

Synthesis and Characterization and Crystal Structure of New Oxime-Type Mononuclear Nickel(II) Complex with 1-[4-((E)-4-Methoxyl-2-hydroxybenzylidene)]oxime

L. ZHAO*, P. WANG, Q. CHENG, H.-X. GUO and X.-L. YAN

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P.R. China

*Corresponding author: E-mail: zhaoli_72@163.com

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A new Ni(II) complex, $[\text{Ni}(\text{L})_2]$, has been synthesized *via* the complexation of nickel(II) acetate monohydrate with a new oxime-type ligand (HL = 1-[4-((E)-4-methoxyl-2-hydroxybenzylidene)]oxime). X-ray crystal structure determination of the Ni(II) complex shows that the Ni(II) complex is mononuclear, the Ni(II) atom is four-coordinated by the phenolate O atoms and imine N atoms from two deprotonated oxime-type ligands L^- , in a square-planar geometry.

Keywords: Oxime-type compound, Synthesis, Crystal structure.

INTRODUCTION

As is well known, Schiff base compounds have been playing an important role in the development of coordination chemistry^{1,2}. During the past few years, a large number of Schiff base complexes have been studied extensively for their facile synthesis and easily tunable steric position and application³. Many Schiff base complexes have been structurally characterized⁴, but only a relatively small number of oxime-type compounds have been characterized⁵⁻⁷. Here, we report the synthesis and crystal structure of a new oxime-type Ni(II) complex.

EXPERIMENTAL

4-Methoxyl-2-hydroxybenzylidene and hydroxylamine hydrochloride were purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory.

Elemental analysis for Ni was detected by an IRIS ER/S-WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (4000-500 cm^{-1}) and CsI (500-100 cm^{-1}) pellets. UV-visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. X-ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. Melting points were obtained by use of an X₄ microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected.

Synthesis of HL: To a hot water (4 mL) solution of hydroxylamine hydrochloride (73.35 mg, 1.1 mmol) was added sodium bicarbonate (84 mg, 1 mmol). The solution is clarified and added an ethanol (4 mL) solution of 4-methoxyl-2-hydroxybenzylidene after stirring the reaction mixture at 338 K for 5 h. The solvent was removed under reduced pressure and the residue was recrystallized from ethanol to give the title compound HL. Yield 77.4 %. m.p. 438-439 K. Anal. Calcd. for $\text{C}_8\text{H}_9\text{NO}_3$ (%): C, 57.48; H, 5.43; N, 8.38. Found (%): C, 57.45; H, 5.36; N, 8.44.

Synthesis of the Ni(II) complex: A solution of nickel(II) acetate monohydrate (2.5 mg, 0.01 mmol) in methanol (2 mL) was added dropwise to a solution of HL (3.3 mg, 0.02 mmol) in methanol (5 mL) at room temperature. The colour of the mixing solution turned to brown immediately and then continued to stirring for 4 h at room temperature. The mixture solution was filtered and the filtrate was allowed to stand at room temperature for about four weeks, the solvent was partially evaporated and obtained several green prismatic single crystals suitable for X-ray crystallographic analysis. Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_6\text{Ni}$ $[\text{Ni}(\text{L})_2]$ (%): C, 49.15; H, 4.12; N, 7.16; Ni, 15.01. Found: C, 49.32; H, 4.09; N, 6.96; Ni, 15.13.

X-ray structure determination: Details of the crystal parameter, data collection and refinements for the Ni(II) complex are summarized in Table-1.

The X-ray diffraction measurement for the Ni(II) complex was performed on Bruker Smart 1000 CCD diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.071073$ nm) at 298(2) K. Empirical absorption correction was applied

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR THE Ni(II) COMPLEX

Empirical formula	C ₁₆ H ₁₆ N ₂ O ₆ Ni
Formula weight	391.02
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Cell dimensions, (Å, deg)	a = 6.4406(8), b = 18.356(2), c = 8.2859(11), β = 124.633(2)
Volume (Å ³)	806.02(18)
Z	2
Density (calculated) (mg/m ³)	1.611
Absorption coefficient (mm ⁻¹)	1.240
F ₍₀₀₀₎	404.0
Crystal size	0.28 × 0.11 × 0.07
Index ranges	-7 ≤ h ≤ 7, -20 ≤ k ≤ 21, -9 ≤ l ≤ 7
Reflections collected	3980 (R _{int} = 0.0775)
Independent reflections	1419
Reflections observed [I > 2σ(I)]	824
Data/restraints/parameters	1419 / 0 / 116
Goodness of fit indicator	1.034
R [I > 2σ(I)]	R ₁ = 0.0600, wR ₂ = 0.1193
Largest diff. peak and hole (e Å ⁻³)	0.645, -0.828

to the data using SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares method on F² using the SHELXL program. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. CCDC: 989207.

RESULTS AND DISCUSSION

FT-IR spectra: The main FT-IR spectral data of the free ligand HL and its corresponding Ni(II) complex in the 4000-400 cm⁻¹ region is given in Fig. 1.

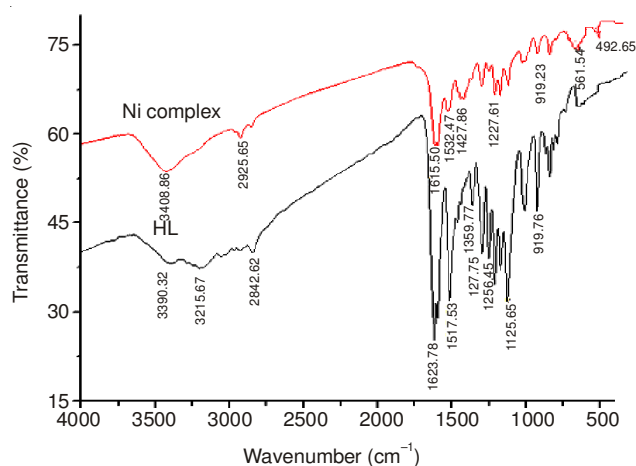


Fig. 1. FT-IR spectra of the free ligand HL and its Ni(II) complex

The free ligand HL exhibits characteristic (C=N) stretching band at 1623.78 cm⁻¹, while the (C=N) stretching band of the Ni(II) complex was observed in the 1615.50 cm⁻¹. The (C=N) stretching frequency is shifted to lower frequency by about 8 cm⁻¹ upon complexation, indicating the behavior between the free ligand and the corresponding Ni(II) atom

resulting in weakening the force constant of C=N bond. Meanwhile, the Ar-O stretching frequency appears as a strong band in the 1256.45 cm⁻¹ in the free ligand HL and the toward lower wavenumber of the Ar-O absorption shift about 29 cm⁻¹ indicating that Ni-O bonds are formed between the Ni(II) atoms and the oxygen atoms of the phenolic groups^{8,9}.

The N-O stretching frequencies of the oxime group in the free ligand and its Ni(II) complex appear as a strong band in the 919.23 cm⁻¹ indicating that the oxime N atoms do not involve in coordination. In the 1591-1460 cm⁻¹ region, the observed bands were attributed to aromatic C=C vibrations. Upon coordination these bands shift to lower frequencies for the Ni(II) complex. In addition, the O-H stretching frequency of the free ligand HL appears at 3390.32 and 3215.67 cm⁻¹. The out-of-plane bending vibration of phenolic alcohol in the free ligand HL at 1277 cm⁻¹, which disappears in the Ni(II) complex, indicating the oxygen in the phenolic alcohol of the Ni(II) complex has been deprotonated and coordinated to the Ni(II) atoms.

The far-infrared spectrum of the Ni(II) complex was also obtained in the region 500-100 cm⁻¹ in order to identify frequencies due to the Ni-O and Ni-N bonds. The FT-IR spectrum of the Ni(II) complex shows ν(Ni-N) and ν(Ni-O) vibration absorption frequencies at 561.54 and 492.65 cm⁻¹, respectively.

UV-visible spectra: The UV-visible absorption spectra of the free ligand HL and its Ni(II) complex in diluted chloroform solution are shown in Fig. 2.

It can be seen that the absorption peaks of the Ni(II) complex are obviously different from those of the free ligand HL upon complexation. The spectrum of the free ligand HL consists of two relatively intense bands centered at 287.55 and 354.81 nm, assigned to the π-π* transitions of the benzene ring of the salicylaldehyde and oxime groups¹⁰. These peaks are shifted to 302.61 and 357.20 nm in the Ni(II) complex, respectively and a new absorption peak at 429.22 nm was observed in the Ni(II) complex, indicating that the coordination of the Ni(II) atom with the free ligand HL.

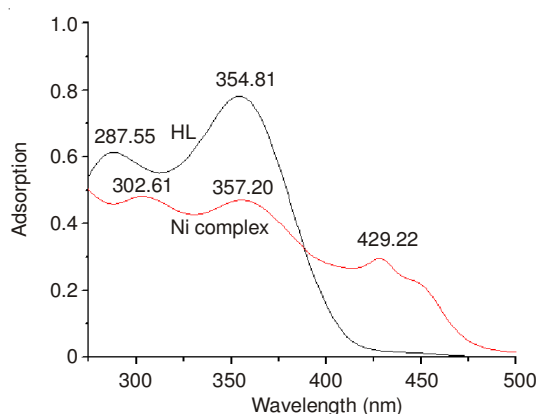


Fig. 2 UV-visible data for the ligand HL and its Ni(II) complex

Crystal structure of [Ni(L)₂]: X-ray crystallographic analysis of [Ni(L)₂] reveals formation of a mononuclear structure. The Ni(II) complex crystallizes in the monoclinic system, space group P2(1)/c and Z = 2. The Ni(II) complex consists of one Ni(II) atom, two bidentate L⁻ units, The molecular structure of the Ni(II) complex is shown in Fig. 3, selected bond distances and angles are listed in Table-2.

TABLE-2
 SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE Ni(II) COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Ni1-O2 ^{#1}	1.828(4)	Ni1-O2	1.828(4)	Ni1-N1	1.869(4)
Ni1-N1 ^{#1}	1.869(4)	-	-	-	-
Bond	Angles	Bond	Angles	Bond	Angles
O2 ^{#1} -Ni1-O2	180.0	O2 ^{#1} -Ni1-N1	87.3 (2)	O2-Ni1-N1	92.7(2)
O2 ^{#1} -Ni1-N1 ^{#1}	92.7(2)	O2-Ni1-N1 ^{#1}	87.3(2)	N1-Ni1-N1 ^{#1}	180.0
C1-N1-Ni1	128.9(4)	O1-N1-Ni1	117.4(3)	C3-O2-Ni1	129.9(3)

 Symmetry transformations used to generate equivalent atoms: ^{#1} -x-1, -y+1, -z+1

 TABLE-3
 DATA FOR HYDROGEN-BONDING INTERACTIONS (Å, °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
O1-H1...O1	0.82	2.56	3.057(7)	120
C1-H1A...O1	0.93	2.48	3.313(8)	149
O1-H1...O2	0.82	1.87	2.496(6)	132

In symmetric molecule unit of the Ni(II) complex, the Ni(II) center is *tetra*-coordinated by the phenolate O atoms and imine N atoms from two oxime-type ligands L⁻, in a square-planar geometry. The dihedral angle between the coordination plane of O2-Ni1-N1^{#1} and that of O2^{#1}-Ni1-N1 is 180°, while another dihedral angle between the coordination plane of N1-Ni1-O2 and that of N1^{#1}-Ni1-O2^{#1} is also 180°.

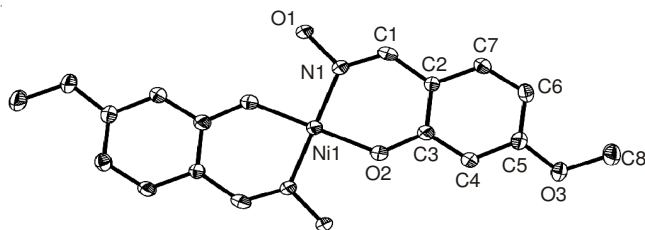


Fig. 3. Crystal structures of the Ni(II) complex with the atom numbering. Thermal ellipsoids are plotted at 30 % probability level. Symmetry code: ^{#1} -x-1, -y+1, -z+1; Hydrogen atoms are omitted for clarity

As illustrated in Fig. 4, There is an intramolecular hydrogen bond O1-H1...O2 between hydroxyl O1-H1 group and phenolic O2 atom. While the hydroxyl -O1H1 bonded to the phenolate O1 atom and the -C1H1A group of the oxime-type ligand L⁻ is hydrogen-bonded to the O1 atom of the phenolate, which are intermolecular hydrogen bonds (Table-3).

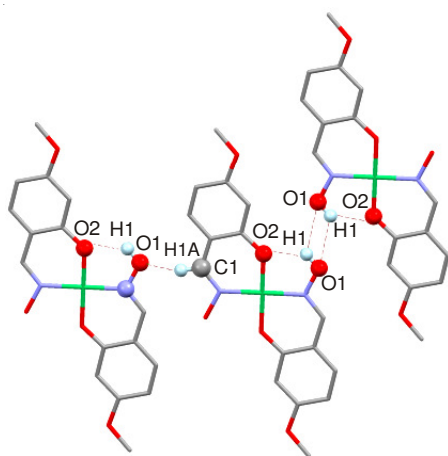


Fig. 4. Molecular hydrogen bonds of the Ni(II) complex. Hydrogen atoms are omitted for clarity

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