

Hydrothermal Synthesis, Crystal Structure and Properties of a New Binuclear Nickel(III) Complex with 3-(Pyridin-2-yl)-1,2,4-triazole^①

LI Chang-Hong^{a②} LI Yu-Lin^{b②}
LI Wei^{b②} KUANG Yun-Fei^b

^a (School of Materials and Chemical Engineering, Hunan Institute of Technology, Hengyang 421002, China)

^b (School of Chemistry and Materials Science, Hengyang Normal University, Hengyang 421008, China)

ABSTRACT A new binuclear nickel(II) complex Ni₂(HPT)₄(H₂O)₃ (**1**) has been hydrothermally synthesized with nickel hydroxide, 3,4-pyridine dicarboxylic acid and 3-(pyridin-2-yl)-1,2,4-triazole (HPT) in the mixed solution (the volume ratio of methanol and water is 1:4). It crystallizes in tetragonal space group $P4_2/n$, with $a = 20.844(1)$, $b = 20.844(1)$, $c = 7.2463(7)$ Å, $V = 3148.2(5)$ Å³, $D_c = 1.587$ g/cm³, $Z = 4$, $\mu(\text{MoK}\alpha) = 1.257$, $F(000) = 1544$, the final $GOOF = 1.043$, $R = 0.0437$ and $wR = 0.1297$. The crystal structure shows that the whole molecule consists of two nickel ions which are bridged by four $\mu_2\text{-}\eta^1:\eta^0$ -3-(pyridin-2-yl)-1,2,4-triazole anions. The coordination environment of Ni(II) ion is NiN₆, giving a distorted octahedral geometry. The thermal stability and fluorescent and magnetic properties of the complex were investigated.

Keywords: binuclear nickel(II) complex, thermal stability, fluorescent and magnetic properties;

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1 INTRODUCTION

The design and construction of coordination polymers are a fascinating area because of their interesting molecular topologies and potential applications such as gas adsorption and separation, luminescent sensors, molecule magnets, and catalysts^[1-3]. Triazoles and their derivatives are very important ligands with N–N donor centers that produce interesting network structures with novel topologies, which can adopt monodentate terminal or bidentate N,N'-bridging coordination mode and produce interesting network structures with novel topologies. It makes them easily link two adjacent metal ions to yield dinuclear, linear trinuclear, or linear polymeric metal compounds with double or triple triazole bridges^[4-6]. A large number of mononuclear, oligonuclear, and polynuclear metal coordination compounds with 1,2,4-triazole derivatives have been prepared and characterized because of their interesting properties^[7, 8]. Those compounds are mainly concentrated in copper complexes^[9-12], while coordination with nickel is relatively less investigated^[13-15]. 2,3-Pyridine

dicarboxylic acid which contains nitrogen atoms and carboxylic acid groups can participate in coordination to construct molecular structures of the complexes. As a very good organic ligand, 2,3-pyridine dicarboxylic acid is also an intermediate of niacin, nicotinamide, nikethamide, etc., and it has a very important application in industry^[16]. In this article, we use 3-(pyridin-2-yl)-1,2,4-triazole(HPT) as the main ligand and 2,3-pyridinedicarboxylic acid as the auxiliary ligand to react with nickel ion, and expect to obtain the complexes with novel structures. However, it is a pity that 2,3-pyridine-dicarboxylic acid failed to participate in the coordination, and only a binuclear nickel coordination polymer was obtained. We will continue to explore the reaction conditions in the future research and expect to obtain the ideal nickel complex structure.

2 EXPERIMENTAL

2.1 Materials and instruments

All reagents were of analytical grade and used as obtained

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② Corresponding authors. E-mail: lichanghong4444@126.com or li_weihnx@163.com

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from commercial sources without further purification. HPT was synthesized with the reference^[17]. Crystal structure determination was carried out on a Bruker SMART CCD 6000 single-crystal diffractometer. Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer. XT4 binocular microscope melting point apparatus was used to measure the melting point with thermometer unadjusted. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrophotometer using KBr discs. The fluorescent spectra for the powdered samples were measured on a RF-5301PC spectrofluorometer with a xenon arc lamp as the light source. Magnetic measurements in the range of 2~300 K were performed on a MPMS-SQUID magnetometer at a field of 2 kOe on a crystalline sample in the temperature settle mode. Thermogravimetric analyses were performed on a simultaneous SPRT-2 pyris1 thermal analyzer at a heating rate of 10 K/min.

2.2 Synthesis of 1

A mixture of 3,4-pyridine dicarboxylic acid (33.4 mg, 0.2 mmol), HPT (29.2 mg, 0.2 mmol), and Ni(OH)₂·4H₂O (27.6 mg, 0.3 mmol) was dissolved in 25 mL hydrothermal vessel of mixed solvent (The volume ratio of methanol and water is 1:4). The pH value of the resultant mixture was adjusted to 6.5 by adding ammonium hydroxide. The reaction was kept at 433 K for 72 h, and cooled to room temperature at the speed of 10 K·h⁻¹. Green crystals of **1** suitable for X-ray diffraction analysis were obtained in 72.65% yield based on the nickel element. m.p.: 569 K. Anal. Calcd. (%) for C₁₄H₁₃N₈NiO_{1.50}: C, 44.72; H, 3.48; N, 29.80. Found (%): C, 44.54; H, 3.47; N,

29.92. Main IR (KBr, cm⁻¹): IR (ν/cm⁻¹): 3323(s), 1609(vs), 1593(vs), 1481(vs), 1478(vs), 1373(m), 1265(w), 1144(m), 1022(w), 795(m), 725(vs), 677(w), 492(w).

2.3 Determination of the crystal structure

A single crystal with dimensions of 0.24mm × 0.23mm × 0.22mm was put on a Bruker SMART CCD 6000 diffractometer equipped with a graphite-monochromatic MoK α radiation ($\lambda = 0.71076 \text{ \AA}$) using an ω scan mode at 296(2) K. A total of 15383 reflections were collected in the range of $2.76 \leq \theta \leq 23.40^\circ$, of which 2768 were independent ($R_{\text{int}} = 0.0464$) and 2038 were observed ($R_{\text{sigma}} = 0.0335$, $I > 2\sigma(I)$). All data were corrected by Lp factors and empirical absorption. The crystal structure was solved directly by program SHELXS-2014, and refined by program SHELXL-2014^[18]. The hydrogen and non-hydrogen atoms were corrected by isotropic and anisotropic temperature factors respectively through full-matrix least-squares method. The final $R = 0.0437$, $wR = 0.1297$ ($w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 4.1029P]$, where $P = (F_o^2 + 2F_c^2)/3$), $(\Delta/\sigma)_{\text{max}} = 0.001$, $S = 1.043$, $(\Delta\rho)_{\text{max}} = 0.74$ and $(\Delta\rho)_{\text{min}} = -0.49 \text{ e \AA}^{-3}$.

3 RESULTS AND DISCUSSION

3.1 Crystal structure of 1

The coordination structure of **1** is revealed in Fig. 1, the one-dimensional chain of water with hydrogen bond of **1** is shown in Fig. 2, and its packing diagram is given in Fig. 3. Selected bond lengths and bond angles are shown in Table 1, and hydrogen bonds of the complex in Table 2.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) of Complex 1

Bond	Dist.	Bond	Dist.	Bond	Dist.
Ni(1)–N(5)	1.969(3)	Ni(1)–N(3)	1.987(3)	Ni(1)–N(2 ⁱ)	2.012(3)
Ni(1)–N(4)	2.086(3)	Ni(1)–N(6 ⁱⁱ)	2.359(3)	Ni(1)–N(8)	2.546(3)
Angle	(°)	Angle	(°)	Angle	(°)
N(5)–Ni(1)–N(3)	166.17(12)	N(5)–Ni(1)–N(2 ⁱ)	90.72(12)	N(3)–Ni(1)–N(2 ⁱ)	96.42(11)
N(5)–Ni(1)–N(4)	92.62(12)	N(3)–Ni(1)–N(4)	79.62(12)	N(4)–Ni(1)–N(2 ⁱ)	175.21(12)
N(5)–Ni(1)–N(6 ⁱⁱ)	100.77(11)	N(3)–Ni(1)–N(6 ⁱⁱ)	90.35(11)	N(2 ⁱ)–Ni(1)–N(6 ⁱⁱ)	95.54(11)
N(4)–Ni(1)–N(6 ⁱⁱ)	87.23(11)				

Symmetry transformations used to generate the equivalent atoms: i: 1 - x, 1 - y, 1 - z; ii: 1 - x, 1 - y, -z

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°)

D–H···A	D(D–H)	D(H···A)	D(D···A)	∠DHA
O(1)–H(1A)···O(2) ^a	0.85	1.994	2.746	147
O(1)–H(1B)···O(2) ^b	0.85	2.007	2.746	145
O(2)–H(2A)···N(1)	0.782	2.176	2.942	166
O(2)–H(2B)···O(1)	0.759	2.020	2.711	151

Symmetry transformations used to generate the equivalent atoms: (a): x - 1/2, -y + 1, z - 1/2; (b): -x + 1, y + 1/2, z - 1/2

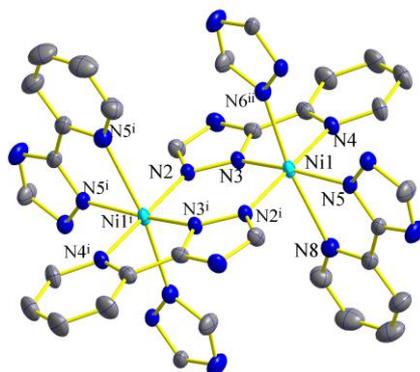


Fig. 1. Molecular structure with thermal ellipsoids drawn at the 30% probability level (The water molecules are deleted.) Symmetry codes: i: $1-x, 1-y, 1-z$; ii: $1-x, 1-y, -z$

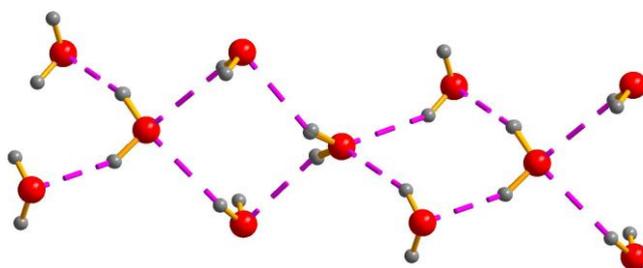


Fig. 2. One-dimensional chain of water with hydrogen bond of **1**

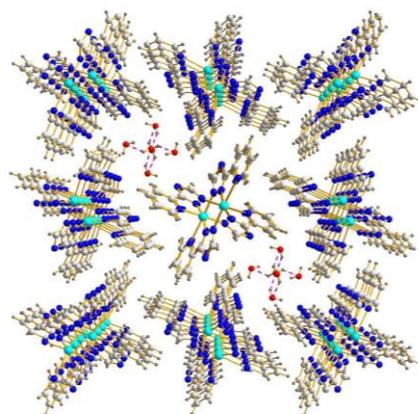


Fig. 3. Packing of complex **1**

Fig. 1 shows that the whole molecule of the complex consists of two nickel ions, four HPT anions and two water molecules. In the independent unit, two nickel ions are bridged by four $\mu_2\text{-}\eta^1\text{:}\eta^0$ 3-(pyridin-2-yl)-1,2,4-triazole anions with the Ni \cdots Ni distance to be 4.125 Å, which is close to that of the similar complex $[\text{Ni}_2(\text{C}_7\text{N}_4\text{H}_5)_3(\text{C}_9\text{H}_9\text{O}_2)]_n$ (Ni(1) \cdots Ni(2) = 4.230 Å)^[10] and $[\text{Cu}_2(\text{Hpt})(\text{CO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (Cu(1) \cdots Cu(2) = 4.065 Å)^[19]. The Ni(1) ion is coordinated with six nitrogen atoms from triazole rings (N(3), N(5), N(6A)) and pyridine rings (N(4), N(2A), N(8)) of four Hpt anions, forming distorted octahedral geometry. The Ni–N

bond lengths range from 1.970 to 2.546 Å, averaged by 2.160 Å which is longer than the value for the similar Ni(II) complex $[\text{Ni}_2(\text{C}_7\text{N}_4\text{H}_5)_3(\text{C}_9\text{H}_9\text{O}_2)]_n$ (Ni–N = 1.999 Å)^[10]. As shown in Fig. 2, there are clusters of water molecules in the molecule forming one-dimensional chains. From Table 2 and Fig. 3, another noticeable characteristic of **1** is the strong hydrogen bonding interactions, which exist between water and HPT molecules such as O(1)–H(1A) \cdots O(2A) (2.746 Å, 147°), O(1)–H(1B) \cdots O(2B) (2.746 Å, 145°), O(2)–H(2A) \cdots N(1) (2.942 Å, 166°), O(2)–H(2B) \cdots O(1) (2.711 Å, 151°). The shortest center distance between adjacent HPT group is

4.144 Å, larger than 3.700 Å, indicating a weak π - π stacking interaction between pyridine rings^[20]. These hydrogen bonding interactions and water molecule groups form a three-dimensional network structure.

3.2 Fluorescence of 1

The emission spectra of Ni(II) complexes **1** were studied in the solid state at room temperature and depicted in Fig. 3. There are emission bands at 435 nm ($\lambda_{\text{ex}} = 332$ nm) for **1**.

Such fluorescence emissions may be assigned to intra-ligand π - π^* transitions because the free HPT ligand exhibits a similar broad emission at 450 nm upon excitation at 340 nm. The emission band of **1** is blue-shifted by 15 nm as compared to the HPT ligand, which is attributed to the coordinative interactions between the metal atom and the ligand. Such emission bands may be tentatively assigned to ligand-to-metal charge transfer (LMCT)^[21].

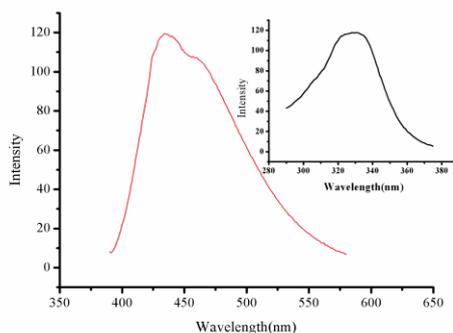


Fig. 4. Fluorescence of **1** in the solid state at room temperature
(Curve red: emission spectrum. Curve black: absorption spectrum)

3.3. Magnetic properties of 1

The temperature dependence of the magnetic susceptibility of **1** was investigated from 300 to 2 K with an applied magnetic field of 2 kOe. The $X_M T$ vs. T and $1/X_M$ vs. T curves are in Fig. 5. $X_M T$ of **1** increases with decreasing the temperature. It is $1.834 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 300 K, which is slightly larger than that for the same complex $[\text{Ni}_4(\text{L})_2(\text{m}_2\text{-OAc})_2(\text{m}_3\text{-OAc})_2] \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ ($X_M T = 3.42 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$)^[22] and $[\text{Ni}(\text{5-Br-ip})(\text{bib})]_n$ ($X_M T = 2.51 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$)^[23]. The linear regression equation is $1/\chi_M = 0.5434T + 0.0931$ with a

correlation coefficient of 0.9998. According to the Curie-Weiss law, from $\chi_M = C/(T-\theta)$, the Weiss constant θ can be obtained, $C = 1.840$ and $\theta = -0.17132$ K. These magnetic behaviors show that the title complex exhibits antiferromagnetism. In this work, the main magnetic interactions may be considered to occur between adjacent nickel(II) ions bridged by triazole rings (N(3), N(5), N(6A)) and pyridine rings (N(4), N(2A)), which is the same type of bridge in Cu(II) complexes^[24].

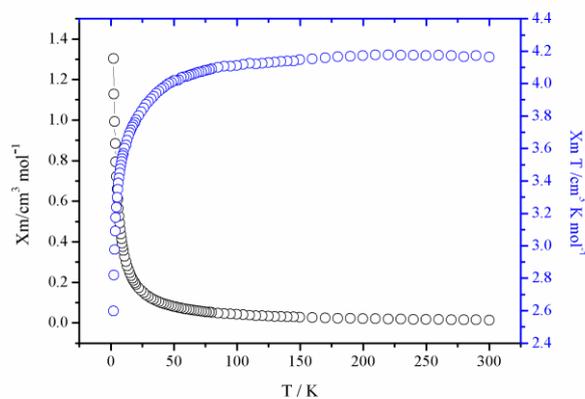


Fig. 5. Temperature dependence of the magnetic susceptibility of **1** in the form of $X_M T$ vs. T and $1/X_M$ vs. T

3.4 Thermal stability of **1**

The thermogravimetric analysis (Fig. 6) of **1** demonstrated that the weight loss of the complex in the air from room temperature to 873 K occurred mainly in 2 stages. The first stage occurs from 453~513 K with the weight loss of 4.81% resulting from the loss of one and half water molecules (calcd.:

4.79%). The second stage takes place from 513 to 693 K with the weight loss of 75.29% due to the departure of two HPT anions (calcd.: 77.65%). In air, the final product is nickel oxide with the final residual rate to be about 19.90% (calcd.: 17.56%).

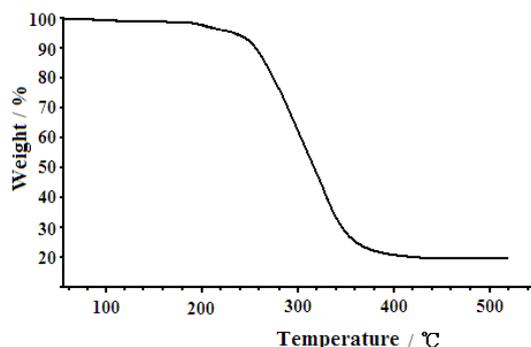


Fig. 6. TG of complex **1**

4 CONCLUSION

A new binuclear nickel(II) complex has been prepared by hydrothermal reaction and characterized by single-crystal X-ray diffraction. Our research shows that the thermal

stability shows that **1** is stabilized under 453 K, and gives off an intense fluorescence at around 332 nm. Magnetic properties indicates that **1** exhibits antiferromagnetism properties.

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