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Spectroscopic studies and biological evaluation of transition metal complexes of Schiff bases derived from 5-nitro-o-vanilline

K.R.Joshi, J.H.Pandya, A.J.Rojivadiya*

M.D. Science College, Porbandar, Gujarat, (INDIA)

E-mail : jhpandya@gmail.com; lekhrajr@gmail.com

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ABSTRACT

Two new series of cobalt(II), nickel(II) and copper(II) complexes with two Schiff base, HL^1 and HL^2; ligands have been prepared. The Schiff base, HL^1 and HL^2, ligands were synthesized by the condensation of 5-nitro-o-vanilline with 5-chloro-o-anisidine and 2,5-dichloroaniline respectively. All compounds were characterized by spectroscopy, elemental and thermal analyses techniques. This azomethine compounds were found to form complexes readily with cobalt(II), nickel(II) and copper(II). From IR and electronic spectral studies, the phenolic oxygen and imine nitrogen of the ligand were found to be the coordination sites. The structure of the complex obtained was confirmed by FT-IR, electronic spectra, ESI Mass and ^{1}H NMR. The metal complexes exhibit different geometrical arrangements such as square planar, tetrahedral, and distorted octahedral arrangement. These ligands as well as their metal complexes were also evaluated for their antimicrobial activity against several bacterial strains, such as *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *E. coli*. and also such funguses, *candida albicans* and *aspergillus-niger*.

KEYWORDS

Schiff base complexes;
Didentate ligand;
Antimicrobial activity.

INTRODUCTION

Schiff base metal complexes have been of interest in coordination chemistry for many years due to their facile synthesis and wide applications[1-3]. Many Schiff base complexes with metal ions have been studied because they possess diverse spectra due to biological and pharmaceutical activity, such as antitumour and antioxidative activity[4-5]. Schiff bases and their metal complexes have been prepared because of their interesting and important properties, e.g., their ability to bind toxic and heavy metal ions, exhibit catalytic reduction and photochromism[6]. Recently, cobalt(II), nickel(II) and copper(II) complexes involving Schiff base ligands of different denticity have been investigated in this laboratory[7-9]. The present investigation involves the synthesis, characterization and biological screening of cobalt(II), nickel(II) and copper(II) Schiff base complexes involving 5-nitro-o-vanillin and disubstituted anilines.

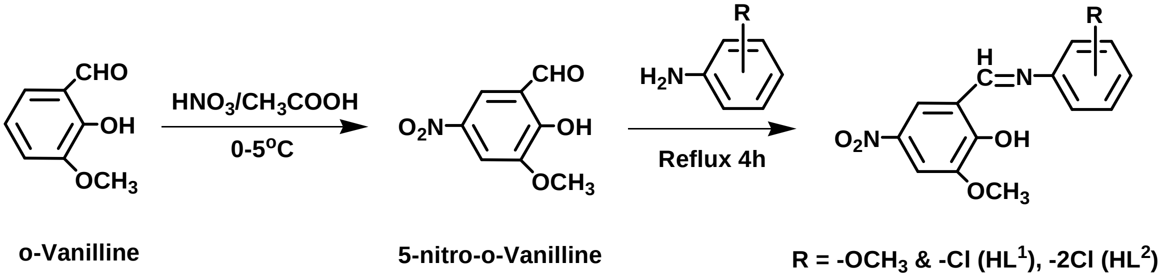
EXPERIMENTAL

1. Physical measurements

All chemicals (reagent grade) used were commercially available. IR spectra of the ligands and their metal complexes, as KBr discs, were recorded on an 8400 FTIR Simadzu Spectrometer. ^{1}H NMR spectra of the ligand and complexes, in DMSO-d6, were recorded on a Bruker Avance II 400 Spectrometer at room temperature using TMS as internal standard. Mass spectra were recorded at QP 2010 Shimadzu GCMS and ESI Mass VG-70-S Spectrometer, electronic spectra of the metal complexes in DMF were recorded on a perkin elmer lambda 19 Spectrophotometer, and ESR was recorded on E-112 ESR Spectrometer, Thermal analyses have been carried out by using Perkin Elmer (Pyris 1 TGA) from room temperature to 800°C under heating rate of 20°C/min. Elemental analysis of ligand and metal complexes carried out by Perkin Elmer PE 2400 elemental analyzer. Analyses of the metals were carried out by dissolving the complexes in concentrated nitric acid, neutralizing the diluted aqueous solutions with ammonia and titrating the metal solutions with EDTA.

2. Preparation of Schiff base ligand, HL

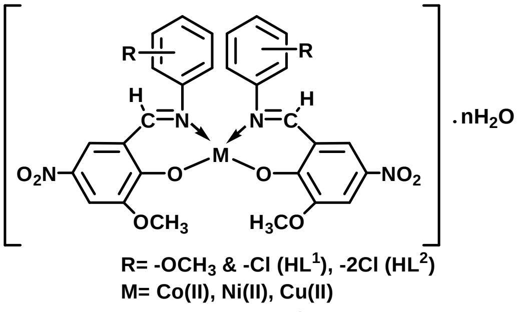
The ligands HL^1 and HL^2 both were prepared in two steps. The first step involved the nitration of o-vanilline in the presence of glacial acetic acid at 0-5^{0}C temp. in ice bath[10]. The second step involved the ethanolic solution of 5-nitro-o-vanilline (4.92g, 25.0 mmol)) with ethanolic solution of 5-chloro-o-anisidine (3.92g, 25.0 mmol) and 2,5- dichloro aniline (4.00 g, 25.0 mmol) was boiled under reflux in the presence of glacial acetic acid separately for 4 h. The products obtained were filtered off and washed several times with a few amount of EtOH then ether and air dried. The products were kept in a desiccators until used. Recrystallization was carried out in EtOH. A general chemical reaction for ligand is formulated as in (Scheme 1).



Scheme 1 : A general chemical reaction for ligand

3. Preparation of metal complexes

The solution of cobalt(II) chloride, nickel(II) nitrate and copper(II) nitrate (1.0 mmol) in EtOH (15 mL) was added dropwise to an ethanolic solution (25 mL) of Schiff base (2.0 mmol) and stirred at room temperature for an hour. The resulting mixture was allowed to reflux on a water bath at 70^{0}C for 2 h and cooled to room temperature. The precipitate was filtered, and then washed with cold alcohol. The resulting precipitate was recrystallized from MeOH and dried in a vacuum desiccators (Scheme 2).



Scheme 2 : Structure of metal complex

4. Testing of the Antimicrobial Activity

All of the compounds synthesized were tested for their antibacterial activities against *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *E. coli* and antifungal activity against *candida albicans* and *aspergillus-niger*. The method used for evaluate the antimicrobial activity is 'Broth Dilution Method'. It is one of the non-automated *invitro* susceptibility tests. Serial dilutions were prepared in primary and secondary screening[15, 16]. The MBC (minimal bactericidal concentration) of the control organism is read to check the accuracy of the drug concentrations. The lowest concentration inhibiting growth of the organism is recorded as the MBC/MFC.

RESULTS AND DISCUSSION

The structure of the ligands and the complexes were determined by a combination of elemental analysis, IR, ^{1}H NMR spectra, electronic spectra, Mass, ESI Mass and thermo gravimetric analyses (TGA). The analytical and physical data of ligands and metal complexes are given in TABLE 1.

TABLE 1 : The analytical and physical data of ligands and metal complexes

Ligand or Complex	Formula	Color	Yield	M.P. ^{0}C	Elemental analysis, %, Found/Calcd			
					C	H	N	M
HL^1	$C_{15}H_{13}ClN_2O_5$	Reddish brown	85%	170	53.48(53.50)	3.85(3.89)	8.31(8.32)	-
HL^2	$C_{14}H_{10}Cl_2N_2O_4$	Reddish brown	83%	140	49.26(49.29)	2.92(2.95)	8.20(8.21)	-
$[CoL^1]$ nH_2O	$C_{30}H_{24}Cl_2CoN_4O_{10}$	Reddish brown	68%	-	49.30(49.33)	3.30(3.31)	7.65(7.67)	8.04(8.07)
$[NiL^1]$ nH_2O	$C_{30}H_{24}Cl_2N_4NiO_{10}$	Green	74%	-	49.32(49.35)	3.30(3.31)	7.64(7.67)	8.00(8.04)
$[CuL^1]$ nH_2O	$C_{30}H_{24}Cl_2CuN_4O_{10}$	Bluish brown	81%	-	48.98(49.02)	3.27(3.29)	7.59(7.62)	8.63(8.65)
$[CoL^2]$ nH_2O	$C_{28}H_{18}Cl_4CoN_4O_8$	Reddish brown	69%	-	45.45(45.49)	2.43(2.45)	7.57(7.58)	7.93(7.97)
$[NiL^2]$ nH_2O	$C_{28}H_{18}Cl_4N_4NiO_8$	Green	72%	-	45.50(45.51)	2.43(2.46)	7.55(7.58)	7.90(7.94)
$[CuL^2]$ nH_2O	$C_{28}H_{18}Cl_4CuN_4O_8$	Bluish brown	79%	-	45.18(45.21)	2.40(2.44)	7.50(7.53)	8.52(8.54)

1. Spectral characterization of ligand and metal complex

IR and electronic spectra

TABLE 2 presents the most important bands of the infrared spectra of the compounds with their assignments[11, 12]. The bands at 1625 cm^{-1} of the ligands are assigned to the stretching vibration of the azomethine group. When the spectra of the complexes are compared with those of the uncomplexed Schiff base ligands the ν(C=N) band is shifted to lower frequency, this indicates that the imine nitrogen is coordinated to the metal ion. Very strong bands at 1270 cm^{-1} were assigned to in-plane bending (O–H) vibration of the ligands. This band is shifted in the complexes toward lower frequencies as a result of the coordination of the nitrogen to the metal ion. The infrared spectra of the ligand and complexes exhibit broad bands in the 3227–3351 cm^{-1} range and this may be attributed to the stretching vibration of the O–H groups. This band is ascribed to the O–H stretching vibration, which is known to shift significantly to lower frequencies because of OH—-N intramolecular hydrogen bonding. The bands between 575–435 cm^{-1} are assigned to vibrations that are probably coupled metal-nitrogen and metal-oxygen bonds.(Figure 1&2)

The electronic spectra of the Schiff base ligands and the complexes in EtOH are shown[13] in TABLE 2. In the Schiff base, the band at 334 nm is attributed to the azomethine chromophore π-π* transition. The bands at higher energies (212 and 281 nm) are associated with the benzene π-π* transition. In the spectra of the complexes, however, the azomethine chromophore π-π* transition is shifted to 300-320 nm, indicating that the imino nitrogen is involved in coordination to the metal ion. The absorption frequencies ascribed to the benzene π-π* transition (at ca. 218-223 and 265-270 nm) are slightly changed, representing an influence on the benzene ring due to the coordination interaction. The Schiff bases are capable of coordinating to the metal ion occupying four coordination sites preferably with

TABLE 2 : Infrared and electronic spectral data of ligand and complexes

Ligand/ Complex	IR spectra (cm^{-1})					λ_{max} (nm)
	ν (OH)	ν (C=N)	ν (C-O)	ν (M-O)	ν(M-N)	
HL^1	3400	1625	1235	-	-	212, 281, 334
HL^2	3350	1616	1225	-	-	212, 281, 334
$[CoL^1]$ nH_2O	3157	1610	1226	453	541	219, 267, 317
$[NiL^1]$ nH_2O	3227	1600	1231	451	533	219, 270, 300
$[CuL^1]$ nH_2O	3319	1605	1232	452	530	218, 265, 322
$[CoL^2]$ nH_2O	3340	1598	1229	448	535	219, 268, 316
$[NiL^2]$ nH_2O	3220	1610	1226	447	540	220, 270, 310
$[CuL^2]$ nH_2O	3320	1608	1230	450	538	218, 265, 324

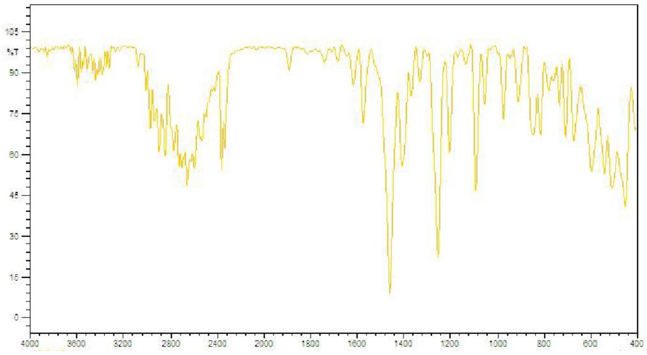


Figure 1 : IR spectra of ligand

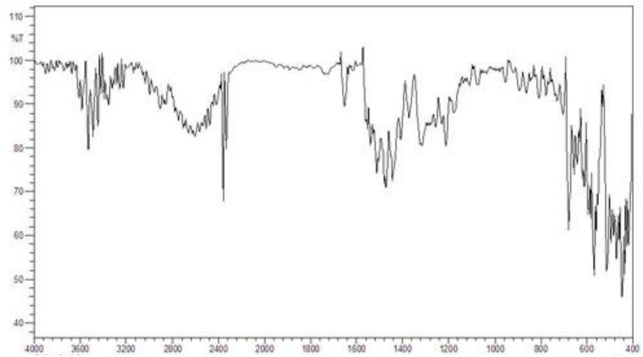


Figure 2 : IR spectra of metal complex

cis-nitrogen atoms. Hence, one can postulate that the structure of the complexes is square planar, -ONNO-donor atoms occupying the four sites of the plane. The tentative structure for the complexes is shown in Figure 1. The water molecules may be in the lattice.

^{1}H NMR Spectra

The ^{1}H NMR spectra of the ligand (HL^1 & HL^2) and complex were obtained (Figure 3). The ligand HL^1 exhibits signals at δ (ppm) 8.15 (1H, s, CH), 7.91–6.76 (m, ArH), 3.83 and 3.96 (3H, s, -2-OCH_3), and 10.19 (1H, s, -OH), and HL^2 exhibits signals at δ (ppm) 8.15 (1H, s, CH), 7.91–6.76 (m, ArH), 3.96 (3H, s, -OCH_3), and 10.19 (1H, s, -OH). While in the complex the signals are at 7.83-6.71, 3.83 and 3.96 δ (ppm). The proton peak of the -OH group had disappeared, which suggests that the hydroxyl group coordinates to the metal ions. The signal at 8.15 (s, 1H) attributed to the imine hydrogen in the ligand, shifts to 8.30 (s, 1H) in the complexes, which proves that imine nitrogen took part in the coordination. Thus, the ^{1}H NMR studies reinforce the conclusions drawn from the IR spectra.

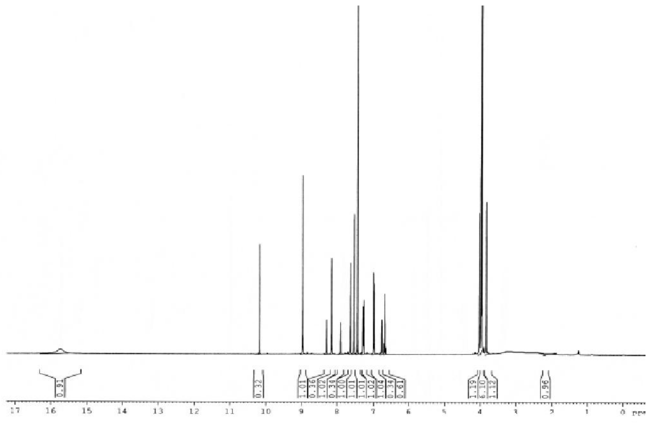


Figure 3 : ^{1}H NMR spectra of ligand

Mass spectra

Mass spectroscopy was performed on the HL ligand to determine its molecular weight and fragmentation pattern. The molecular ion peaks for HL^1 were observed at m/e 337, 301, 271, 241, 225, 149, 135, 122, 77, 63, 44 and the molecular ion peaks for HL^2 were observed at m/e 341, 305, 271, 241, 225, 149, 135, 122, 77, 63, 44. The formula weight (FW) for HL^1 and HL^2 are 336 and 340 respectively. Which are same as the calculated m+ values. Mass spectroscopy of complexes was taken by ESI mass, which shows the total mass of complex with lattice water molecule.

Thermal Analysis

Thermal methods of analysis open a new possibility for the investigation of metal complexes[14]. The thermal behavior of all the metal complexes was studied by using thermo gravimetric techniques at a 40–700°C temperature range. The data from the thermo gravimetric analyses indicated that the decomposition of the complexes proceeds in three steps (Figure 4). The complexes lost water molecules between 40–200°C, the decomposition of ligand between 200-500°C and formed metal oxides above 500°C for the Cu(II), Ni(II) and Co(II) complexes. Water of hydration is associated with complex formation and is found outside the coordination sphere formed around the central metal ion.

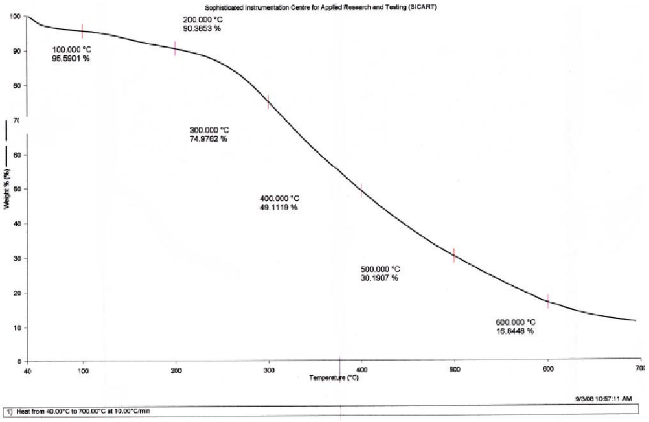


Figure 4 : TG analysis of metal complex

2. Biological evaluation of ligand and metal complex

Anti bacterial and antifungal activities of the ligand and its complexes were carried out against the bacteria *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *E. coli*. And fungi *candida albicans* and *aspergil-*

lus-niger by the ‘broth dilution method’ with MIC using Gentamycin and Nystatin as standards. The results of the antibacterial and antifungal study are given in TABLE 3. The study indicates that the Co(II), Ni(II) and Cu(II) complexes show moderate antibacterial and good antifungal activity in comparison with standard drugs[15, 16].

TABLE 3 : Antimicrobial activities of ligands and their complexes at different concentrations

Compound	Antibacterial activity			Antifungal activity	
	Concentration (μg/ml)				
	E. coli	***S. aureus***	***P. aeruginosa***	***Candida albicans***	***Aspergillus-niger***
HL^1	++	+++	++	+	+
HL^2	+	+	+	+	+
$[CoL^1]\ nH_2O$	+	+++	++	+	+
$[NiL^1]\ nH_2O$	+	+++	++	++	+
$[CuL^1]\ nH_2O$	++	++	++	++	+
$[CoL^2]\ nH_2O$	+++	++	+++	+	++
$[NiL^2]\ nH_2O$	++	+++	++	+	+
$[CuL^2]\ nH_2O$	+	+++	+++	+	++

+++ - 100 μg/ml, ++ - 250 μg/ml, + -500 μg/ml

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