II) complex.

2. Results and Discussion

2.1. Structural Description of Zn(II) Complex (1)

Zn(II) complex 1 crystallizes in triclinic system, space group $P\bar{1}$, and the crystallographic independent unit contains one *N*-nicotinoylglycine anion ligands, two coordinated water molecules, a lattice water molecule and one Zn(II) ion located on symmetry center. The coordination environment of the Zn(II) ion in 1 is shown in Figure 1, and a selection of bond lengths (Å) and angles (°) is listed in Table 1. From Figure 1, it can be seen that the Zn(II) ion is six-coordinated by the pyridine-N atoms of two *N*-nicotinoylglycine anion ligands and by four O atoms of water molecules, thus adopting an octahedral coordination geometry. The COO-groups of *N*-nicotinoylglycine ligand does not coordinate with Zn(II) ion, and the coordination environment in complex 1 is the same as that reported in literature for the nicotinoyl-glycine Mn(II) complex [21]. Complex 1 is linked by O-H···O hydrogen bonds to form 1D chained structure (Figure 2). The 1D chains further expand into a 3D network structure by hydrogen bonds and $\pi\cdots\pi$ stacking interactions (Figure 3). Details of the hydrogen bonds geometry for the Zn(II) complex are given in Table 2.

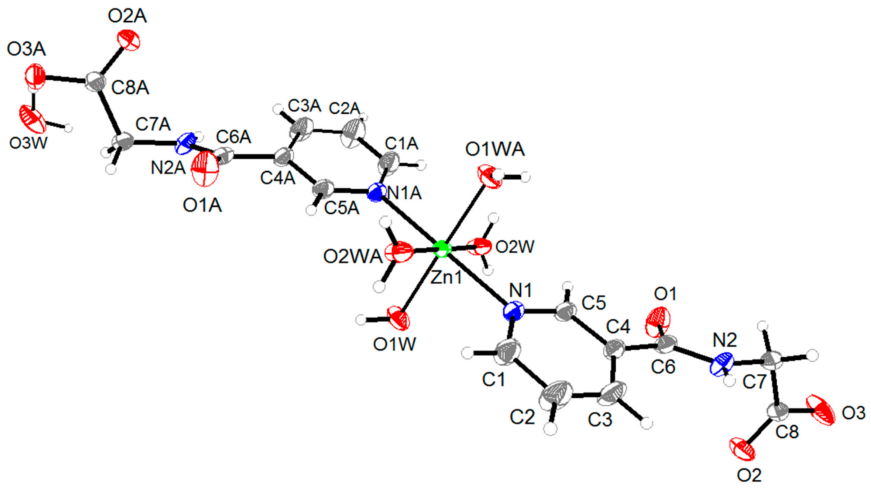


Figure 1. The coordination environment of Zn(II) ion, where the thermal ellipsoids were drawn at 30% possibility.

Table 1. Selected bond lengths (Å) and bond angles (°) for Zn(II) complex.

Bond	*d*	Bond	*d*
Zn1-O1W	2.067 (2)	Zn1-O2W	2.069 (2)
Zn1-N1	2.254 (3)	C7-N2	1.445 (4)
C6-O1	1.227 (4)	O2-C8	1.234 (4)
C8-O3	1.259 (4)	C1-N1	1.338 (5)
C5-N1	1.342 (4)	N2-C6	1.338 (4)
Angle	ω	Angle	ω
O1WA-Zn1-O1W	180.00 (14)	O1WA-Zn1-O2WA	89.89 (10)
O2WA-Zn1-O1W	90.11 (10)	O2W-Zn1-O2WA	180.0
O1WA-Zn1-N1	88.36 (11)	O1W-Zn1-N1	91.64 (11)
O2WA-Zn1-N1	89.84 (10)	O2W-Zn1-N1	90.16 (10)
N1A-Zn1-N1	180.00 (1)		

Symmetry transformation: A: $-x+2, -y+2, -z-1$.

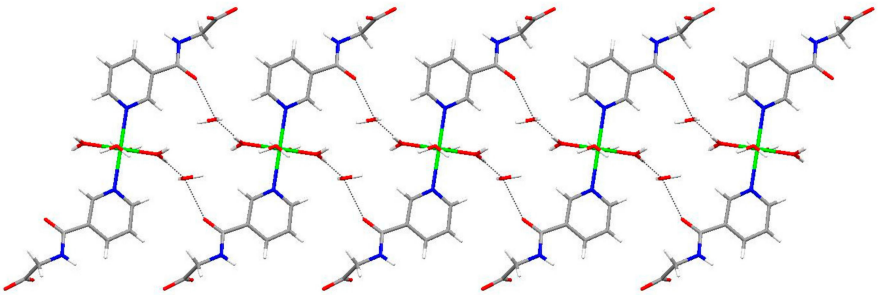


Figure 2. 1D chained structure by the hydrogen bonds.

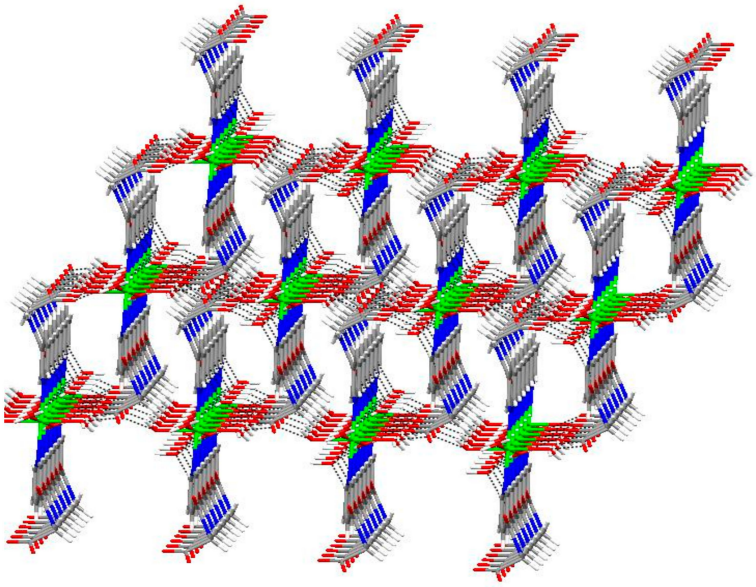


Figure 3. 3D supramolecular network structure by hydrogen bonds and π-π stacking.

Table 2. Hydrogen bonds data for Zn(II) complex.

Donor-H ... Acceptor	D-H	H ... A	D ... A	∠D-H ... A	Symmetry Transformation
O1W-H1WB ... O3	0.96	1.95	2.699 (4)	133	$-x+1, -y+1, -z$
O1W-H1WC ... O3	0.96	2.05	2.676 (4)	122	$x, y+1, z-1$
O2W-H2WA ... O2	0.86	1.81	2.649 (4)	164	$x, y+1, z-1$
O2W-H2WB ... O3W	0.86	1.82	2.672 (4)	168	$x+1, y+1, z-1$

2.2. IR Characterization of Zn(II) Complex

The IR spectrum of Zn(II) complex is shown in Figure 4. The characteristic absorption bands of Zn(II) complex appear at 3317 cm^{-1} (ν (N-H)), 1641 cm^{-1} (ν (C=O), 1577 cm^{-1}, 1471 cm^{-1} (pyridine) and 1236 cm^{-1} (ν (C-N)). The corresponding absorption peaks of *N*-nicotinoylglycine appear at 3309, 1643, 1598, 1431, and 11,238 cm^{-1}, respectively. It can be seen that only absorption peaks of pyridine changed, indicating that the N atom of pyridine takes part in coordination with Zn(II) ions [22]. The result of IR has been confirmed by single-crystal X-ray diffraction.

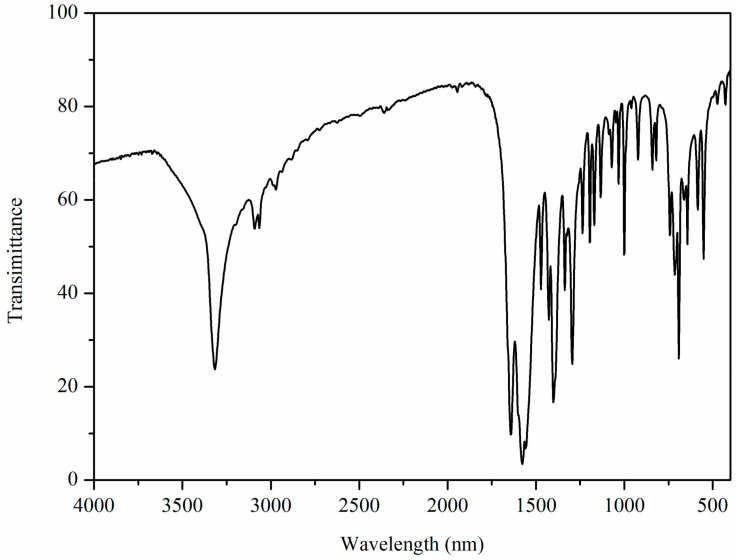


Figure 4. The IR spectrum of Zn(II) complex.

2.3. Fluorescent Properties

The fluorescent behaviors of Zn(II) complex in solid state and in ethanol solution have been investigated. The fluorescent spectra are shown in Figure 5. The Zn(II) complex exhibits fluorescent maximum peak at 461 nm (in solid state) and 441 nm (in ethanol solution) upon excitation at 391 nm. However, the *N*-nicotinoylglycine ligand does not have luminescent peak [23]. Indicating that the Zn(II) takes part in coordination with N-nicotinoylglycine ligand and Zn (II) complex can stably exist in ethanol solution.

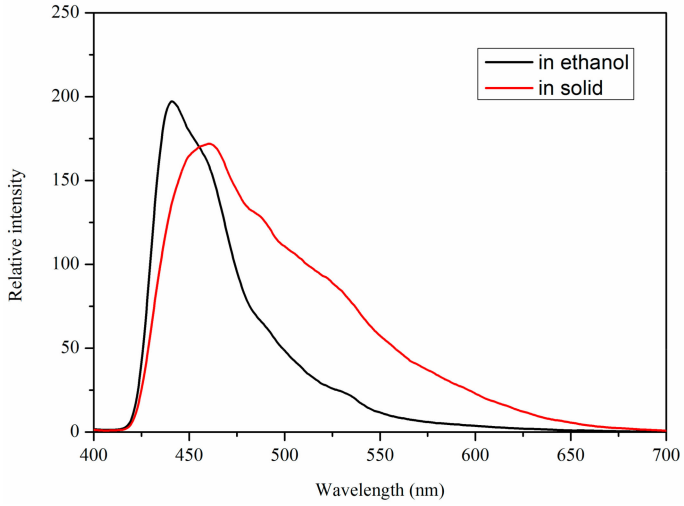


Figure 5. The fluorescent spectra of Zn(II) complex in solid and in ethanol. The excitation and emission slit widths were 5 nm.

3. Experimental Section

3.1. Materials and Instrumentation

The ligand *N*-nicotinoylglycine (A.R.) was obtained from Xi'ya Chemical Reagent Company (Jinan, China). $Zn(OAc)_2 \cdot 2H_2O$ (A.R.) and other chemicals were purchased from Shanghai Chemical Reagent Company (Shanghai, China). The elemental analysis for C, H, and N was carried out on an Elementar Vario III EL elemental analyzer (Hanau, Germany). IR spectra were recorded on a Nicolet

AVATAR 360 FTIR spectrophotometer (Nicolet Instrument Inc., Madison, WI, USA) (range 4000 cm^{-1} ~400 cm^{-1}) using KBr discs. Crystal data of $[ZnL_2(H_2O)_4]\cdot H_2O$ (**1**) was collected on a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA). Fluorescent spectra were performed on a PE LS-55 spectrometer (PerkinElmer, Waltham, MA, USA).

3.2. Synthesis of $[ZnL_2(H_2O)_4]\cdot H_2O$ (1)

The ligand *N*-nicotinoylglycine (1.0 mmol, 0.1802 g), $Zn(OAc)_2\cdot 2H_2O$ (0.5 mmol, 0.1097 g), and NaOH (1.0 mmol, 0.040 g) were added to 95% ethanol solution. The mixtures were stirred for 7 h at 60 °C. After cooling to room temperature, the mixtures were filtered, and then the filtrate was transferred to a 20 mL beaker. Light yellow crystals of $[ZnL_2(H_2O)_4]\cdot 2H_2O$ (**1**) were gained from filtrate after one month. Yield ca. 60%. Anal. Calcd. for $C_{16}H_{26}N_4O_{12}Zn$: C, 36.11; H, 4.89; N, 10.53. Found: C, 35.95; H, 5.07; N, 10.61. IR: 3317 cm^{-1} (s), 1641 cm^{-1} (s), 1577 cm^{-1} (s), 1471 cm^{-1} (m), 1471 cm^{-1} (s), 1336 cm^{-1} (w), 1294 cm^{-1} (m), 1236 cm^{-1} (m), 1195 cm^{-1} (w), 1170 cm^{-1} (w), 1134 cm^{-1} (w), 1070 cm^{-1} (w), 1031 cm^{-1} (w), 1001 cm^{-1} (w), 995 cm^{-1} (w), 922 cm^{-1} (w), 840 cm^{-1} (w), 692 cm^{-1} (s), 642 cm^{-1} (m), 549 cm^{-1} (m).

3.3. Crystal Data Collection and Structure Determination

The intensity data of single crystal of $[ZnL_2(H_2O)_4]\cdot 2H_2O$ (**1**) were collected on a Brucker Smart Apex CCD diffractometer using graphite-monochromated Mo*Kα* radiation (λ = 0.71073 Å) at 293 (2) K. Diffraction data were collected using ϕ-ω scan mode. Cell parameters were refined using Bruker SMART program. The Bruker SAINT program was used for data reduction. The structure was solved by direct method using the SHELXS-97 program [24], and refined on F^2 by full-matrix least squares with the SHELXL-97 program [24]. The key information of the crystal structure solutions and refinements is listed in Table 3. Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1540290. 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).

Table 3. Crystallographic data and structure refinement for Zn(II) complex.

Empirical formula	$C_{16}H_{26}N_4O_{12}Zn$
Formula weight	531.78
Temperature/K	293 (2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	7.7490 (15)
b/Å	8.8265 (18)
c/Å	8.9520 (18)
α/°	82.84 (3)
β/°	64.89 (3)
γ/°	80.80 (3)
Volume/Å^3	546.18 (19)
Z	1
ρ_{calc}mg/mm^3	1.617
μ/mm^{-1}	1.195
S	1.125
F(000)	276
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 10$, $-10 \le l \le 10$
Reflections collected	4227
Independent reflections	1910 [R (int) = 0.0669]
Data/restraints/parameters	1910/3/151
Goodness-of-fit on F^2	1.097
Final R indexes [I > = 2σ (I)]	R_1 = 0.0551, wR_2 = 0.1362
Final R indexes [all data]	R_1 = 0.0563, wR_2 = 0.1369
Largest diff. peak/hole/e Å^{-3}	0.641/−1.296

4. Conclusions

In summary, a new Zn(II) complex has been synthesized by $Zn(OAc)_2 \cdot 2H_2O$ with *N*-nicotinoylglycine in 95% ethanol solution. The complex **1** formd 1D chained structure and 3D network structure by hydrogen bonds and $\pi \cdots \pi$ stacking. The Zn(II) complex showed blue fluorescence both in solid state and in ethanol.

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Author Contributions: Zhang Yun-Chen synthesized the Zn(II) complex and wrote the manuscript.

Conflicts of Interest: The author declares no conflict of interest.

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