

Template Synthesis of Un-Symmetrical Tetradentate Schiff Base Complexes of Ni(II), Co(II), Zn(II) and X-ray Structure of Ni(II) Complex

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Abstract

Metal complexes, ML (M=Ni, Cu, Co and Zn) of unsymmetrical tetradentate schiff base have been synthesized by the template reaction of the half-units N-(1-hydroxy-2-acetonaphthone)-1-amino-2-phenyleneimine)(HL¹) with 2-Pyrrolecarbaldehyde. The complexes have been characterized by elemental analysis, IR, ¹H NMR and UV spectroscopy. The crystal structure of the Ni(II) complex has been determined by X-ray and exhibits distorted square-planar conformation. Crystals of NiL are orthorhombic, space group P2₁2₁2₁, with a = 7.1635(6), b = 11.6815(10), c = 20.7217(17) Å and Z = 4. The Ni-O and Ni-N bonds have very similar lengths and form a regular square-planar structure.

Keywords: Template; Unsymmetrical; Tetradentate

Introduction

The design, synthesis and characterization of dissymmetrical Schiff base ligands derivative from appropriate amines for transition metal ion complex has become from the realization that coordination ligand around central metal ions in natural systems is asymmetric [1-4]. Un-symmetrical Schiff bases are used as ligands in metal coordination chemistry due to the wide application of their complexes in biological systems [5, 6] and catalytic reaction [7, 8]. In the present paper, as a part of our study was to determine metal ions of various ligands towards transition metal ions. We have synthesized Ni(II), Co(II) and Zn(II) complexes with the condensation products N-(1-hydroxy-2-acetonaphthone)-1-amino-2-phenyleneimine)(HL¹) and 2-Pyrrolecarbaldehyde.

Attempt to prepare free ligand was unsuccessful.

Materials and Methods

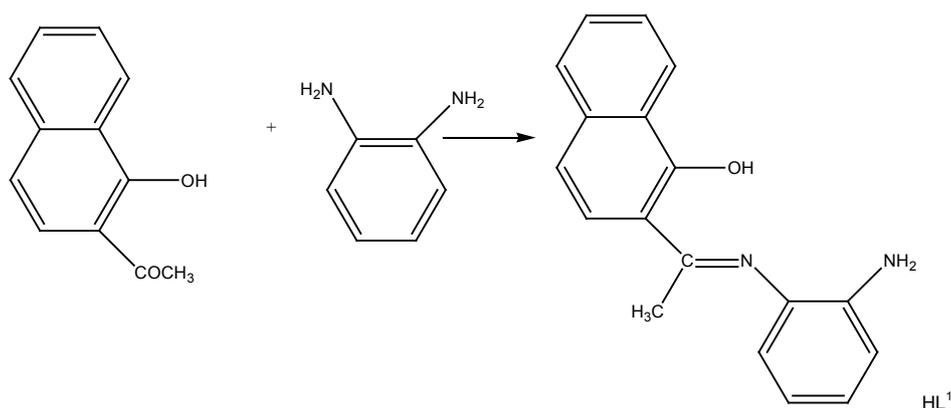
Experimental

All melting points were analyzed with an electrothermal melting point apparatus. FT-IR spectra were recorded using a Bruker Tensor 27 spectrometer. The visible spectra were determined using a Perkin Elmer, Lambda 35 UV/Vis spectrometer. ¹HNMR spectra were obtained on a Bruker Avance 300 MHz spectrometer using TMS as internal standard.

Preparation of the Half-Unit HL¹

It was prepared by previous method [9].

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Scheme 1. Preparation of HL¹.

Preparation of ML

Methanolic solution (15 mL) of the metal acetate salt (1 mmol) was added to a solution of HL¹ (1 mmol) and 2-pyrrolicarbaldehyde (1 mmol) in methanol (15 mL). This mixture was refluxed for 1h and then left to cool to allow the precipitation of the complex. The precipitate was filtered and washed with methanol.

X-ray Crystallography

Single crystals were mounted with oil on a quartz fibre and transferred into the cold nitrogen stream on a Siemens SMART (Siemens, 1994) three-circle system with CCD area detector. The crystal was held at 220 (2) K with the Oxford Cryosystem Cryostream cooler (Cosier & Glazer, 1986). The structures were solved by direct methods using SHELXS (sheldrick, 1990) (TREF) with light atoms found by Fourier methods.

Results and Discussion

Half ligand (HL¹) has been prepared by the reaction of *o*-hydroxyacetophenone and phenylenediamine under reflux conditions (Scheme 1). Then one equivalent of (HL¹) in the presence of 2-Pyrrolicarbaldehyde and metal acetate reflux for one hour which gave complexes ML (M = Ni, Zn and Co). Infrared spectra of ML showed the characteristic band [10] assignable to ν (C = N) at ca. 1614 and 1615 cm⁻¹. Their electronic spectra consist of a shoulder of intense UV or broad band in the visible region assignable to a d-d transition [11]. The d-d band maxima for complexes NiL and CoL are at λ_{max} (nm); 523 (sh), 530(sh), respectively.

The ¹H NMR spectrum of HL¹ gives direct evidence of the formation half ligand. As anticipated, the spectrum consists of one methyl at δ 2.3, one hydroxy hydrogen at δ 14.8 and aromatic protons at δ 6.7-8.6 signals. On formation of ML (M = Ni and Zn) complexes the signals of the methyl group are shifted to δ 2.7 and the signals of the OH group have disappeared. The obtained data confirm distorted square-planar geometry for nickel complex. It seems that cobalt (II) and zinc (II) complexes also have distorted square-planar environment. Details on single crystal of NiL complex is as follows:

Red plate-like crystals of NiL suitable for the X-ray analysis (0.7, 0.14, 0.06 mm) were obtained by recrystallization from chloroform/ethanol (3:1). The resolution of the structure is correct as confirmed by the acceptable R (F) (0.0487) and goodness-of-fit (1.016) values and by the consistency of the structural parameters (bond distances and angles).

Structure of NiL Complex

Figure 1 shows ORTEP drawing of NiL complex. The present X-ray analyses verified that the structure of Ni(II) with unsymmetrical tetradentate ligand is composed of the condensation products of *o*-hydroxyacetophenone, phenylenediamine and 2-Pyrrolicarbaldehyde in the mole ratio 1:1:1. The crystal structure analysis of this compound reveals that it contains a tetradentate ligand in which three nitrogen and one oxygen atoms are co-ordinated to the nickel atom.

The nickel atom is in distorted square-planar environments. Selected bond lengths (Å) and bond angle (°) of NiL complex are shown in Table 1. The Ni-O and Ni-N distances are close to the limits of ranges

1.83-1.87 and 1.83-1.89 Å for Ni-O and Ni-N distances, respectively. This behaviour is normally observed in N_3O square-planar nickel (II) complexes [12]. The crystal data and the most relevant experimental parameter used in the X-ray measurements and in the crystal structures analyses are reported in Table 2.

IR Spectra

IR spectral data of the compounds and their relative assignments are shown in Table 3. The infrared spectrum of the “half-unit” (HL^1) shows two bands at 3338 and 3200 cm^{-1} . These two bands are assigned to the primary amine stretching, on the basis of their absence in the spectrum of ML. An intense sharp band at 1615 cm^{-1} in the spectrum of HL^1 and a broad intense band at 1600-1607 cm^{-1} in the spectrum of ML are tentatively assigned to azomethine vibrations. The absorption values of the C=N vibration at about 1600-1607 cm^{-1} for the complexes are lower by about 8-15 cm^{-1} than for the free half ligand. A comparison between the IR spectra of HL^1 and complexes also showed that a band characterizing $\nu C-O$ at 1307 cm^{-1} was shifted to higher frequency by about 46-62 cm^{-1} in the spectrum of the complexes which indicated the formation of C-O-M bond [13].

1H NMR Spectra

The 1H NMR spectral data of the half ligand (HL^1) and their Ni(II) and Zn(II) complexes are given in Table 4. The signal at δ 3.7 in the spectrum of HL^1 is assigned to the NH_2 group on the observation of loss of this signal in the spectra of NiL and ZnL. The 1H NMR spectra of ZnL and NiL complexes in $CDCl_3$ solution have peaks at δ 8.0 and 7.4, respectively which are assigned to the hydrogen of azomethine resonance of

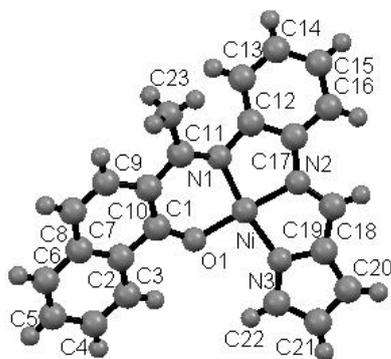


Figure 1. ORTEP drawing of NiL with the atom numbering scheme.

Table 1. Selected bond Lengths (Å) and Bond Angle ($^\circ$) for Complex NiL

Ni-O1	1.802(2)	Ni-O1	1.841(3)
Ni-N1	1.866(3)	Ni-N3	1.884(3)
O1-Ni-N2	176.59(12)	O1-Ni-N1	96.40(12)
N2-Ni-N1	86.56(13)	O1-Ni-N3	93.78(12)
N2-Ni-N3	83.43(14)	N1-Ni-N3	168.56(14)

Table 2. Experimental data for the X-ray diffraction studies

Formula weight	$C_{23}H_{17}N_3NiO$
Molecular weight	410.11
Wavelength	0.71073 Å
Temperature	220(20) K
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	7.1635(6)
b (Å)	11.6815(10)
c (Å)	20.7217(17)
Z	4
Dc(g/cm^3)	1.571 mg/m^3
F (000)	848
Crystal size	0.7 x 0.14 x 0.06 mm
min, min/ θ	1.97 to 28.47 $^\circ$
Total reflection	10756
Independent reflections	4064 ($R_{int} = 0.0883$)
Absorption Correction	SADABS
Max. and min. transmission	0.928 and 0.766
Refinement method	Full-matrix least-squares on F^2
R (F)[$I > 2\sigma(I)$]	$R1 = 0.0478$, $wR2 = 0.0864$
Rw (F)	$R1 = 0.0887$, $wR2 = 0.1010$
Goodness of fit on F^2	1.016

Table 3. Important IR absorption bands (cm^{-1}) of the ligand and their complexes

Compounds	$\nu(O-H)$	$\nu(C=N)$	$\nu(C-O)$
HL^1	-	1615	1307
NiL	3448	1607	1353
CoL	3461	1607	1369
ZnL	-	1600	1369

Table 4. ¹HNMR chemical shifts δ (ppm) of HL¹ and ML in CDCl₃

Compounds	NH ₂	O-H	CH=N	CH ₃	Aromatic Hydrogen
HL ¹	3.7(2H, s)	16.9(1 H, s)	--	2.4(3H, s)	6.7 - 8.5(10 H, m)
ZnL	--	--	8.0(1 H, s)	2.7(3H, s)	6.5 - 7.5(13 H, m)
NiL	--	--	7.4(1 H, s)	2.7(3H, s)	6.9 - 8.6(13 H, m)

pyrrolcarbaldehyde. The signals of methyl hydrogen group due to complexation were shifted, and the signals of the OH group were disappear. From these data we can conclude that the ligand is tetradentate and the nickel(II) complexes are diamagnetic, which indicates a square planar or distorted square planar structure.

Electronic Spectroscopy

For the Ni(II) complexes, d-d transition (Table 5) appears below 600 nm, which is a characteristic of square planar or distorted square planar [14].

For the CoL, d-d transition was appeared below 600 nm, which is characteristic of square-planar or distorted square-planar structure [15-16]. The bands at 384-480 nm were assigned to ($n-\pi^*$) transitions for the aromatic moiety of the ligand [17].

Supplementary Material

CCDC 827636 contains the supplementary crystallographic data for NiL complex. These data can be obtained free of charge via <http://www.ccdc.com.ac.uk/conts/retrieving.html> or e-mail: deposit@ccdc.com.ac.uk.

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