

Synthesis and Characterization of Co(II), Ni(II), Cu(II) and Cd(II) Complexes of Schiff Base Derived from 1,8-Diaminonaphthalene

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A new Schiff base 8-amino-[1-(2-hydroxyphenyl)imino]naphthalene (LH) has been synthesized by the condensation of 1,8-diaminonaphthalene and salicylaldehyde. The complexes of the Schiff base were prepared with Co(II), Ni(II), Cu(II), Cd(II) chlorides in ethanol. The ligand and its metal complexes have been characterized by elemental analyses, magnetic susceptibility, molar conductance, IR, ¹H NMR and UV-Vis spectroscopy. The magnetic moment and electronic spectral data suggest tetrahedral structure for Ni(II) and Cd(II) complexes, square-planar geometry for Co(II) and Cu(II) complexes.

Key Words: 1,8-Diaminonaphthalene, Salicylaldehyde, Schiff base, Metal complexes.

INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and find extensive application in different fields^{1,2}. A large number of Schiff base compounds are often used as ligands in coordination chemistry by considering their metal binding ability³. Metal complexes with Schiff base have been widely studied subject because of their industrial, antifungal, antibacterial and biological applications⁴⁻⁸. Schiff bases obtained from 1,8-diaminonaphthalene can be used in optical materials and conducting polymers⁹. Thus new optical and organic conducting materials can be produced by these compounds.

The present investigation is concerned with the synthesis and characterization of Co(II), Ni(II), Cu(II) and Cd(II) complexes with Schiff base ligand derived from condensation of 1,8-diaminonaphthalene and salicylaldehyde.

EXPERIMENTAL

All chemicals and solvents were obtained from Merck, Aldrich or Alfa Aesar. The chemicals were used without further purification.

The electronic spectra of the ligand and the complexes in the UV-Vis region were recorded in acetone and chloroform solutions using a pharmacia LKB-Ultraspac III. UV Spectrophotometer. The IR spectra of the ligand and the complexes were recorded with Ati Lnicam Mattson 1000 Series instrument. ¹H NMR spectra were recorded

on a Jeol FX 90 Q, 90 MHz in DMSO- d_6 , magnetic susceptibilities measurements were performed using the standard Gouy tube technique using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant. The elemental analyses were conducted on a leco 932 CHNS-o instrument.

Synthesis of Schiff base ligand: 3.16 g (0.02 mol) of 1,8-diaminonaphthalene was dissolved in 50 mL ethanol, was added with constant stirring to a solution of 2.44 g (0.02 mol) of salicylaldehyde in ethanol (10 mL). The pH was adjusted to ≈ 5 using glacial acetic acid (3-4 drops). The reaction mixtures were refluxed for 6 h. The resulting solution was allowed to stand at ambient temperature for 24 h. Brown coloured precipitate was filtered and washed with ethanol and ether, respectively. It was then dried at room temperature¹⁰. Yield: 3.93 g (75.0 %).

Synthesis of the Co(II), Ni(II), Cu(II) and Cd(II) complexes: The ligand 0.52 g (0.002 mol) was dissolved in 30 mL absolute ethanol in a 100 mL round bottom flask. A solution of 0.001 mol of metal salts [$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24 g), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.17 g)] in 10 mL absolute ethanol was added dropwise in a 10 min period with continuous stirring at room temperature. The mixture was refluxed for 12 h at 90 °C. The precipitated complex was filtered, washed with ethanol dried in room temperature.

The complexes Cu(II) and Cd(II) were prepared by same method using an aqueous solution (10 mL) of [$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 0.26 g (0.001 mol), $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ 0.26 g (0.001 mol)] and ethanol solution (50 mL) of the ligand L (0.001 mol). Yields: 0.35 g (61.0 %) for Co(II), 0.33 g (57.0 %) for Ni(II), 0.26 g (52.0 %) for Cu(II), 0.31 g (58.0 %) for Cd(II).

RESULTS AND DISCUSSION

The Schiff base ligand was prepared by condensation of salicylaldehyde with 1,8-diaminonaphthalene in absolute ethanol by the reaction of shown in Fig. 1.

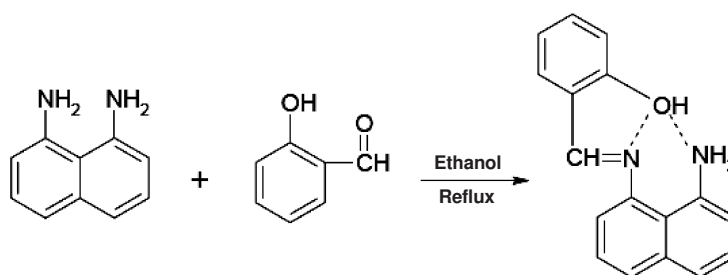
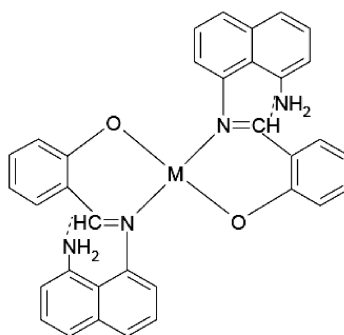


Fig. 1. Synthesis scheme for the reaction of the 1,8-diaminonaphthalene and salicylaldehyde

The elemental analysis results and some physical properties of the ligand and its complexes are listed in Table-1. The ligand LH on reaction with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ yields complexes corresponding to the formulae [CoL_2], [NiL_2], [Cu_2LCl_3] and [$\text{Cd}_2\text{L}(\text{OH})_3$] (Fig. 2 and 3).

TABLE-1
COLOURS, FORMULA, FORMULA WEIGHT, YIELDS, MAGNETIC MOMENTS
AND ELEMENTAL ANALYSES RESULTS OF THE SCHIFF BASE AND
ITS METAL COMPLEXES

Compounds	FW (g/mol)	Yield (%)	Elemental analyses (%): Calcd. (Found)			μ_{eff} (BM)
			C	H	N	
Ligand (Brown)	262.00	75.0	77.86 (77.62)	5.34 (5.48)	10.69 (10.47)	–
$\text{C}_{17}\text{H}_{14}\text{N}_2\text{OH}$						
$[\text{CoL}_2]$ (Dark Green)	580.93	61.0	70.23 (70.34)	4.48 (4.48)	9.64 (9.66)	1.72
$\text{C}_{34}\text{H}_{26}\text{N}_4\text{O}_2\text{Co}$						
$[\text{NiL}_2]$ (Dark Green)	580.71	57.0	70.26 (70.37)	4.48 (4.40)	9.64 (9.60)	3.90
$\text{C}_{34}\text{H}_{26}\text{N}_4\text{O}_2\text{Ni}$						
$[\text{Cu}_2\text{LCl}_3]$ (Black)	494.58	52.0	41.25 (41.30)	2.63 (2.43)	5.66 (5.68)	Diamag.
$\text{C}_{17}\text{H}_{13}\text{N}_2\text{OCl}_3\text{Cu}_2$						
$[\text{Cd}_2\text{L}(\text{OH})_3]$ (Pale pink)	536.80	58.0	38.00 (38.06)	2.98 (2.86)	5.22 (5.18)	Diamag.
$\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_4\text{Cd}_2$						



M = Co(II) and Ni(II)

Fig. 2. Suggested structure of the square-planar Co(II) and tetrahedral Ni(II) complexes of the ligand

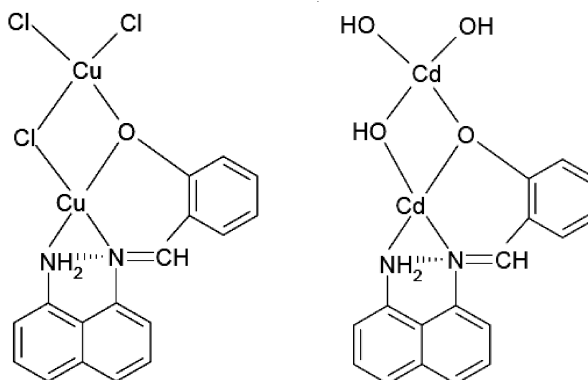
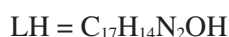
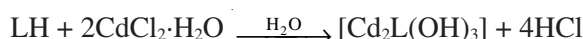
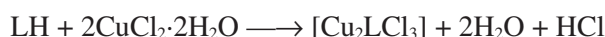
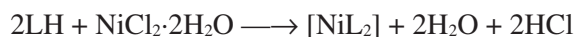
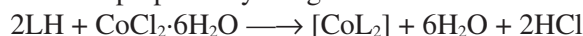


Fig. 3. Suggested structure of the square-planar Cu(II) and tetrahedral Cd(II) complexes of the ligand

The complexes were prepared by the general reactions shown below.



All metal complexes of this Schiff base was air stable and prepared by the stoichiometric reactions of the corresponding metal(II) chloride with the Schiff base ligand, in molar ratio M:L of 1:2 or 2:1. The Schiff base is sparingly soluble in hot ethanol, methanol, acetone, chloroform and benzen, while the complexes are soluble in acetone, chloroform and DMF.

Conductance measurements: According to the molar conductivity measurement Co(II), Ni(II), Cu(II) and Cd(II) complexes haven't an important conductivity and shows that the complexes are non-ionic structure¹¹.

Magnetic data: The Co(II) and Ni(II) complexes are paramagnetic and their magnetic susceptibilities are 1.72 and 3.90 BM, respectively^{12,13}. Cu(II) and Cd(II) complexes are diamagnetic^{11,14}. It was concluded that there was Cu-Cu effect in Cu(II) complex. It was determined that Cu(II) complex has dimeric structure and Cd(II) complex has tetrahedral geometry¹³ with coordination number 4.

Infrared spectra: Important IR bands of the Schiff base ligand and its metal complexes are given Table-2. The broad band is observed at 3000-2666 cm^{-1} in IR spectrum of ligand belonged to intramolecular hydrogen-bonding vibration (O-H...N). Spectra of $[\text{CoL}_2]$, $[\text{NiL}_2]$, $[\text{Cu}_2\text{LCl}_3]$ and $[\text{Cd}_2\text{L}(\text{OH})_3]$ observed a broad band at 3666-2610 cm^{-1} prevented extension vibrations belong to NH_2 . This is indicating that strong intramolecular and between molecular hydrogen-bonding¹¹.

TABLE-2
CHARACTERISTIC IR BANDS (cm^{-1}) OF THE LIGAND (LH)
AND ITS METAL COMPLEXES IN KBr PELLETS

Assignment	Ligand (LH)	$[\text{CoL}_2]$	$[\text{NiL}_2]$	$[\text{Cu}_2\text{LCl}_3]$	$[\text{Cd}_2\text{L}(\text{OH})_3]$
Intramolecular H-bounded (OH...N)	3000-2666	3500-2660	3500-2610	3666-2700	3530-2800
$\nu(\text{CH}=\text{N})$ azomethine	1621	1602	1604	1612	1606
$\delta(\text{NH})$	1600	—	—	1589	1586
Phenolic C-O stretching	1270	1165	1165	1153	1167
$\nu(\text{M}-\text{N})$	—	532	530	536	540
$\nu(\text{M}-\text{O})$	—	444	440	450	475

The band at 1621 cm^{-1} assigned to the stretching vibration of the azomethine group of the ligand. This band shifted in the complexes toward lower frequencies (1612-1602 cm^{-1}) because of the coordination of the ligand to the metal atoms by the nitrogen of azomethine^{15,16}.

IR spectrum of the ligand exhibited a band 1600 cm^{-1} attributed to $\delta(\text{N-H})$ band. The band observed at 1600 cm^{-1} in the free ligand assigned to $\delta(\text{NH})$ is shifted to lower frequencies in Cu(II) and Cd(II) complexes. This suggests that this amine group is involved in metal ion coordination¹⁷.

The infrared spectra of Schiff base ligand showed band at 1270 cm^{-1} assigned to the phenolic C-O vibration. However, in the spectra of the metal complexes the C-O band shifted to the lower region $1167\text{-}1153\text{ cm}^{-1}$. These changes suggest that the OH group of this Schiff base moiety has taken part in complex formation¹⁸.

The infrared spectra of all metal complexes showed two new bands at $540\text{-}530$ and $475\text{-}440\text{ cm}^{-1}$ assigned to $\nu(\text{M-N})$ and $\nu(\text{M-O})$, respectively¹⁹.

¹H NMR Spectra: ¹H NMR spectra of the ligand and its the Cu(II) complex was recorded using DMSO-*d*₆ as a solvent. ¹H NMR spectrum of ligand showed a singlet at 9.85 ppm that was assigned to the OH proton and multiplets at 7.60-6.40 ppm were assigned to the aromatic protons. The singlet at 8.25 ppm was attributed to the proton of the azomethine group and NH₂ protons were observed at 4.1 ppm²⁰. The NH₂ and OH protons disappeared on addition of D₂O. The ¹H NMR spectrum of Cu(II) complex showed almost the same values as that of the ligand with the exception of phenolic group. The phenolic-OH signal, appeared in the spectrum of ligand (LH) at 9.85 ppm is completely disappeared in the spectra of its Cu(II) complex indicating that the OH protons are removed by the chelation with Cu(II) ions. In the spectra of Schiff bases proton of the azomethine group undergo downfield shift in the Cu(II) complex indicating participation of this group in coordination of the metals ions. Since the Cd(II) complex is insoluble, its ¹H NMR spectra could not be obtained.

Electronic spectra: The UV-vis spectra of the ligand and its complexes were recorded in the acetone and chloroform solutions in the wavelength range from 200 to 800 nm.

In the ligand and its metal complexes were determined between 275-521 nm $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ transitions. In the spectrum of the Schiff base ligand, the aromatic bands at 250-360 nm are attributed to a benzene $\pi \rightarrow \pi^*$ transition. The band at 425 nm is assigned to the imino $\pi \rightarrow \pi^*$ transition. Compared to the free ligand, the imine $\pi \rightarrow \pi^*$ transition of the complexes were shifted to some extent, probably because of coordination of the nitrogen atom of the ligand imine group to the metal ion. The spectra of the complexes further display a bands in the range 404-521 nm, which might be assigned to charge transfer transition from the ligand to metal ions (L \rightarrow M)¹⁰.

In electronic spectrum of Co(II) complex showed absorption bands at 560 nm and 766 nm, attributed to the ${}^2A_{1g} \rightarrow {}^2E_g$ and ${}^2A_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively which is compatible with this complex having a square-planar structure²¹.

In electronic spectrum of the Ni(II) complex showed absorption bands at 637 and 728 nm attributed to the ${}^3T_1({}^3F) \rightarrow {}^3T_1({}^3P)$ and ${}^3T_1({}^3F) \rightarrow {}^3T_2({}^3F)$ transition, which is compatible with this complex having a tetrahedral structure^{10,22}.

Copper(II) complex has dimeric structure. $[\text{Cu}_2\text{LCl}_3]$ could be attributed to molecular association and/or strong anti-ferromagnetic interaction between Cu(II) centers, occurring through either Cu-Cu bonding or through a bridging ligand. The elemental analysis suggests that copper exists in the oxidation state of +2 in complex, excluding the possibility of direct Cu-Cu bonding. The electronic spectrum of $[\text{Cu}_2\text{LCl}_3]$ displayed intraligand bands range 404-526 nm and a new shoulder at 728 nm. The shoulder could be assigned to MLCT and/or no *d-d* transitions. Such spectral features and the zero magnetic moment observed for this complex suggest the existence of copper as Cu(II). Elemental analysis and electronic spectral data support the existence of Cu(II) in this complex. Based on the mentioned this data, the square-planar structure can be assumed to be obtained *via* the chloride bridge structure^{23,24}.

Electrons in $3d^{10}$ orbitals of the Cd(II) ions were showed diamagnetic behaviour and transfer in 687 nm belongs to bimetalic Cd(II) complex, that this transfer was observed shows that the structure is tetrahedral^{12,25}.

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