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TEMPLATE SYNTHESIS, CHARACTERIZATION OF HIGHLY UNSYMMETRICAL TETRADENTATE SCHIFF BASE COMPLEXES OF NICKEL (II) AND COPPER (II)

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Abstract

Nickel (II) and copper (II) complexes of highly unsymmetrical tetradentate Schiff base have been synthesized by the template reaction of half-units N-(1-hydroxy-2-acetonaphtone)-1-amino-2-phenyleneimine (HL) and N-(2-hydroxy-acetophenone)-1-amino-2-phenyleneimine (HL^1) with the glyoxalphenylhydrazone. The complexes have been characterized by elemental analyses, conductance, IR, ^{1}H NMR and UV spectroscopy.

Introduction

Recent interest in the synthesis and characterization of unsymmetrical tetradentate Schiff base complexes [1-4] has been prompted by the belief that systematic investigation of these complexes may shed light on the nature of complexes of biological interest. In these compounds, the metal is in an unsymmetrical ligand environment. Many hydrazine derivatives have been reported to inhibit the numerous reactions catalyzed by pyridoxal 5-phosphate as coenzyme [5]. The amino-oxidase enzyme requires such a coenzyme besides copper (II) ions for catalytic activity.

At this point, it seems necessary to investigate the reaction of derivative of hydrazine with divalent metal ions, especially Cu(II), to gain information concerning the coordination chemistry of these molecules in the highly unsymmetrical environment. In this paper, we report the synthesis of mono-Schiff bases N-(1-hydroxy-2-acetonaphtone)-1-amino-2-phenyleneimine (HL) and N-(2-hydroxyacetophenone)-1-amino-2-phenyleneimine (HL^1) by condensation of *o*-phenylenediamine with 1-hydroxy-2-acetonaphtone and *o*-hydroxyacetophenone, respectively (Figure 1). Non-symmetric Schiff base complexes were then obtained by the reaction of half-units with glyoxalmono-phenylhydrazone (HL^2) in methanol in the presence of the desired metal acetate.

Keywords: Template, Tetradentate, Unsymmetrical, Schiff-base

Experimental Section

Microanalyses were performed by the Microanalytical Laboratory, Research Institute of Petroleum Industry of the Islamic Republic of Iran. Conductivity was measured using a Jenway-4010 conductivity meter. IR spectra as KBr discs were recorded using a Mattson 1000 FT-IR spectrometer, the visible spectra were determined using a Unicam 8700 series UV/Vis spectrometer and proton NMR spectra were run on a Bruker FT AC-80. All chemical shifts are given in ppm *vs.* TMS.

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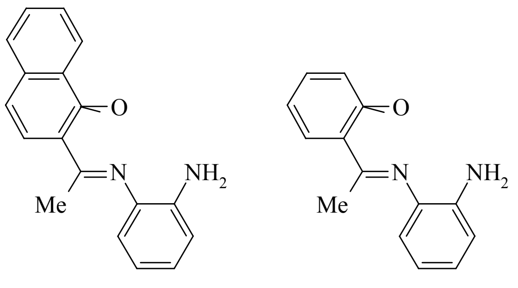
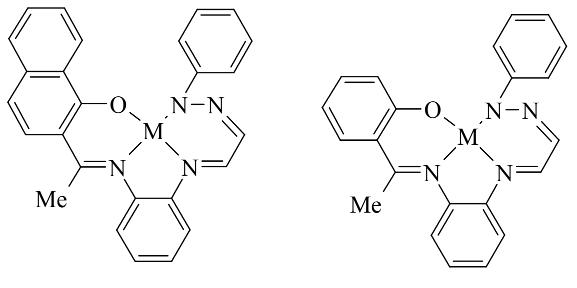


HL HL^1

Figure 1. Structures of half-unit ligands.



M(L-L^2) M(L^1-L^2)

Figure 2. Structures of highly unsymmetrical Schiff base complexes M = Cu and Ni.

Preparation of HL

1-Hydroxy-2-acetonaphtone (0.19 g, 1 mmol) and *o*-phenylenediamine (0.11 g, 1 mmol) in absolute ethanol (30 ml) was refluxed while being stirred for 6 h. Evaporation of the ethanolic solution gave a yellow solid which was filtered, recrystallized in ethanol and analyzed.

Preparation of HL^1

O-hydroxyacetophenone (0.14 g, 1 mmol) and *o*-phenylenediamine (0.11 g, 1 mmol) in absolute ethanol (30 ml) were stirred and refluxed for 5 h. The yellow solution was concentrated to approximately 5 ml by evaporation and then 5 ml of n-hexane was added. The resulting yellow solid was separated by filtration and recrystallized from n-hexane-ethanol.

Preparation of HL^2

HL^2 was prepared by the method of Chiwell [6].

Preparation of Ni (L-L^2) and Cu (L-L^2)

To a solution of HL (0.29 g, 1 mmol) and HL^2 (0.15 g, 1 mmol) in methanol (30 ml) methanolic solution (10 ml) of the desired metal acetate salt (1 mmol) was added. This mixture was refluxed for 2 h. the solution was left at room temperature for one night. The dark solution deposited a black solid that was filtered and washed with methanol and air-dried.

Preparation of Ni (L^1-L^2) and Cu (L^1-L^2)

These compounds were prepared similarly except that HL^1 (0.23 g, 1 mmol) was used.

Results and Discussion

As a possible route to obtain non-symmetrical Schiff bases, a two-step process may be considered according to the Equations 1 and 2.

$$R_1R_2C{=}O+H_2N\text{-}(CH_2)_n\text{-}NH_2 \rightarrow R_1R_2C{=}N\text{-}(CH_2)_n\text{-}NH_2 \quad (1)$$

$$R_1R_2C{=}N\text{-}(CH_2)_n\text{-}NH_2+O{=}C\,R_3R_4 \rightarrow R_1R_2C{=}N\text{-}(CH_2)_n\text{-}N{=}C\,R_3R_4 \quad (2)$$

The major difficulty was expected to occur in preparing and isolating the intermediary 1:1 species, $R_1R_2C{=}N\text{-}(CH_2)_n\text{-}NH_2$. When 1-Hydroxy-2-acetonaphtone or *o*-Hydroxyacetophenone reacts in ethanol with *o*-phenylenediamine, Schiff base condensation occurs at only one of the two available amino groups, even in the presence of a large excess of ketones (Eq. 3).

$$RCOCH_3+H_2N\text{-}C\,(CH)_4C\text{-}NH_2 \rightarrow RCH_3\,C{=}N\text{-}C\,(CH)_4C\text{-}NH_2 \quad (3)$$

$R{=}C_6H_4OH,\ C_{10}H_6OH$

These half-units are easily isolated as solids, which can further be used by recrystallization. The free amino groups of HL and HL^1 are sufficiently reactive to condense with appropriate aldehyde [7]. For the preparation highly unsymmetrical Schiff base complexes; these half-units react with another half-unit which is obtained by the condensation of glyoxal hydrate with phenylhydrazine [8] in the presence of metal acetates (Figure 2). All the unsymmetrical chelates are stable crystalline solids insoluble in water and soluble in organic solvents. Attempts to obtain the free ligands ($H_2L\text{-}L^2$) and ($H_2L^1\text{-}L^2$) were unsuccessful. The presence of metal atom appears to stabilize the highly unsymmetrical ligands.

The complexes were characterized by elemental analyses, ^{1}H NMR, IR and UV spectroscopy. Moreover, molar conductance in CH_2Cl_2 indicates that all complexes are non-electrolytes, which requires that the Schiff bases coordinate as dibasic ligands. The elemental analyses and physical properties of the half-units and their complexes are listed in Table 1.

^{1}H NMR Spectroscopy

The values of the chemical shifts are reported in Table 2. They are fully consistent with the structures depicted. Particular attention has been paid to the NH_2 signal, which is absent in the complexes, due to condensation with carbonyl group. No NH and OH

Table 1. Analytical data of the half-units and their complexes

Formula	**m.p. (°C)**	**Yield**	**Found (Calcd.)%**		
Compound	**(dec.p.)**	**(%)**	**C**	**H**	**N**
HL $C_{18}H_{16}N_2O$	162	60	78.2 (78.0)	5.8 (6.0)	10.1 (10.1)
HL^1 $C_{14}H_{14}N_2O$	95	45	74.3 (74.3)	6.2 (6.2)	12.3 (12.4)
Ni(L-L^2) 1.5H_2O $C_{26}H_{23}NiN_4O_{2.5}$	(>250)	51	63.2 (63.6)	4.6 (4.6)	10.9 (11.4)
Cu(L-L^2) H_2O $C_{26}H_{22}CuN_4O_2$	(>250)	45	63.6 (63.2)	4.6 (4.4)	11.4 (10.9)
Ni(L^1-L^2) $C_{22}H_{18}NiN_4O$	(>170)	61	62.4 (62.6)	4.6 (4.5)	13.1 (13.3)
Cu(L^1-L^2) $C_{22}H_{18}CuN_4O$	(>180)	40	62.7 (63.2)	4.3 (4.3)	13.4 (13.4)

Table 2. ^{1}H NMR chemical shifts (ppm) of the half-units and the Ni(II) complexes

Compound	**NH_2**	**O-H**	**CH=N**	**CH_3**	**Aromatic group**
HL	3.7 (s, 2 H)	16.9 (s, 1 H)	–	2.4 (s, 3 H)	6.7-8.5 (m, 10 H)
HL^1	3.5 (s, 2 H)	14.7 (s, 1 H)	–	2.2 (s, 3 H)	6.2-7.7 (m, 8 H)
Ni(L-L^2)	–	–	A	2.9 (s, 3 H)	6.5-7.4 (m, 17 H)
Ni(L^1-L^2)	–	–	5.9(d, 1 H) 6.5(d, 1 H)	2.8 (s, 3 H)	6.7-7.4 (m, 15 H)

A: under aromatic region; d: doublet; m: multiplet; s: singlet

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

Compound	**ν(H_2O)**	**ν(NH_2)**	**ν(C=N) ν(C=C)**	**ν(C-O)**
HL	–	3346 3230	1646 1584	1323
HL^1	–	3338 3200	1615 1500	1307
Ni(L-L^2) 1.5H_2O	3461	–	1615 1561 1515	1338
Cu(L-L^2) H_2O	3438	–	1607 1561 1515	1330
Ni(L^1-L^2)	–	–	1600 1546 1515	1330
Cu(L^1-L^2)	–	–	1600 1553	1330

resonance is present in the Ni (L-L^2) and Ni (L^1-L^2) spectra as a result of deprotonation upon complexation. These results indicate that the ligands behave as dibasic ligands [9].

In the proton spectrum of Ni (L^1-L^2) two distinct doublets are observed at 5.9 and 6.5 ppm, which are assigned to the two-unequal C-H groups on the glyoxalmonophenylhydrazone residue. For the Ni (L-L^2) these two C-H resonances are under the aromatic region [10].

Infrared Spectroscopy

Important IR absorption frequencies of the half-units and their complexes are given in Table 3. The infrared spectra of HL and HL^1 exhibit two bands in the region 3200-3350 cm^{-1} [11]. Both bands are absent from the spectra of the M (L-L^2) and M (L^1-L^2), thus they are assigned to the primary amine NH_2 stretching. A relatively intense band at 3215 cm^{-1} in the spectrum of HL^2 is assigned to the NH stretch [6] of the hydrazine residue, on the basis that no band exists in this region for the metal complexes. On the basis of ^{1}H NMR evidence, it is proposed that deprotonation of this group occurs upon complexation. The infrared spectra of all of the Ni(II) and Cu(II) complexes are very similar. In the IR spectra of the complexes, new bands appear at a lower frequency (~1600 cm^{-1}). This indicates that condensation of the free amino group of the half-units with the carbonyl group (ν C=O 1669 cm^{-1}) has taken place and is assigned to ν C=N. The 1600 cm^{-1} region, however, is far more complicated, being overlapped by ring vibrations, three C=N vibrations and C=C vibrations making band assignment tentative. A comparison between the IR spectra of HL and HL^1 and the respective complexes M(L-L^2) and M(L^1-L^2) also show that a band, characteristic of νC-O at ~1310 cm^{-1}, is shifted to ~1330 cm^{-1}. This band moves to a higher frequency in the spectra of the complexes. These changes can be due to the C-O-M bond formation [12].

Electronic Spectroscopy

Figures 3 and 4 show the electronic spectra of Ni(II) and Cu(II) complexes. The bands observed in the visible region (Table 4). For the nickel complexes are due to transition from d_π (dxz and dyz) to the d_σ (dxy) orbital [13]. The other intense bands are due to charge transfer transitions. Diamagnetism of the nickel complexes (Ni(L-L^2) and Ni(L^1-L^2)) and lack of the absorption above 650 nm, in their electronic spectra are indicative of the square-planar or distorted square-planar geometry in both complexes [14].

For the copper complexes, the d-d transitions apparently all occur under a broad envelop (Table 4). The peaks have maxima at 414 and 460 nm for Cu(L-L^2) and Cu(L^1-L^2), respectively. This position is consistent with a planar geometry around the copper ion [15,16]. The other intense bands are due to charge transfer transitions.

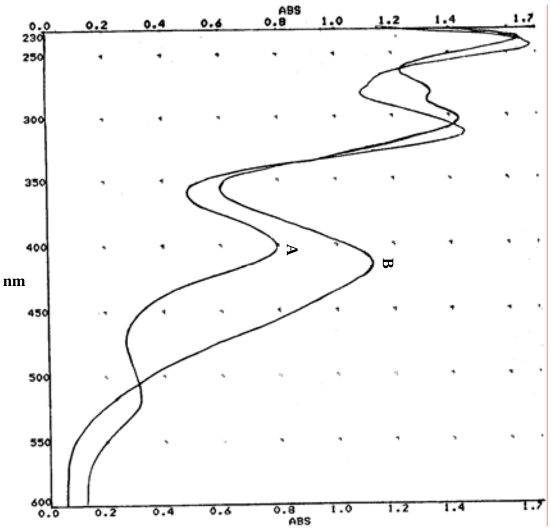


Figure 3. Electronic spectra of Ni(L-L^2) (A) and Cu(L-L^2) (B) in dichloromethane.

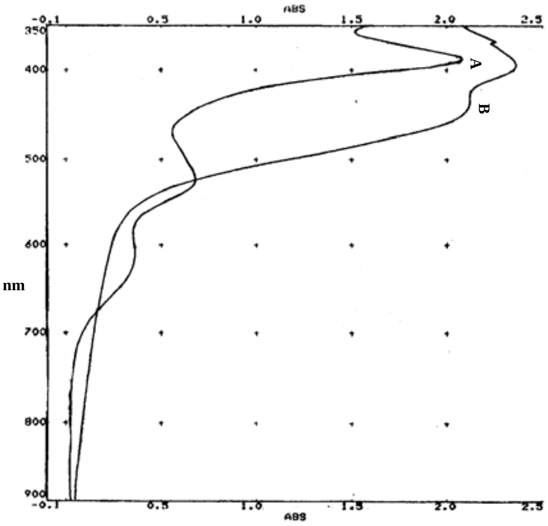


Figure 4. Electronic spectra of Ni(L^1-L^2) (A) and Cu(L^1-L^2) (B) in dichloromethane.

Table 4. Electronic spectral bands in CH_2Cl_2

Compound	Bands, nm (ε)
Ni(L-L^2)	514(3.8), 403(4.2), 314(4.5)
Cu(L-L^2)	414(4.3), 302(4.4), 280(4.3)
Ni(L^1-L^2)	611(3.4), 522(3.6), 387(4.2)
Cu(L^1-L^2)	460(sh), 393(4.2), 368(4.2)

$\varepsilon = mol^{-1}l^{-1}cm^{-1}$; sh = shoulder

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