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Synthesis and identification of several new complexes of Co (II), Ni (II) and Cu (II) with a bidentate Schiff base ligand

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ABSTRACT

This paper reports the synthesis of Co (II), Ni (II) and Cu (II) complexes of N, N- bis (2-nitrocinnamaldehydene)phenylene-1,2-diamine (L). The compounds so obtained have been characterized by elemental analyses, molar conductance, magnetic measurements, infrared and electronic spectral studies and decomposition temperatures. The results suggest pseudotetrahedral geometry for cobalt and copper while octahedral structure for nickel complexes. Therefore general formulas of these complexes are suggested as NiL_2X_2 and MLX_2, wherein M = Co (II) and Cu (II) and X = Cl^-, Br^-, I^-,$N3^-$, SCN^-.

KEYWORDS

Schiff base;
Cobalt;
Nickel and copper complexes;
Symmetrical.

INTRODUCTION

Schiff bases offer versatile and flexible ligands capable of binding with metal cations to yield complexes[1]. The field of Schiff base complexes was fast developing on account of the wide variety of possible structures for the ligands depending upon the aldehydes and amines[2-4]. Many attempts were done to prepare symmetric polydentate ligands in order to achieve rare coordination number with Ni (II) and Co (II) ions whose importance was mainly due to their ability to form metal chelates[5]. Synthesis of these Schiff base complexes is achieved through the template reaction[6] or transmetallation reactions[7] which are used when the transition metal cations are ineffective as templates. These ligands and their metal complexes have different applications in fields such as bioinorganic chemistry, material science, catalysis, separation and encapsulation processes, hydrometallurgy, formation of compounds with unusual properties and metal–metal interactions[8-11]. New efficient antidepressants, anticonvulsants, antimicrobial and other medical agents have been detected on the basis of azomethines[12-14].

The aim of this present study is to synthesize and characterize of new Ni (II), Co (II) and Cu (II) complexes with bidentate Schiff base derived from 2- nitrocinnamaldehyde and 1,2-phenylendiamine. The general formula of these complexes are NiL_2X_2 and MLX_2 wherein M = Co (II) and Cu (II) and X = Cl^-, Br^-, I^-, N_3^-, SCN^-. The ligand and complexes were characterized by physical and spectral data such as FT-IR, UV-Vis, magnetic moment, ^1H and ^{13}C NMR and conductivity measurements.

EXPERIMENTAL

Materials

2-nitrocinamaldehyde and 1,2-phenylendiamine, cobalt, nickel and copper salts and other chemicals were obtained from Aldrich and Merck. Solvents were purified by standard methods[15].

Physical measurements

IR spectra in the 4000-400 cm^{-1} range were obtained as KBr pellets on a JASCO-680 model FT-IR spectrometer. UV–Vis spectra were recorded using a JASCO-V570 model spectrophotometer in DMF. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300MHz FT-NMR spectrometer with the samples dissolved in DMSO-d$_6$ using TMS as internal standard. MS (m/z) of ligand was obtained on Shimadzu model GC-MS QP5050. Elemental analyses (CNHS) of dried samples were performed using a CHNS-932 (leco) elemental analyzer by central instrumental laboratory of Tarbiat Moallem University of Tehran. The melting points (°C) of the compounds were recorded on a BI Barnstead electrothermal instrument. The molar conductivity of the ligands and their complexes were determined in DMF (1.0 × 10^{-3} M) at room temperature using a Metrohm 712 conductometer with a dip-type conductivity cell made of platinum black. Magnetic susceptibility data for the metal complexes were recorded on a magnetic susceptibility MS-model (made in Iran).

Synthesis of ligand

N, N- bis (2-nitrocinnamaldehydene)phenylene-1,2-diamine (L) as a bidentate Schiff-base was prepared by mixing 2:1 ratio of 2- nitrocinnamaldehyde (1 mmol, 0.177 g) and 1,2-phenylendiamine (0.5 mmol, 0.054 g) in methanol solvent under reflex and severe stirring condition for 4-5h as reported in our previous report[16]. The product was characterized by spectral and analytical data as reported previously.

Synthesis of complexes

A solution of 0.5mmol ligand (0.213 g) (1 mmol ligand for Ni (II) complexes) in dicholoromethane/methanol mixture was added slowly to a magnetically stirred solution of 0.5 mmol MX$_2$ (M= Co (II), Ni (II) and Cu (II) and X= Chloride, bromide, iodide, thiocyanate and azide). The mixture was vigorously stirred at room temperature for 4–6 h. The complexes were filtered as a colored precipitates and for more purification washed twice with warm methanol. The physical, IR and electronic spectral data have been collected in TABLE 1 and 2.

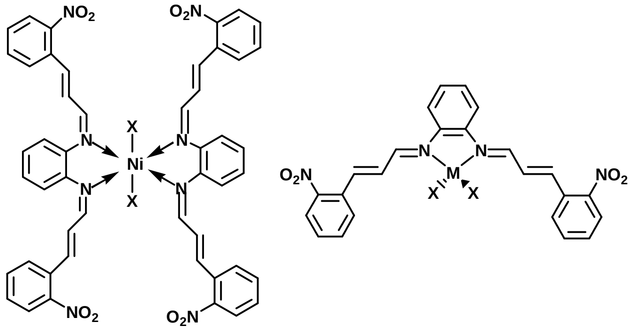
TABLE 1 : Synthetic, analytical, magnetic moment and conductivity data for the ligand and its complexes.

	Compound	Color	M.p.(°C)	Yield (%)	Found (Calcd.) (%)			ΛM(cm^2 Ω^{-1}M^{-1})	μ$_{eff}$ (B.M.)
					C	N	H		
1	Ligand	Yellow	146-148	68	66.8(67.60)	13.2(13.14)	4.2(4.25)	2.18	-
2	CoLCl$_2$	Dark yellow	220(dec.)	79	52.16(51.82)	10.20(10.07)	3.19(3.26)	18.77	3.81
3	CoLBr$_2$	Orange	223(dec.)	82	-	-	-	73	3.72
4	CoLI$_2$	Orange	225(dec.)	80	-	-	-	121	3.50
5	CoL(SCN)$_2$	Yellow	212(dec.)	76	52.30(51.91)	13.10(13.97)	3.20(3.02)	60.09	3.35
6	CoL(N$_3$)$_2$	Orange	195(dec.)	72	-	-	-	52.10	3.85
7	NiL$_2$Cl$_2$	Yellow	258(dec.)	79	57.71(58.68)	11.27(11.41)	3.50(3.69)	50.8	2.71
8	NiL$_2$Br$_2$	Yellow	255(dec.)	78	-	-	-	95.5	2.60
9	NiL$_2$I$_2$	Orange	260(dec.)	81	49.1(49.47)	9.3(9.62)	3.40(3.11)	128	2.65
10	NiL$_2$(SCN)$_2$	Pale yellow	224(dec.)	72	-	-	-	46.55	2.55
11	NiL$_2$(N$_3$)$_2$	Orange	203(dec.)	68	56.72(57.91)	19.33(19.70)	3.37(3.64)	34.6	2.68
12	CuLCl$_2$	Brown	224(dec.)	74	44.93(44.36)	8.34(8.62)	2.78(2.79)	51.6	1.71
	CuLBr$_2$	Brown	227(dec.)	75	-	-	-	47.6	1.61
13	CuL(SCN)$_2$	Brown	209(dec.)	69	50.90(51.52)	13.30(13.86)	2.70(2.99)	26.35	1.63

RESULTS AND DISCUSSION

Synthesis

By condensation reaction between 2-nitrocinnamaldehyde and 1,2-phenylendiamine, the Schiff base of N(1), N(2) -bis (2-nitrocinnamaldehydene)-1,2-phenylenediamine (L) was prepared. The Schiff-base is soluble in dichloromethane, chloroform, acetone, dimethylsulfoxide, dimethylformamide, and less soluble in alcohols. The detailed spectral data of ligand has been reported previously[16]. New complexes with general formula MLX_2 for Co (II) and Cu (II) and NiL_2X_2 wherein X= Cl^-, Br^-, I^-, SCN^- and N_3^- were synthesised and the stoichiometries of the ligand and its complexes were confirmed by their elemental analyses. The analytical and physical data of the Schiff base ligand and its complexes are given in TABLE 1 and 2. The analytical data show that the metal to ligand ratio for Ni (II) complexes is 1:2 and for Co (II) and Cu (II) complexes is suggested to be 1:1 (Scheme 1).



Scheme 1 : Suggested structure of the NiL_2X_2 and MLX_2 complexes M=Co(II) and Cu(II) and X=Cl^-, Br^-, I^-, SCN^-, N_3^-.

Molar conductivity

The molar conductance measurements of the prepared complexes were carried out in 10^{-3}M solutions of the complexes in DMF at room temperature. The obtained values (in the 18.77-128 $cm^2\Omega^{-1}M^{-1}$ range) were taken as a good evidence for the existence of a non-electrolyte nature of all complexes meaning the coordination of ligand and anions to metal centers in inner sphere coordination space[17]. Except for cobalt and nickel iodide complexes that is suggested to be dissociated in DMF solution probably to two mols of ions.

IR spectra

Comparably difference in the location of picks in IR spectrum before and after complexation is a good evidence that show the ligand is coordinated to metal in all complexes. The most characteristic absorptions of the bidentate Schiff base ligand and its complexes are summarized in TABLE 2. The IR spectra of ligand and some metal complexes are depicted in Figure 1. The FT-IR spectrum of the Schiff base ligand showed the stretching frequencies at 3057, 2916 and 2856 cm^{-1} assigned to C-H of aromatic, aliphatic and iminic groups, respectively, smoothly affected by coordination of the ligand. The absorption band in the 1609 cm^{-1} is assigned to the existence of ν (HC=N-) group of the azomethine as function group for Schiff base compound. The shifting to the higher frequecy 1617-1624 cm^{-1} indicated this group was affected by complexation. The very strong bands at 1519 and 1347 cm^{-1} for the ligand can be attributed to the asymmetric

TABLE 2 : Infra-red (cm^{-1}) and UV–Visible (nm) spectral data of the Schiff-base ligand and its complexes.

Compounds	$\nu CH_{arom.}$	$\nu CH_{aliph.}$	νCH_{imin}	νC=N	ν (–NO2)	νCH arom(oop)	νC-C arom(oop)	νM–N	$–SCN/–N_3$	λ_{max}
Ligand	3057	2916	2856	1609	1519, 1347	734	698	-	-	278, 374
$CoLCl_2$	3058	2912	2854	1623	1522, 1343	743	698	460	-	284, 372, 608, 674
$CoLBr_2$	3058	2910	2853	1623	1523, 1343	742	698	464	-	284, 368, 612, 666
$CoLI_2$	3061	2917	2856	1622	1523, 1344	741	698	457	-	282, 372, 608, 672
$CoL(SCN)_2$	3070	2917	2859	1621	1521, 1343	741	698	459	2066	284, 372, 596, 654
$CoL(N_3)_2$	3068	2925	2856	1619	1523, 1340	741	697	455	2035	282, 372, 594, 676
NiL_2Cl_2	3059	2912	2848	1624	1522, 1344	742	698	472	-	288, 352
NiL_2Br_2	3058	2917	2854	1623	1523, 1343	742	698	464	-	288, 348
NiL_2I_2	3062	2912	2854	1621	1523, 1344	741	698	472	-	288, 352
$NiL_2(SCN)_2$	3078	2914	2859	1620	1520, 1343	741	699	477	2083	288, 348
$NiL_2(N_3)_2$	3066	2921	2854	1621	1523 and 1341	741	697	462	2035	288, 348
$CuLCl_2$	3063	2912	2854	1618	1516, 1347	736	691	455	-	280, 508
$CuLBr_2$	3058	2912	2850	1623	1523, 1343	742	698	458	-	284, 508
$CuL(SCN)_2$	3061	2913	2850	1617	1514, 1344	739	681	455	2111	282, 374, 522

(ν_{asym}) and symmetric stretching (ν_{sym}) of $-NO_2$ groups. As shown in TABLE 2, in the complexes these strong bands shift a few wave numbers. The very strong out-of-plane bending of the aromatic C-H and C-C at 734 and 698 cm^{-1} are shifted to higher or lower frequencies after coordination. Evidences for bonding in

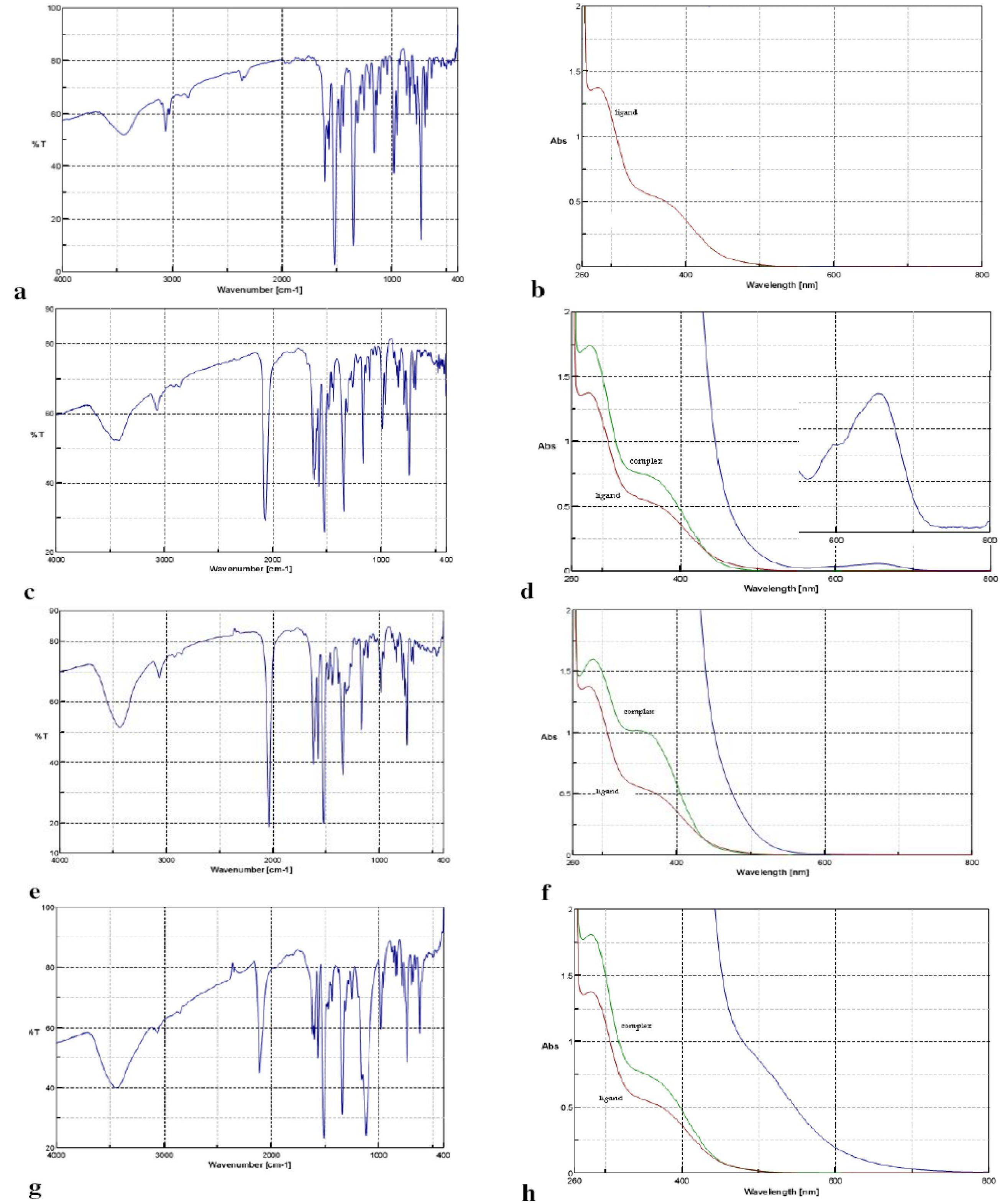


Figure 1 : The IR and UV-Visible spectra of ligand(a, b), cobalt thiocyanate complex(c, d), nickel azide complex(e, f) and copper thiocyanate complex(g, h).

the complexes is also shown by observation of new bands in the spectra of the metal complexes at 455–477 cm^{-1} assigned to ν (M–N)[18]. The absorption bond at 2066, 2083 and 2111 cm^{-1} in the IR spectrum of CoL $(SCN)_2$, $NiL_2(SCN)_2$ and CuL $(SCN)_2$ assigned to coordinated SCN- to metal as N- linkage for two first and S-linkage for the third respectively[19,20]. The absorption frequency at 2035 cm^{-1} in azid complexes of Co (II) and Ni (II) confirmed coordination of N_3^- to metal ion[19,21,22].

Electronic spectral studies

All complexes are insoluble in nonpolar solvents like benzene, toluene and petroleum ether as well as polar solvents like ethyl alcohol, methyl alcohol, dichloromethane, chloroform, acetonitrile and acetone but they are soluble in DMF and DMSO. The electronic spectra of the complexes were obtained in DMF solution with 10^{-4} M concentration at room temperature. The spectral data have been recorded in TABLE 2. The electronic spectra of ligand and some metal complexes are illustrated in Figure 1. The spectrum of free Schiff base exhibits two absorption bands. The first band in region 278 nm attributed to $\pi \rightarrow \pi^*$ transition of banzene ring and second band in region 374 nm assigned to $\pi \rightarrow \pi^*$ transition of imine group. After coordination in all complexes, the $\pi \rightarrow \pi^*$ transition band of banzene ring is shifted to longer wavelenght and the imino $\pi \rightarrow \pi^*$ transition is shifted to a shorter wavelength. These chenges in UV spectra of complexes confirm the formation of Schiff base metal complexes. The electronic spectra of the Cobalt complexes exhibit an absorption band with fine structure at 594-676 nm attributed to the d-d electron transition (A_2 to T_1 (F)). Two other bands is expected for this type of complexes that fall out of the visible region and are not shown by our instrument. A band related to d-d electron transfer is the characteristic for Ni (II) complexes in octahedral geometry in the 400-800 nm but in this record, this band is not appeared because the structure of these Schiff base Ni (II) complexes are rigid leading to shift of related transition to shorter wavelengths and probably converge with ligand transitions. The Cu (II) complexes show a broad band in the visible region of the electronic spectra at 508-522 nm. This is the characteristic d-d transition band in distorted pseudo-tetrahedral Cu (II) complexes.

Magnetic susceptibility

All the Co (II), Ni (II) and Cu (II) complexes were found to be paramagnetic as seen in TABLE 1. The values of the magnetic moment (μ_{eff}) are 3.35-3.85 B.M. for cobalt complexes, 2.55-2.71 B.M. for nickel complexes and 1.61-1.71 for cooper complexes. The magnetic moment values confirm pseudo-tetrahedral geometry for cobalt and copper complexes. Also the found magnetic moment values of nickel complexes suggest the octahedral geometry for them[23].

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