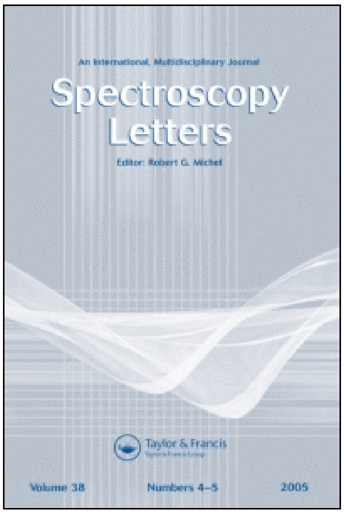

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THE SYNTHESIS AND SPECTRAL CHARACTERIZATION OF NEW Cu(II), Ni(II), Co(III), AND Zn(II) COMPLEXES WITH SCHIFF BASE

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ABSTRACT

Cu(II), Ni(II), Co(III) and Zn(II) complexes with Schiff base have been prepared. Ligand is derived from condensation of 1,2-bis(*p*-aminophenoxy)ethane and 2- hydroxynaphthalin-1-carbaldehyde. The complexes have been characterized by elemental analyses, Λ_M, IR, UV-VIS, ^{1}H NMR, ^{13}C NMR and magnetic measurements. The ligand is coordinated to the central metal as a tetradentade ONNO ligand. The four bonding sites are the azomethine nitrogen and aldehydic -OH groups.

Key Words: Schiff bases; Transition metals

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INTRODUCTION

The metal complexes with Schiff bases as ligands have been playing an important part in the development of coordination chemistry as a whole. However, it was not until the 1950s that concrete and rapid advances in this field became evident. In the early days the main efforts were directed toward synthesis and characterization of rather fundamental complexes, which do not look striking nowadays but were strongly needed in those days. Schiff base metal complexes have been a widely studied subject because of their industrial, antifugal and biological applications[1–7].

In the present paper Cu(II), Ni(II), Zn(II) and Co(III) complexes of Schiff base derived from 2- hydroxynaphthalin-1-carbaldehyde and 1,2-bis-(*p*-aminophenoxy)ethane are reported. Based on the physical and chemical data of some of these complexes and adducts, schematic structures for these compounds are proposed. As far as we know, this is the first report on this ligand. The structure of the Schiff base ligand is shown in Fig. 1.

EXPERIMENTAL

Reagents and Measurements

All the chemicals were obtained from Aldrich and used without further purification. The electronic spectra of the complexes in UV-Vis region were recorded in DMF solutions using Shimatzu Model 160 UV Visible

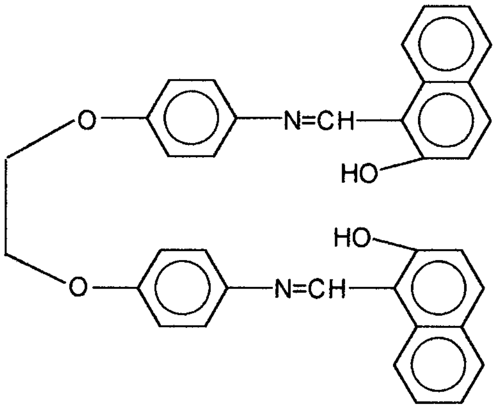

Figure 1. N,N′-*bis*-(2-hydroxynaphthalin-1-carbaldehydene)-1,2-*bis*-(*p*-aminophenoxy)ethane.

Spectrophotometer. The IR spectra of the complexes were recorded with Midac 1700 instrument in KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker GmbH DPX-400 MHz Digital FT-NMR spectrometer in DMSO-d_6, magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model NO: MK1) at room temperature (23°C) using $Hg[Co(SCN)]_2$ as a calibrant: diamagnetic corrections were calculated from Pascal's constants[8]. The elemental analyses were conducted on Carlo Erba instrument.

Synthesis of Schiff Base Ligand

N,N′-bis-(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis-(*p*-aminophenoxy) ethane was prepared by equimolar amounts of 1,2-bis-(*p*-aminophenoxy)ethane (2.44 g, 10 mmol) and 2- hydroxynaphthalin-1-carbaldehyde (3.44 g, 20 mmol) in 100 mL absolute ethanol under reflux for 2 h. The crystals of the Schiff base that separated on cooling were recrystallized from DMF, m.p: 265°C (yield %82).

Synthesis of the Metal Complexes

A solution of metal acetate (20 mmol) in DMF was mixed with the Schiff base ligand (20 mmol) in DMF 1:1 (M:L) ratio and contents were refluxed in 150 mL DMF on an oil-bath for 2–3 h. The solid complexes that separated out were filtered, washed with ethanol and dried in desiccator over silica gel. The decompose at 275–300°C and are almost insoluble in water but partially soluble in polar solvents (DMF and DMSO).

RESULTS AND DISCUSSION

The analytical data for all these complexes were presented in Table 1. The Schiff base ligand was prepared by condensation of 2-hydroxynaphthalin-1-carbaldehyde with 1,2-bis-(*p*-aminophenoxy)ethane in absolute ethanol as yellow (see Fig. 2).

The metal to ligand ratio of the Ni(II), Co(III), Cu(II), and Zn(II) complexes was found to be 1:1; in addition Ni(II), Cu(II) and Zn(II) complexes were present one additional molecules of water of crystallization, but the Co(III) complex has two additional coordinated water molecule and hydroxo (see Fig. 3).

Table 1. The Colors, Formulas, Formula Weight, Yields, Melting Points, and Elemental Analyses Results of the Ligand and Its Complexes

Compound	F.W g/mole	M.P. (°C)	Yield (%)	Elemental Analyses % Calculated (Found)			Λ_M $\Omega^{-1}cm^{-2}mole^{-1}$	μ_{eff} (B.M)
				C	H	N		
Ligand (H_2L) (Yellow)	552.00	265.0	82.0	78.26	5.07	5.07	–	–
$C_{36}H_{28}N_2O_4$				(78.08)	(5.16)	(5.13)		
[CuL]H_2O (Brown)	631.55	275.0	63.0	65.40	4.43	4.43	2.7	1.72
$C_{36}H_{28}N_2O_5Cu$				(65.46)	(4.29)	(4.52)		
[NiL]H_2O (Green)	626.71	295.0	53.0	68.93	4.47	4.47	4.1	Dia
$C_{36}H_{28}N_2O_5Ni$				(68.88)	(4.60)	(4.46)		
[CoLH_2O(OH)] (Red)	661.93	289.0	50.0	65.26	4.38	4.23	3.0	Dia
$C_{36}H_{30}N_2O_6Co$				(65.41)	(4.42)	(4.08)		
[ZnL]H_2O (Dark White)	635.38	300.0	53.0	68.20	4.42	4.42	5.8	Dia
$C_{36}H_{28}N_2O_5Zn$				(68.37)	(4.40)	(4.20)		

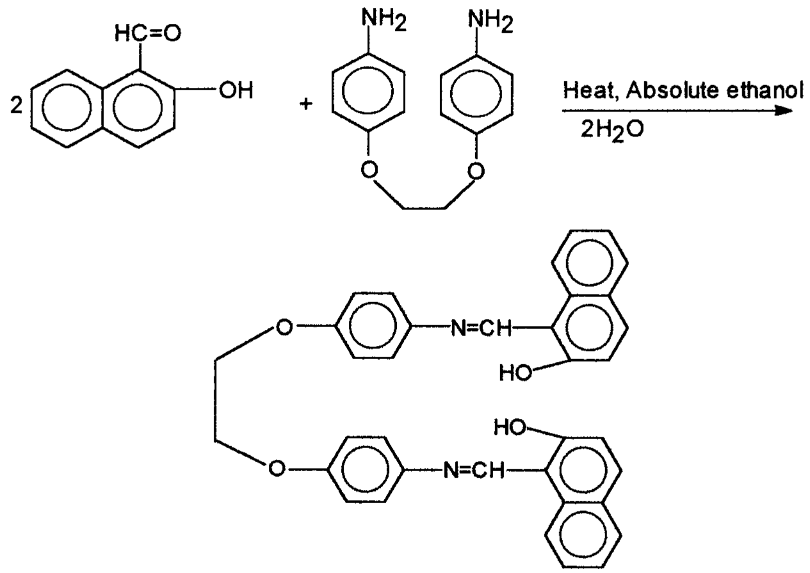

Figure 2. Synthesis scheme for the reaction of the 2-hydroxynaphthalin-1-carbaldehyde and 1,2-*bis*(*p*-aminophenoxy)ethane (H_2L).

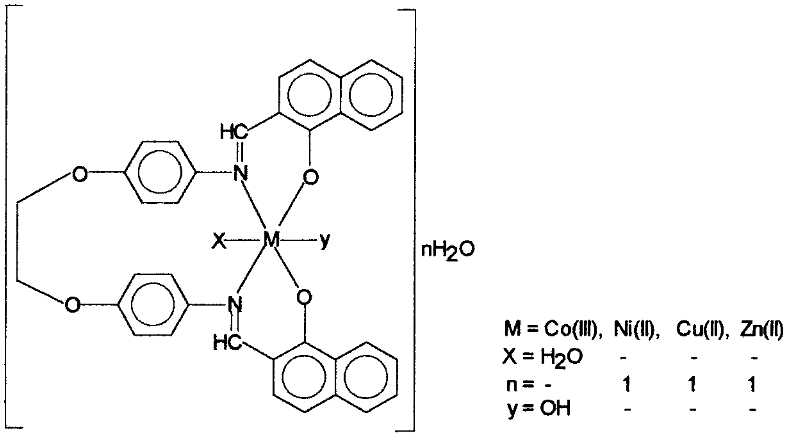

Figure 3. Suggested structure of the tetrahedral Zn(II), square-planar Cu(II), Ni(II), and octahedral Co(III) complexes of the ligand H_2L.

Their formation can be presented by the following general equations:

$$H_2L + Cu(CH_3COO)_2H_2O \rightarrow [CuL]H_2O + 2CH_3COOH$$

$$H_2L + Ni(CH_3COO)_2 4H_2O \rightarrow [NiL]H_2O + 2CH_3COOH + 3H_2O$$

$$H_2L + Zn(CH_3COO)_2 2H_2O \rightarrow [ZnL]H_2O + 2CH_3COOH + H_2O$$

$$H_2L + Co(CH_3COO)_2 4H_2O + 1/2O_2$$
$$\rightarrow [CoLH_2O(OH)] + 2CH_3COOH + 2H_2O + H_2O_2$$

Conductance Measurements

The Ni(II), Zn(II), Co(III) and Cu(II) complexes are non-electrolytes as shown by their molar conductivity (Λ_M) measurements in DMF, which are in the range[9] 2.7–5.8 Ω^{-1} cm^2 mol^{-1}.

Magnetic Susceptibility

The Cu(II) complex is paramagnetic and their magnetic susceptibility is 1.72 B. M., respectively. Since the Cu(II) complex is paramagnetic[10–12], their ^{1}H NMR spectra could not be obtained. The Zn(II), Ni(II) and Co(III) complexes are diamagnetic. These ^{1}H NMR and ^{13}C NMR spectra were being obtained.

IR Spectra

Important IR bands of the Schiff base ligand and its complexes are given in Table 2. A broad and weak band occurring around 3400 cm^{-1} may be attributed to the OH vibration of water molecules in the complexes[13]. The broad band that appeared in the IR spectrum of the Schiff base at 2887 cm^{-1} is assigned to the stretch vibration of the intramolecular hydrogen bonded -OH exist that in the molecule. Similar bands were observed at the same frequency in the IR spectra of salicylideneanilines[11]. This band disappeared in the IR spectra of the complexes. The band at 1285 cm^{-1} in the IR spectrum of the ligand is ascribed to the phenolic C-O stretching vibration[4]. This band is found in the region 1280–1283 cm^{-1} in the IR spectra of the complexes. These changes suggest that the *o*-OH group of this Schiff base moiety has taken part in complex formation. The coordination though the imine nitrogen is inferred from the shift of 1616 cm^{-1} of the ligand to 1613–1620 cm^{-1} of

Table 2. Some IR Frequencies (in cm^{-1}) of Schiff Base and Its Complexes

Ligand(H_2L)	[CuL]H_2O	[NiL]H_2O	[CoLH_2O(OH)]	[ZnL]H_2O	Assignment
–	3430 w	3440 w	3441 m	3445 w	H_2O
2887 m	–	–	–	–	Intramolecular H-bounded-OH
1616 s	1613 s	1617 s	1615 s	1620 s	Central C=N stretching
1285 m	1283 s	1280 s	1281 s	1282 s	Phenolic C-O stretching
–	505 w	557 w	506 w	500 w	ν(M-N)
–	455 w	475 w	459 w	461 w	ν(M-O)

[a] s (strong), m (medium), w (weak).

the complexes[14–16]. Conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of the metal complexes appear at 455–475 cm^{-1} and 500–557 cm^{-1} assigned to (M-O) and (M-N) stretching vibrations which are not observed in the spectra of the Ligand[16].

Electronic Spectra

The electronic spectra of all the complexes were recorded in 10^{-3} M DMF at room temperature. The spectra of free Schiff base exhibit two absorption bands in regions 265–275 and 318–326 nm. These bands are attributed to $\pi \rightarrow \pi^*$ transitions, the first with this of benzene ring and the second with this of the imino group. In the complexes, the imino $\pi \rightarrow \pi^*$ transition is shifted to a longer wavelength as a consequence of coordination when binding with the metal, confirming the formation of Schiff base metal complexes[17]. The electronic spectrum of the Ni(II) complex shows an absorption band at 444 nm ($\varepsilon = 405$ L $mol^{-1} cm^{-1}$) attributed to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition, which is compatible with this complex having a square-planar structure[18]. The electronic spectrum of the Cu(II) complex shows an absorption band at 600 nm ($\varepsilon = 290$ L $mol^{-1} cm^{-1}$) attributed to the $^2T_{2g} \rightarrow {}^2E_g(G)$ transition, which is compatible with this complex having a square-planar structure[19]. The electronic spectrum of the Co(III) complex shows an absorption bands at 424 nm ($\varepsilon = 600$ L $mol^{-1} cm^{-1}$) and 458 nm ($\varepsilon = 400$ L $mol^{-1} cm^{-1}$) attributed to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition, which is compatible with this complex having a octahedral structure[20]. The electronic spectrum of the Zn(II) complex shows an absorption band at 444 nm ($\varepsilon = 1395$ L $mol^{-1} cm^{-1}$) attributed to the L→M (charge transfer) transition, which is compatible with this complex having a tetrahedral structure[21,22].

^1H NMR and ^{13}C NMR Spectra

The ^1H NMR spectra (in DMSO-d_6) of the ligand H2L showed signals at 3.57 (s, 2H) Ar-OH; 4.42 (s, 4H) O-CH_2; 7.04 (d, 2H, J: 9.12 Hz), 7.14 (d, 4H, J: 8.92 Hz), 7.35 (t, 2H, J: 7.36 Hz), 7.54 (t, 2H, J: 7.21 Hz), 7.64 (d, 4H, J: 7.21 Hz), 7.80 (d, 2H, J: 7.72 Hz), 7.92 (d, 2H, J: 9.16 Hz), 8.51 (d, 2H, J: 8.52 Hz) Ar-H; 9.66 (s, 2H) HC = N ppm.

The ^1H NMR spectra (in DMSO-d_6) of the Zn(II) complex showed signals at 3.40 (br. 2H) H_2O; 4.42 (s, 4H) O-CH_2; 7.04 (d, 2H, J: 9.18 Hz), 7.14 (d, 4H, J: 8.84 Hz), 7.35 (t, 2H, J: 7.38 Hz), 7.55 (t, 2H, J: 7.91 Hz), 7.64 (d, 4H, J: 8.80 Hz), 7.80 (d, 2H, J: 7.96 Hz), 7.92 (d, 2H, J: 9.12 Hz), 8.51 (d, 2H, J: 8.50 Hz) Ar-H; 9.66 (s, 2H) HC = N ppm.

The ^{1}H NMR spectra (in DMSO-d_6) of the Ni(II) complex showed signals at 3.45 (br. 2H) H_2O; 4.42 (s, 4H) O-CH_2; 7.04 (d, 2H, J: 9.15 Hz), 7.14 (d, 4H, J: 8.88 Hz), 7.35 (t, 2H, J: 7.38 Hz), 7.55 (t, 2H, J: 7.90 Hz), 7.64 (d, 4H, J: 8.82 Hz), 7.80 (d, 2H, J: 7.92 Hz), 7.92 (d, 2H, J: 9.13 Hz), 8.51 (d, 2H, J: 8.50 Hz) Ar-H; 9.66 (s, 2H) HC = N ppm.

^{13}C NMR spectra (in DMSO-d_6) of the ligand H_2L showed signals at 109.48, 116.39, 121.23, 122.63, 122.91, 124.18, 127.58, 128.79, 129.81, 133.92, 136.91, 138.55, 155.69,158.16 ppm.

^{13}C NMR spectra (in DMSO-d_6) of the Zn(II) complex showed signals at 109.48, 116.39, 121.23, 122.62, 122.91, 124.19, 127.58, 128.79, 129.81, 133.92, 136.92, 138.52, 155.67, 158.16 ppm.

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