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antitumor activities<sup>[6-8]</sup>. Hydrazone Schiff base has long been paid considerable attention for its fascinating chemical behavior<sup>[9-10]</sup> and biological essentiality<sup>[11-13]</sup>. Of interest to structural chemists is the coordination ability of the hydrazone ligand through the nitrogen or oxygen electron-donating atoms that allows it to serve as either a multidentate or a bridging building block in structural assemblies.

In this paper, we describe the synthesis of Ni(II) complex with Hydrazone Schiff base ligand, and the crystal structure of the complex is reported.

## 1 Experimental

### 1.1 Materials and physical measurements

All reagents used were of analytical grade. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Vario EL III Elemental Analyzer. The infrared spectra (4 000~400 cm<sup>-1</sup>) were recorded by using KBr pellets on FTIR-8400 spectrometer. The crystal was determined on a AFC10/Saturn724 + diffractometer equipped with a graphite-monochromatized Mo K $\alpha$  ( $\lambda=0.071\ 073\ \text{nm}$ ). Thermal stability (TG-DTG) was recorded on a STA-449 instrument in Nitrogen atmosphere at a heating rate of 5 K·min<sup>-1</sup> in the temperature range 20~800 °C using platinum crucibles.

### 1.2 Synthesis of the title complex

A mixture of 2-(2-[[2-(3-Pyridylcarbonyl)hydrazone]methyl]phenoxy)acetic acid (0.1 mmol, 29.9 mg) and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.1 mmol, 24.9 mg) in 10 mL *N,N*-

dimethylformamide was placed in a Teflon-lined stainless steel vessel, heated to 120 °C for 5 d, and then cooled to room temperature over 48 h. The green suitable crystals for X-ray diffraction were obtained. (Yield: 58%). Anal Calcd for C<sub>21</sub>H<sub>25</sub>N<sub>5</sub>NiO<sub>6</sub> (%): C: 50.31, H: 4.89, N: 14.03; found (%):C: 50.18, H: 4.98, N: 13.92.

### 1.3 Crystallographic data collection and structure determination

A green single crystal of title complex was put on a AFC10/Saturn724 + diffractometer equipped with a graphite-monochromatic Mo K $\alpha$  ( $\lambda=0.071\ 073\ \text{nm}$ ) by using an Multi-scan mode at 93(2) K. In the range of 3.09° ≤  $\theta$  ≤ 27.50°, a total of 17 357 reflections were collected including 5 027 unique ones ( $R_{\text{int}}=0.029\ 6$ ), of which 4 601 were observed with  $I>2\sigma(I)$ . The structure was solved by direct methods with SHELXS-97<sup>[14]</sup>. All non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-squares technique using the SHELXL-97<sup>[15]</sup> program. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. The final  $R=0.028\ 6$ ,  $wR=0.067\ 3$  ( $w=1/[\sigma^2(F_o^2)+(0.033\ 6P)^2+0.639\ 0P]$ , where  $P=(F_o^2+2F_c^2)/3$ ,  $S=0.999$ ,  $(\Delta/\sigma)_{\text{max}}=0.001$ ,  $(\Delta\rho)_{\text{max}}=378$  and  $(\Delta\rho)_{\text{min}}=-348\ \text{e}\cdot\text{nm}^{-3}$  for the complex. A summary of the crystallographic data and details of the structure refinements are listed in Table 1 and the elected bond lengths and bond angles of the complex are listed in Table 2.

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Table 1 Crystallographic data for the complex

Empirical formula	C <sub>21</sub> H <sub>25</sub> N <sub>5</sub> NiO <sub>6</sub>	Size / mm	0.43×0.27×0.20
Formula weight	502.17	Limit indices	-18 ≤ $h$ ≤ 13, -21 ≤ $k$ ≤ 21, -12 ≤ $l$ ≤ 11
Color	Green	Absorption coefficient / mm <sup>-1</sup>	0.922
Temperature / K	93(2)	F(000)	1048
Wavelength / nm	0.071 073	$\theta$ range / (°)	3.09 ≤ $\theta$ ≤ 27.50
Crystal system	Orthorhombic	Reflections collected	17357
Space group	<i>Pna</i> 2 <sub>1</sub>	Independent reflections	5 027
$a$ / nm	1.444 4(2)	Reflections observed ( $I>2\sigma(I)$ )	4 601
$b$ / nm	1.622 1(3)	Goodness-of-fit on $F^2$	0.999
$c$ / nm	0.94795 (14)	$R_1, wR_2$ ( $I>2\sigma(I)$ )	0.028 6, 0.067 3
$V$ / nm <sup>3</sup>	2.221 1(6)	$R_1, wR_2$ (all data)	0.032 1, 0.068 7
$Z$	4	Largest diff. peak and hole / (e·nm <sup>-3</sup> )	378 and -348
$D_c$ / (g·cm <sup>-3</sup> )	1.502		

Table 2 Selected bond lengths (nm) and bond angles ( $^\circ$ )

Ni(1)-N(3)	0.197 2(2)	Ni(1)-O(2)	0.209 45(13)	Ni(1)-O(3)	0.198 16(16)
Ni(1)-N(1)#1	0.212 8(2)	Ni(1)-O(1)	0.202 58(15)	Ni(1)-O(5)	0.215 00(17)
N(1)-Ni(1)#2	0.212 8(2)				
N(3)-Ni(1)-O(3)	169.07(7)	O(3)-Ni(1)-N(1)#1	92.21(7)	N(3)-Ni(1)-O(1)	80.78(7)
O(1)-Ni(1)-N(1)#1	91.83(7)	O(3)-Ni(1)-O(1)	108.68(6)	O(2)-Ni(1)-N(1)#1	92.52(7)
N(3)-Ni(1)-O(2)	88.58(7)	N(3)-Ni(1)-O(5)	90.70(8)	O(3)-Ni(1)-O(2)	81.56(6)
O(3)-Ni(1)-O(5)	83.85(8)	O(1)-Ni(1)-O(2)	168.70(7)	O(1)-Ni(1)-O(5)	90.81(6)
N(3)-Ni(1)-N(1)#1	92.94(9)	O(2)-Ni(1)-O(5)	85.48(7)	N(1)#1-Ni(1)-O(5)	175.80(8)
C(3)-N(1)-Ni(1)#2	123.75(15)	C(7)-O(1)-Ni(1)	107.54(13)	C(9)-N(3)-Ni(1)	129.72(16)
C(5)-N(1)-Ni(1)#2	118.69(15)	N(2)-N(3)-Ni(1)	114.23(14)		

Symmetry transformation used to generate the equivalent atoms: #1:  $-x+1, -y+1, z+1/2$ ; #2:  $-x+1, -y+1, z-1/2$ .

## 2 Results and discussion

### 2.1 Crystal structure

Single-crystal X-ray diffraction analysis reveals that the title complex is a three-dimensional coordination polymer. It crystallizes in the Orthorhombic system, space group  $Pna2_1$ . The asymmetric unit consists of one Ni(II) atom, one 2-(2-[[2-(3-Pyridylcarbonyl)hydrazono]methyl]phenoxy)acetic acid ( $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_5$ ) ligand, one coordinated and one solvated *N,N*-dimethylformamide (DMF) molecules. As shown in Fig.1, Each Ni(II) ion is six-coordinated by three oxygen atoms and one nitrogen atom from 2-(2-[[2-(3-Pyridylcarbonyl)hydrazono]methyl]phenoxy)acetic acid molecule and one oxygen atom from *N,N*-dimethylformamide molecule and one nitrogen atom of adjacent pyridine ring, generating a distorted octahedral coordination geometry. In the  $\text{NiN}_2\text{O}_4$  octahedral, O(1), O(2), O(3) and N(3) locate at the equatorial plane, but O(5) and N(1#1) occupy the axial position. Bond angles O(3)-Ni(1)-O(2), N(3)-Ni(1)-O(2), N(3)-Ni(1)-O(1), O(3)-Ni(1)-O(1) are  $81.56(6)^\circ$ ,

$88.58(7)^\circ$ ,  $80.78(7)^\circ$  and  $108.68(6)^\circ$ , respectively. The sum of these angles is  $359.60^\circ$  (close to  $360^\circ$ ), suggesting a planar nature of O(1), O(2), O(3), N(3) and Ni(1). The Ni-O bond lengths, 0.198 16(16), 0.202 58(15), 0.209 45(13) and 0.215 00(17) nm; the Ni-N bond lengths, 0.197 2(2) and 0.212 8(2) nm. The Ni-O and Ni-N bond lengths for the complex are comparable to that found in similar types of Ni(II) octahedral complexes<sup>[16-17]</sup>. The coordination geometry is distorted from octahedral as ascertained by the observed  $\tau$  value of 0.11 (the structure index is defined as  $\tau = (\beta - \alpha)/60$ , where  $\alpha$  and  $\beta$  are the largest coordination angles,  $\beta = \text{N}(1\#1)\text{-Ni}(1)\text{-O}(5)$   $175.8^\circ$  and  $\alpha = \text{N}(3)\text{-Ni}(1)\text{-O}(3)$   $169.1^\circ$ ), such a type of octahedral geometry was observed in similar Ni(II) complexes ( $\tau = 0.07$ )<sup>[18]</sup>.

In this complex, the ligand molecule chelated with one Ni atom to form two five-membered rings and one six-membered rings, which is connected by Ni(1)-N(1#1) to produce a zigzag coordination polymer (Fig. 2). The 2-(2-[[2-(3-Pyridylcarbonyl)hydrazono]methyl]

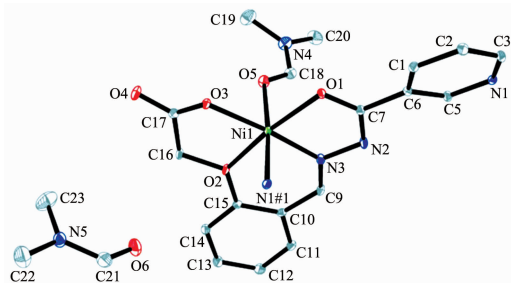


Fig.1 ORTEP diagram showing the coordination environments for Ni atom in the complex

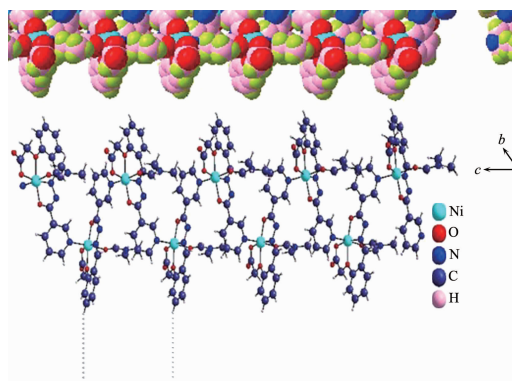


Fig.2 Perspective view of one-dimensional chain

phenoxy)acetic acid ligand in the complex adopts a twist conformation, in which the dihedral angle between pyridine ring and benzene ring is  $29.2^\circ$ , and the Ni(1)-O(5) and Ni(1)-N(1#1) bond form into the rotation axis.

## 2.2 IR spectrum analysis

IR spectra were measured in KBr discs using a FTIR-8400 spectrometer in the range from  $4\,000\sim 400\text{ cm}^{-1}$ . The IR spectra of the complex display a strong absorption at  $1\,630\text{ cm}^{-1}$ , which is assigned to a  $\text{-C=N-}$  group stretching mode in the Schiff base. There are also strong absorption at  $1\,207$ ,  $1\,379$ ,  $1\,518\text{ cm}^{-1}$ , which is assigned respectively to C-O-C of 2-(2-formylphenoxy)acetic acid,  $\text{-CH}_3$  stretching mode in DMF,  $\text{-C=C-}$  double bond in the benzene.

## 2.3 Thermal analysis

In the nitrogen atmosphere, there are three

weight loss stages from room temperature to  $800^\circ\text{C}$ . The first stage occurs at  $140\sim 217^\circ\text{C}$  with weight loss of 14.39%, corresponding to the release of one free *N,N*-dimethyl-formamide molecule (theoretical value: 14.54%). The second takes place from  $217\sim 362^\circ\text{C}$  with weight loss of 39.75%, which could be attributed to the removal of pyridine formyl hydrazine molecule and combined *N,N*-dimethylformamide molecule (theoretical value: 41.22%). The third appears from  $362\sim 650^\circ\text{C}$  with weight loss of 28.93%, resulting from the loss of 2-(2-formylphenoxy)acetic acid molecule (theoretical value: 29.87%). The ultimate 16.93% remains is NiO (theoretical value: 14.37%). The thermal measurement is in good agreement with the structural analysis, so thermal decomposition of the title compound can be regarded as follow:



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