研究简报

N-苯基亚氨基二乙酸镍二维网状配合物的合成及结构表征

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Synthesis and Structure of 2D Nickel(Ⅱ) Coordination Compound with Phenyl-Iminodiacetic Acid

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Abstract: A new nickel(Ⅱ) coordination compound $[Ni(L^{2-})(2,2'\text{-bipy})(H_2O)]\cdot 2H_2O$ (H_2L=phenyliminodiacetic acid) was obtained by self-assembly of phenyliminodiacetic acid, 2,2′-bipy, and $NiCl_2\cdot 6H_2O$ in the mixed solvent of water and ethanol (V:V=1:1). The complex was characterized by elemental analysis, IR spectra, and X-ray crystallography analysis. The crystal is monoclinic, space group $P2_1/c$ with a=0.867 4(2) nm, b=0.907 3(1) nm, c=2.643 5(5) nm, β=91.01(1)°, V=2.080 2(4) nm^3, Z=4, F(000)=992, D_c=1.520 Mg·m^{-3}, R_1=0.027 0 and wR_2=0.067 5. In the complex, nickel (Ⅱ) atom is coordinated with a distorted octahedral geometry and extensive hydrogen bonds link the complexes into a 2D network structure. CCDC: 244926.

Key words: phenyl-iminodiacetic acid; hydrogen bond; crystal structure; Ni(Ⅱ) complex

0 Introduction

The study of amino-acid compounds and their derivatives have received much attention in recent years because of the functional groups on their coordination geometry and biological relevance[1~5]. Amino-acid compounds are excellent complexing agents to chelate metal through its amino and carboxyl groups[6]. It may provide an additional metal binding site or undergo various weak interactions when the side chain has a functional group. Gao and his co-workers[7] have studied the coordination chemistry of several amino-multiacid groups in recent years. The amino-acid derivatives, such as amino-biacid compounds, can provide multi bonding sites, with which metal ions can been coordinated to form many kinds of clusters and 1D, 2D, 3D crystal structures[7~10]. But transitional metal complexes with phenyliminodiacetic acid, a derivative of amino-carboxylic acid, were reported rarely[11]. In this paper, we report the synthesis and structure of a new nickel complex $[Ni(L^{2-})(2,2'\text{-bipy})(H_2O)]\cdot 2H_2O$ (H_2L=phenyliminodiacetic acid). It is shown that the complex was linked into a 2D network structure through extensive hydrogen bonds.

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1 Experiment

1.1 Materials and instrumentation

All materials were of analytical grade and used without further purified. Analyses of C, H, and N were performed on a German Elementar Vario EL instrument. IR spectra were measured using KBr pellets with Avatar 360 spectrophotometer in the range of 400~4 000 cm^{-1}. Thermal analysis was carried out on a Netzsch TG 209 thermal analyzer.

1.2 Synthesis

The ligand phenyliminodiacetic acid (H_2L) was synthesized according to a reported method with minor modification[11]. Phenylamine, chloroacetic acid and sodium carbonate were mixed in a 1:2:2 molar ratio in aqueous solution. The mixture was stirred and refluxed for 4 h, giving a light brown lucid solution. After cooling to room temperature, the solution was acidified with hydrochloric acid till pH≈1. The resulting precipitate was collected and re-crystallized with boil water. H_2L was finally obtained after dried in air. Yield: 83%, Anal. Calcd.(%) for $C_{10}H_{11}NO_4$.: C 57.41, H 5.30, N 6.70; Found(%): C 57.32, H 5.49, N 6.67.

H_2L (0.21 g, 1.00 mmol), 2,2′-bipy (0.18 g, 1.15 mmol) and $NiCl_2·6H_2O$ (0.52 g, 2.19 mmol) were dissolved together in 20 mL mixed solvent of water and ethanol (V:V=1:1). The solution was adjusted carefully to pH=5 using dilute aqueous solution of NaOH, and was kept at room temperature after filtration. After three days, deep blue crystals were obtained by slow evaporation of the solution. The C, H, and N was determined by elemental analysis (Anal. Calcd.(%) for $C_{20}H_{23}N_3NiO_7$: C 50.45, H 4.87, N 8.83; Found(%): C 50.62, H 4.77, N 8.91).

1.3 Crystal structural determination

A single crystal with dimensions 0.52 mm × 0.46 mm × 0.46 mm was used for structural determination at 296(2) K with graphite monochromatic Mo $K\alpha$ radiatio (λ=0.071 073 nm) on a Siemens P4 Four-Circle diffractometer. A total of 4 460 reflections were collected in the range from 1.54° to 25.25° and 3 759 (R_{int}=0.012 9) were unique. The structure was solved by the direct method using SHELXS-97 program, and refinement on F^2 was performed in SHELXL-97[12] program by using full-matrix least-squares. All hydrogen atoms were placed in calculated position. The final refinements converged R_1=0.027 0 and wR_2=0.067 5 with 2 980 ($I>2\sigma$), GOF=1.039. The largest peak and deepest hole are 245 and −243 e·nm^{-3} respectively. The details of the structure collection and refinement are list in Table 1.

Table 1 Crystallographic data for the title compound

Empirical formula	$C_{20}H_{23}N_3NiO_7$
Formula weight	476.12
Temperature / K	296(2)
Wavelength / nm	0.071 073
Crystal system	Monoclinic
Space group	$P2_1/c$
a / nm	0.867 4(2)
b / nm	0.907 3(1)
c / nm	2.643 5(5)
β / (°)	91.01(1)
Volume / nm^3	2.080 2(4)
Z	4
Calculated density / (Mg·m^{-3})	1.520
Absorption coefficient / mm^{-1}	0.981
F(000)	992
Crystal size / mm	0.52 × 0.46 × 0.46
θ range for data collection / (°)	1.54 to 25.25
Limiting indices	$0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 10$, $-31 \leqslant l \leqslant 31$
Reflections collected/unique	4 460 / 3 759 [R_{int}=0.012 9]
Absorption correction	Empirical
Max. and min. transmission	0.847 5 and 0.793 2
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3 759 / 6 / 305
Goodness-of-fit on F^2	1.039
Final R indices [$I>2\sigma(I)$]	R_1=0.0270, wR_2=0.0675
R indices (all data)	R_1=0.0378, wR_2=0.0697
Largest diff. peak and hole / (e·nm^{-3})	245 and −243

CCDC: 244926.

2 Results and discussion

The result of elemental analyses of the title complex is in agreement with the formula [Ni(L^{2-})(2,2′-bipy)(H_2O)]·$2H_2O$ (H_2L=phenyliminodiacetic acid). The complex is extremely stable in solid state, but readily dissolves in neutral, basic and acidic aqueous solution. It also decomposed in polar solvents such as methanol, ethanol, but not in ether and other weak-

polarity organic solvents.

2.1 Crystal structure

Fig.1 shows a perspective views of the complex, with the atomic numbering scheme. Fig.2 shows a perspective view of the crystal packing in the unit cell along c axis. Selected bond distances and angles are collected in Table 2.

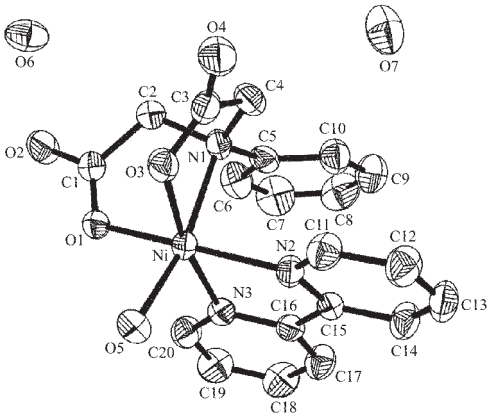

Fig.1　Molecular structure of [NiL(2,2′-bipy)H_2O]·2H_2O with thermal ellipse at the 50% probability

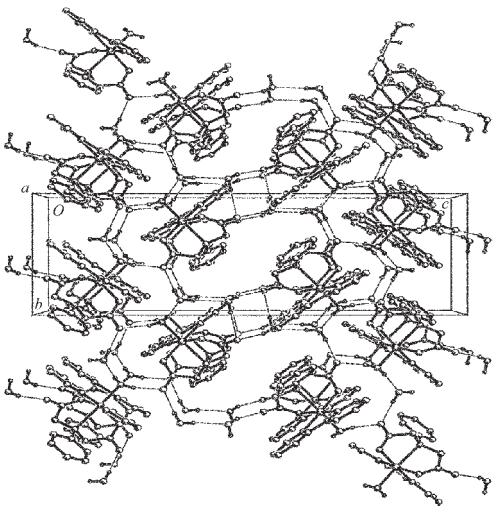

Fig.2　A view of the crystal packing cell along *c* axis

Table 2　Selected bond lengths (nm) and angles(°) of the complex

Ni-O(1)	0.201 16(14)	Ni-N(2)	0.207 31(17)
Ni-O(5)	0.202 42(16)	Ni-N(3)	0.207 68(17)
Ni-O(3)	0.207 20(14)	Ni-N(1)	0.224 65(17)
O(1)-Ni-O(5)	93.75(6)	O(3)-Ni-N(3)	170.01(6)
O(1)-Ni-O(3)	95.10(6)	N(2)-Ni-N(3)	78.49(7)
O(5)-Ni-O(3)	90.36(6)	O(1)-Ni-N(1)	81.43(6)
O(1)-Ni-N(2)	169.79(6)	O(5)-Ni-N(1)	165.69(7)
O(5)-Ni-N(2)	92.05(7)	O(3)-Ni-N(1)	76.75(6)
O(3)-Ni-N(2)	93.26(6)	N(2)-Ni-N(1)	94.83(6)
O(1)-Ni-N(3)	92.58(6)	N(3)-Ni-N(1)	98.15(6)
O(5)-Ni-N(3)	95.52(7)		

In the title compound, the central Ni(Ⅱ) ion is coordinated by two oxygen [Ni-O(1) 0.201 16(14) nm, Ni-O(3) 0.207 20(14) nm] atoms from two carboxylic groups of ligand L^{2-} and another two nitrogen [Ni-N(2) 0.207 31(17) nm, Ni-N(3) 0.207 68(17) nm] atoms of 2, 2-bipy in the quadrilateral positions, and one nitrogen [Ni-N(1) 0.224 65(17) nm] atom of ligand L^{2-} and one oxygen [Ni-O(5) 0.202 42(16) nm] atom of a coordination water molecule at the axial positions. The angles, such as O(1)-Ni-O(3) 95.10(6)°, N(2)-Ni-N(3) 78.49(7)°, O(5)-Ni-N(1) 165.69(7)°, also indicate the resulting coordination geometry is a distorted six-coordination octahedron. Each ligand L^{2-}, as a tridentate ligand, coordinates with Ni^{2+} by N(1), O(1), O(3) , which is different from that observed in [Ni(ADA)$(H_2O)_2$][13]. While, the bond length between Ni and N(1) 0.224 65(17) nm is much longer than other coordinate bonds because of the steric factor which will result in the easy decomposition in thermoanalysis. The bond lengths of C(1)-O(1), C(3)-O(3) [0.125 2(2) nm and 0.126 1(2) nm] are longer than C(1)-O(2), C(1)-O(4) [0.124 3(3) nm, 0.124 2(3) nm], which indicate that each carboxylic group of L^{2-} ligand is a monodentate ligand. The coordinate bond distances between ligand 2,2′-bipyridine and metal atom [Ni-N(2), Ni-N(3)] are similar to those observed in other reports[14,15]. The strong ability of coordination of both H_2L and 2,2′-bipyridine ligands prevent the complex to polymerize, forming discrete molecules.

It is worthy to note that there exists extensive intermolecular hydrogen bonds in the crystal of the complex, which is formed by two kinds of water molecules (coordination water and lattice water) and uncoordinated oxygen atoms of carboxylic group. The hydrogen bond distances and angles are showed in Table 3. One hydrogen in coordinated water molecule is connected with oxygen atom in nearby uncoordinated carboxylic group to form strong bond O(5)–H(5A)⋯O(2), the other hydrogen in the same coordinated water molecule is attached by oxygen atom of one lattice water to form bond O(5)–H(5B)⋯O(6). In the crystal of the complex, the hydrogen bond around the two lattice water molecule is different. As the H-bond donor, one

Table 3 Hydrogen bond distances (nm) and angles (°) in the complex

D–H···A	D-H	H···A	D···A	D–H···A
O(5)–H(5A)···O(2)$^{\#1}$	0.083 2(10)	0.188 4(11)	0.270 7(2)	170(3)
O(5)–H(5B)···O(6)$^{\#2}$	0.082 6(10)	0.191 2(11)	0.273 1(3)	171(3)
O(6)–H(6A)···O(2)	0.082 4(10)	0.190 6(11)	0.272 9(2)	175(4)
O(6)–H(6B)···O(7)$^{\#3}$	0.082 4(10)	0.211 5(14)	0.290 8(3)	161(3)
O(7)–H(7A)···O(4)	0.081 6(10)	0.200 6(11)	0.281 1(3)	169(3)
O(7)–H(7B)···O(4)$^{\#4}$	0.082 3(10)	0.211 0(11)	0.293 1(3)	176(3)

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $y+1/2$, $-z+3/2$; #2: x, $y+1$, z; #3: $-x$, $-y+1$, $-z+1$; #4: $-x$, $-y+2$, $-z+1$.

lattice water is connected with a uncoordinated carboxylic oxygen atom and an oxygen atom of the nearby lattice water respectively [O(6)–H(6A)···O(2), O(6)–H(6B)···O(7)]. As the H-bond acceptor, this lattice water is linked with coordinate water via intermolecular bond. But the other lattice water is linked by two uncoordinated carboxylic oxygen atoms from different complex molecular [O(7)–H(7A)···O(4), O(7)–H(7B)···O(4)]. All above hydrogen bonds link the complex into a 2D network structure (Fig.2), which forms a big ring built by twenty-four-atoms from two complex molecules and four lattice waters. The hydrogen bond distances range from 0.188 4 nm to 0.211 5 nm, and the bond distance O(5)-H(5A)-O(2) 0.270 7(2) nm is shorter than the others, which makes the network structure more stable.

2.2 Infrared absorption spectrum

The IR spectrum of the complex exhibits two strong and broad bands at 3 364 and 3 120 cm^{-1}, which are most likely ascribed to the stretching vibrations of coordinated and crystallized water molecules. Compared with the IR spectrum of free ligand, the disappearance of any bands in the region 1 750~1 700 cm^{-1} of the isolated complex shows the coordination of the COO^- groups in the ligand L^{2-} to the metal ion. As resonances of COO^- group is considered, ν_{as}(COO) red-shift 28 cm^{-1} to the value of 1 605.1 cm^{-1}, and ν_a(COO) blue-shift 20.1 cm^{-1} to 1 398.5 cm^{-1}, which also suggests that the carboxylic oxygen atoms of the ligand L^{2-} are coordinated to the metal ion . The $\Delta\nu_{CO_2}$ ($\nu^{as}_{CO_2}$–$\nu^{s}_{CO_2}$=206.6 nm) between the two bands indicates that the carboxylate is monodentate[16].

2.3 Thermoanalysis

The sample of the complex was heated from 23 ℃ to 730 ℃ at rate of 10.0 ℃ per minute in nitrogen atmosphere. The TG and DTG curves display that two lattice water molecules and one coordinated water are lost at first stage in the temperature range 50~180 ℃ (Found: 11.60% Calculated: 11.35%). The lost rate reaches a maximum at 134.7 ℃. The left framework structure can exist stably in the range of 175~260 ℃, and decomposes slowly when the temperature is over 300 ℃. The final product of thermal decomposition may be Ni (Found: 12.23% Calculated: 12.33%). These values agree well with the elemental analysis.

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