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新型吡啶基羧酸席夫碱配体镍配合物的合成和晶体结构

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摘要:通过新合成的吡啶基羧酸席夫碱配体(5-(吡啶基-3-亚甲基氨基)间苯二甲酸 H_2L),和镍盐反应制备了一个新的镍配合物 $\{[Ni(HL)_2(H_2O)_2]\cdot 2H_2O\}_n$ (**1**),利用元素分析及 X-射线单晶衍射对其进行了表征。结构分析结果表明标题化合物属于三斜晶系,$P\bar{1}$ 空间群,晶胞参数为 a=0.764 79(11) nm,b=0.870 49(13) nm,c=1.081 13(16) nm,α=85.583(2)°,β=82.614(2)°,γ=81.565(2)°,V=0.704 82(18) nm^3,Z=1,D_c=1.586 g·cm^{-3},μ=0.763 mm^{-1},F(000)=350。在配合物的结构中,Ni(Ⅱ)的配位构型为畸变的八面体。配合物中每个配体通过羧酸氧和吡啶氮原子和金属配位形成一维链状结构,并通过体系中丰富的氢键作用链接成为三维框架并加以稳定。

关键词:自组装;晶体结构;镍配合物;席夫碱
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A New Nickel(Ⅱ) Complex Based on Novel Pyridyl-carboxylate Schiff-Base Ligand: Synthesis and Crystal Structure

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Abstract: A novel nickel(Ⅱ) coordination polymer $\{[Ni(HL)_2(H_2O)_2]\cdot 2H_2O\}_n$ (H_2L=5-((pyridin-3-ylmethyl)amino) isophthalic acid) (**1**) has been synthesized by the reaction of $Ni(NO_3)_2\cdot 6H_2O$ and H_2L under hydrothermal condition. The structure of 1 was determined by single-crystal X-ray diffraction. Complex 1 crystallizes in triclinic space group $P\bar{1}$ with a=0.764 79(11) nm, b=0.870 49(13) nm, c=1.081 13(16) nm, α=85.583(2)°, β=82.614(2)°, γ=81.565(2)°, V=0.704 82(18) nm^3, Z=1, D_c=1.586 g·cm^{-3}, μ=0.763 mm^{-1} and F(000)=350. The coordination environment of Ni(Ⅱ) is octahedral, and each ligand links two Ni(Ⅱ) atoms using its pyridyl N atom and carboxylate O atom to generate an infinite one-dimensional (1D) chain structure. The 1D chains are further connected by hydrogen bonds to give a three dimensional structure. CCDC: 769438.

Key words: self-assembly; crystal structure; nickel(Ⅱ) complex; Schiff-base ligand

During the past decade, many chemists have focused their efforts on the synthesis and investigation of highly organized metal-organic frameworks (MOFs) due to their fantastic structural diversities[1-2] as well as potential applications in many areas including gas storage[3], anion exchange[4], catalysis[5] and so on[6-7]. Up to now, multidentate N- or O-donor ligands have been widely used and many MOFs have been constructed by

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the reactions of N-containing or O-containing ligands with corresponding metal salts, such as 1,3,5-Tris (imidazol-1-yimethyl)benzene[8], 1,3,5-benzenetriacetic acid[9], and benzenedicarboxylic acid[10].

Our research is concentrated on the synthesis of coordination polymers based on N,O-bifunctional ligands. Due to the different coordination abilities of N, O atoms to transition or rare-earth metals, the ligands containing both N and O as coordination donors are now often used to synthesize hetero-metallic lanthanide-transition metal complexes[11], which have attracted many attentions due to their special value in investigation on the nature of the magnetic exchange interactions between 3*d* and 4*f* metal ions in magnetic materials that contain rare earth metals[12]. Meanwhile, Schiff-base ligands have also attracted many attentions of chemists in the past few years[13-14] because of the convenience in synthesis, good coordination ability and wide applications of Schiff-base complexes. Herein, we report the hydrothermal synthesis and crystal structure of a new nickel(Ⅱ) complex based on novel pyridyl-carboxylate Schiff-base ligand.

1 Experimental

1.1 General

All commercially available chemicals are of reagent grade and used as received without further purification. Solvents were purified according to the standard methods. C, H and N analyses were made on Elementar Vario EL-Ⅲ elemental analyzer. Infrared (IR) spectra were recorded on Nicolet AVATAR 360 FTIR spectrophotometer by using KBr discs. ^{1}H NMR spectra were recorded on the Bruker DRX-500 spectrometer.

1.2 Structure determinations

A suitable colorless single crystal with dimensions of 0.30 mm×0.30 mm×0.10 mm was selected for data collection at 296 K, using a Bruker Smart Apex Ⅱ CCD equipped with a Mo $K\alpha$ radiation (λ=0.071 073 nm). The structures were solved by direct methods with SHELXS-97 program[15] and refined with SHELXL-97[16] by full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The hydrogen atoms except for those of water molecules were generated geometrically. The details of the crystal parameters, data collection and refinement for the compounds are summarized in Table 1, and selected bond lengths and angels with their estimated standard deviations of **1** are listed in Table 2. The hydrogen bond lengths and bond angles are listed in Table 3.

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Table 1 Crystallographic data for complex 1

Empirical formula	$C_{28}H_{30}N_4NiO_4$	Z	1
Formula weight	673.27	D_c / (g·cm^{-3})	1.586
Temperature / K	293	Absorption coefficient / mm^{-1}	0.763
Crystal system	Triclinic	F(000)	350
Space group	$P\bar{1}$	θ range / (°)	1.90~25.50
a / nm	0.764 79(11)	Reflections collected	3 572
b / nm	0.870 49(13)	Independent reflections	2 448
c / nm	1.081 13(16)	R_{int}	0.022 8
α / (°)	85.583(2)	Goodness of-fit on F^2	0.992
β / (°)	82.614(2)	R (I>2σ(I))	0.035 5
γ / (°)	81.565(2)	wR (I>2σ(I))	0.075 7[a]
V / nm^3	0.704 82(18)		

[a] w=1/[σ^2(F_o^2)+(0.034 9P)^2] where P=(F_o^2+2F_c^2)/3.

Table 2 Selected bond lengths (nm) and bond angles (°) for complex 1

Ni1-O1	0.202 31(15)	Ni1-O1#1	0.202 31(15)	Ni1-O1W	0.209 89(17)
Ni1-O1W#1	0.209 89(17)	Ni1-N1#2	0.210 4(2)	Ni1-N1#3	0.210 4(2)

Continued Table 2

O1-Ni1-O1W	89.58(7)	O1#1-Ni1-O1W	90.42(7)	O1-Ni1-O1W#1	90.42(7)
O1#1-Ni1-O1W#1	89.58(7)	O1W-Ni1-O1W#1	179.999(1)	O1-Ni1-N1#2	90.53(7)
O1#1-Ni1-N1#2	89.47(7)	O1W-Ni1-N1#2	89.50(7)	O1W#1-Ni1-N1#2	90.50(7)
O1-Ni1-N1#3	89.47(7)	O1#1-Ni1-N1#3	90.53(7)	O1W-Ni1-N1#3	90.50(7)
O1W#1-Ni1-N1#3	89.50(7)	N1#2-Ni1-N1#3	180.0		

Symmetry codes: #1: $-x+1, -y+2, -z-1$; #2: $x, y, z-1$; #3: $-x+1, -y+2, -z$.

Table 3　Hydrogen bond lengths and bond angles for 1

D–H…A	*d*(D-H) / nm	*d*(H-A) / nm	*d*(D…A) / nm	∠DHA / (°)
O2W–H2WA…O3#1	0.085(3)	0.219(3)	0.303 4(3)	174(3)
N2–H2…O2#2	0.086	0.210	0.291 6(3)	158
O2W–H2WB…O2#3	0.086(4)	0.202(4)	0.286 2(3)	167(4)
O1W–H1WB…O2W#1	0.092(3)	0.187(3)	0.277 7(3)	171(3)
O4–H4A…O3#4	0.090(4)	0.178(4)	0.267 9(2)	177(3)
C11–H11…O1W#1	0.093	0.257	0.335 5(3)	143

Symmetry codes: #1: $1-x, 1-y, -z$; #2: $-x, 2-y, -z$; #3: $-x, 1-y, -z$; #4: $2-x, 1-y, -z$.

1.3　Synthesis of 5-((pyridin-3-ylmethyl)amino) isophthalic acid (H_2L)

The ligand was synthesized according to the previously reported literatures[17]. To a dry CH_3OH solution (30 mL) of 5-aminoisophthalic acid (50 mmol, 9.050 g) was slowly added 3-picolinaldehyde (50 mmol, 5.360 g) in 25 mL CH_3OH. The resulting yellow solution was stirred over night and then refluxed for 8 h. After been cooled to room temperature, excess $NaBH_4$ was added. The pH value of the solution was adjusted to 5.5 with HCl and the pale yellow precipitate was collected, washed with water and recrystallized in ethanol/H_2O solution. The ligand was obtained in 75% yield. FTIR (KBr pellet, cm^{-1}): 1 677s, 1 672s, 1 566m, 1 525s, 1 469s, 1 437m, 1 421m, 1 315s, 1 288s, 1 174s, 835m, 777m, 763m. ^1H NMR (500 MHz, d_6-DMSO, ppm): δ: 8.52(s, 1H), 8.44(d, 1H), 7.90(t, 2H), 7.58(s, 2H), 7.38(t, 1H), 4.39(s, 2H).

1.4　Synthesis of $Ni(HL)_2(H_2O)_2 \cdot 2H_2O$ (1)

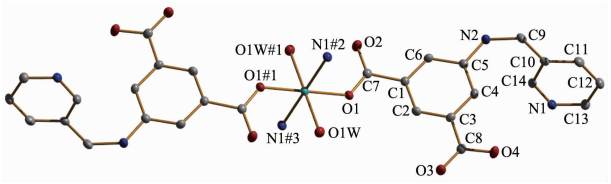
Complex **1** was synthesized by hydrothermal method. To a suspension of H_2L (0.027 g, 0.1 mmol) in 10 mL water was added NaOH (0.008 g, 0.2 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (0.029 g, 0.1 mmol), and 2 mL C_2H_5OH. After being stirred for 30 min, the resulting solution was sealed into a bomb equipped with a Teflon liner and heated at 120 ℃ for 72 h. After slow cooling of the reaction mixture to room temperature, green crystals of **1** suitable for X-ray analysis were obtained in 55% yield. Anal. Calcd. for $C_{28}H_{30}N_4Ni_1O_{12}$(%): C 49.95, H 4.50, N 8.32; found(%): C 50.01, H 4.56, N 8.33.

2　Results and discussion

2.1　Structure description

Complex **1** was prepared by the reaction of $Ni(NO_3) \cdot 6H_2O$ with the sodium salt of H_2L ligand in C_2H_5OH/H_2O system and crystallized in triclinic system, space group $P\bar{1}$. The coordination environment around Ni(Ⅱ) centers are depicted in Fig.1. In complex **1**, the Ni(Ⅱ) ions are six coordinated, where the equatorial plane is completed by two coordinated water molecules and two carboxylic O atoms from two different ligands with Ni-O distance of 0.202 31(15) and 0.209 89(17) nm, respectively. The apical positions are occupied by two N atoms from another two different ligands with Ni-N distance of 0.210 4(2) nm, and the N-Ni-O, O-Ni-O and N-Ni-N bond angles vary from 89.47(7)° to 180°. Thus, the coordination geometry of the six-coordinated Ni(Ⅱ) center can be regarded as a slightly distorted octahedral in N_2O_4 set. It is interesting that although double base has been used, there are still half carboxylate groups are not deprotonated, which just do not participate in the coordination to the metal centers. On the other hand, the deprotonated carboxylate groups coordinate to Ni(Ⅱ) with μ_1-η^1:η^0 coordination mode.

In complex **1**, each ligand coordinates to two Ni(Ⅱ) ions with its pyridyl and deprotonated carboxylate



Symmetry codes: #1: $-x+1, -y+2, -z-1$; #2: $x, y, z-1$; #3: $-x+1, -y+2, -z$; Ellipsoid probability was drawn at 30%, the hydrogen atoms and uncoordinated water molecules were omitted for clarity

Fig.1 Coordination environment around Ni(Ⅱ) center in complex **1**

groups, and each metal ions links two ligand to form a 22-membered macrocycle, where the Ni…Ni distances are 1.081 nm. The two benzene rings in one cycle are parallel to each other with centroid…centroid distance of 0.412 nm, indicating the existence of rather weak π …π interaction between the two aromatic rings (Fig.2)[18]. The dihedral angle of benzene ring and pyridyl ring of the ligand is 73.5°. This macrocycle spread along *c* axis to form a one-dimensional chain structure in **1**.

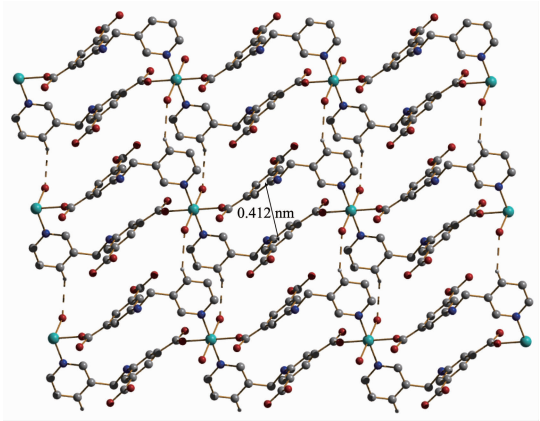


Fig.2 2D network structure of complex **1** linked by C–H …O hydrogen bonds viewing along the *a* axis, where the uncoordinated water molecules were omitted for clarity

The 1D chains are further connected by hydrogen bonds to give a three-dimensional (3D) structure[19-20]. The hydrogen bonding data of **1** are summarized in Table 2. First, the C11…O1W#1 distance of 0.335 3(3) nm and C11-H11-O1W#1 angle of 143° indicate the formation of C11-H11 … O1W#1 hydrogen bond between the neighboring 1D chains, which link the 1D chains to produce a two-dimensional (2D) network (Fig. 2). Furthermore, such 2D networks are linked by another O2W–H2WA…O3#1, N2–H2…O2#2, O2W–H2WB…O2#3, O1W–H1WB…O2W#1, O4–H4A…O3#4 hydrogen bonds (Table 2) to generate 3D framework. The results reveal that the hydrogen bonds play important role in stabilizing the whole structure of complex **1**. The investigations on reactions of ligand H_2L with other metal salts are still in progress.

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