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Synthesis, Structural Characterization and Electrochemical Studies of New Schiff Base Macrocyclic Ligand and Their Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) Metal Complexes

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Abstract - A new macrocyclic ligand (H_2L) was synthesized by reaction of Acenaphthoquinone and o-aminophenol. Then, its Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) complexes were synthesized by the condensation method. Macrocyclic ligand (H_2L) and $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Cu(NO_3)_2.6H_2O$, $ZnCl_2.2H_2O$ and $CdCl_2.2H_2O$ respectively. The ligand and its complexes have been characterized by IR, ^1H, UV–Vis spectra, conductivity measurements, mass spectra, and cyclic voltammetry.

Keywords – Macrocyclic ligand; Schiff base complexes; Spectroscopic characterization.

I. INTRODUCTION

Schiff bases have been of great importance in many of the macrocyclic areas of chemistry and also Schiff base transition metal complexes have been of great interest in view of their structural features such as ligand rigidity, type of donor atoms, their disposition and resemblance to natural systems of metalloenzymes (Chandra et al (2005), Gagne et al (1981),Fry et al (1997)) [1–3]. These transition metal complexes of Schiff bases are used in the agrochemical and pharmaceutical industries [4]. They are extensively used as potential therapeutics [5]. The stability of macrocyclic metal complexes depends upon a number of factors, including the number and type of donor atoms present in the ligand and their relative positions within the macrocyclic skeleton. Over recent years, it has been carried out considerable research involving the interaction between transition and post-transition metals and N_xO_y macrocyclic ligands, combining Schiff-base fragments with other donor groups [6,7]. In the present work, we have synthesized a new macrocyclic Schiff base by reaction of acenaphthoquinone and o-aminophenol. Then, its Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) complexes were synthesized by condensation of acenaphthoquinone and o-aminophenol and $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Cu(NO_3)_2.6H_2O$, $ZnCl_2.2H_2O$ and $CdCl_2.2H_2O$ respectively. Spectral and electrochemical properties of the new compounds were studied in detail.

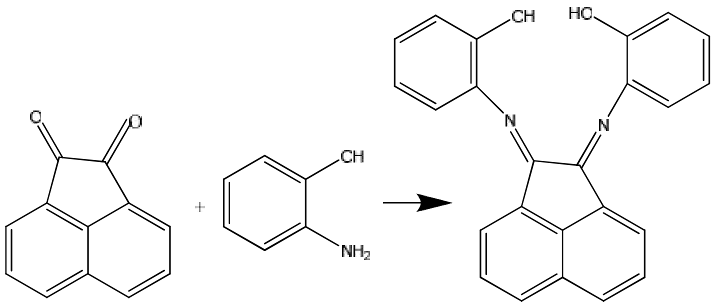
II. EXPERIMENTAL

A. Synthesis of Schiff base macrocyclic ligand (H_2L)

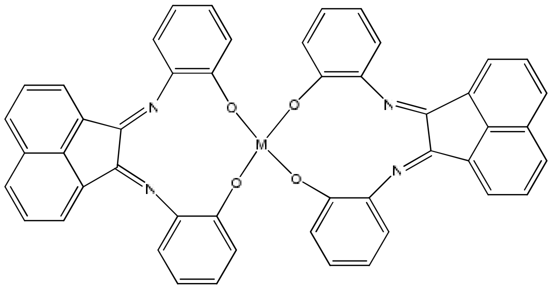
Acenaphthoquinone in acetonitrile was added to o-amino phenol and stirred for 3 hours. The resultant solution stirring was continued for 3 hours. A brown coloured precipitate was filtered. This product was extracted using diethyl ether /methanol mixture and evaporated and obtained as a brown compound. (Scheme1)

B. Synthesis of complexes

To a solution of H_2L in methanol was added a solution of cobalt(II), nickel(II), copper(II) nitrate hexahydrate, zinc(II), cadmium(II) chloride dihydrate in methanol and refluxed for 3 hours. The resultant product was filtered, washed with methanol and dried over anhydrouscalciumchloride.(Scheme2)



Scheme1. Synthesis of Ligand (H_2L)



Scheme2. Synthesis of Complexes M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

III. *RESULT AND DISCUSSION*

The ligand and complexes have been synthesized (Schemes 1 and 2) and characterized by IR, ^{1}H, UV–Vis spectra, conductivity measurements, mass spectra, Luminescence spectral studies and cyclic voltammetry. The corresponding data for the ligand and complexes are presented in Tables 1, 2.

Table:1 IR (cm^{-1}) spectral data for the ligand and its complexes

Compound	ν(C=N)	ν(C-O)	ν(H_2O)	ν(C-H)	δ(N=H)	δ(C-H)	Ionic ν(NO_3^-)
Ligand	1635	1240	3375	3057	1593	750	-
$[Co(L)_2(NO_3)_2].xH_2O$	1625	1263	3330	3100	1585	748	1384
$[Ni(L)_2(NO_3)_2].xH_2O$	1637	1267	3368	3057	1572	750	1384
$[Cu(L)_2(NO_3)_2].xH_2O$	1624	1277	3338	3055	1576	754	1384
$[Zn(L)_2(Cl)_2].xH_2O$	1635	1267	3378	3100	1579	752	-

Table : 2 Electronic absorption spectral data and Molar conductance data for the ligand and its complexes.

Compound	π-π*	n-π*	CT	d-d	Λo $\Omega^{-1}cm^2 mol^{-1}$	Electrolytic Nature	% of Metal
Ligand	326,353	446	-	-	7.9	Neutral	-
$[Co(L)_2(NO_3)_2].xH_2O$	320,345	405,439	570	650	12.6	Neutral	13.0
$[Ni(L)_2(NO_3)_2].xH_2O$	275	326,340	414	604	8.3	Neutral	12.9
$[Cu(L)_2(NO_3)_2].xH_2O$	270	350	436	630	10.2	Neutral	14.0
$[Zn(L)_2(Cl)_2].xH_2O$	320,355	509	610	-	7.8	Neutral	14.2
$[Cd(L)_2(Cl)_2].xH_2O$	310	352	441	655	8.6	Neutral	21.6

A. NMR spectra

^{1}H NMR of the complexes in DMSO-d6 solution shows that they are NMR active. The ^{1}H NMR spectrum of the free ligand showed a signal at 6.71 – 8.25 ppm is due to the aromatic proton. The signals appearing at 1.5 ppm is due to amine group. The ^{1}H NMR spectra of the complexes exhibited almost the same values as that of the ligand. The NMR spectrum of macrocyclic ligand is presented in Fig.1.

B. Electrochemistry

The cyclic voltammograms of complexes of L are recorded using 10^{-3} M solution in DMSO with tetraethyl ammonium bromide (TEAB) was employed as the supporting electrolyte. The scan rate is fixed at 100mV/s and multiple scan is recorded for each complex. The nickel complex of H_2L shows 3 redox peaks and shoulder at $E_{1/2}$ -1.4. The cathodic peak potential of new peaks is -1.44 V and corresponding anodic peaks -1.37 V. This may be due to nickel centered redox process taking place at the electrode surface. The ΔEp of this process is 70mV and ipa/ipc ratio is around 0.76 V. This shows that the redox process is irreversible. The CVs and their data are depicted in Fig.2.

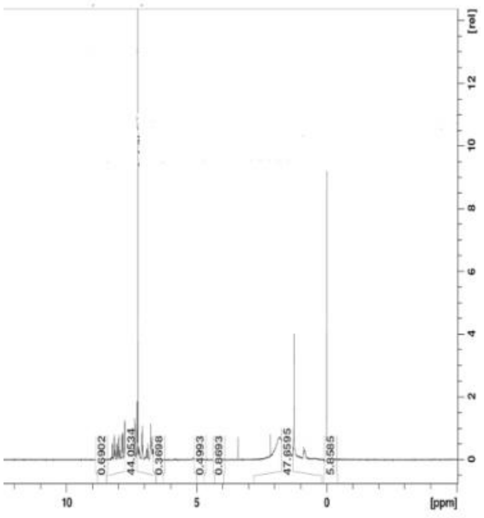


Fig 1: ^{1}H NMR spectrum of ligand (H_2L)

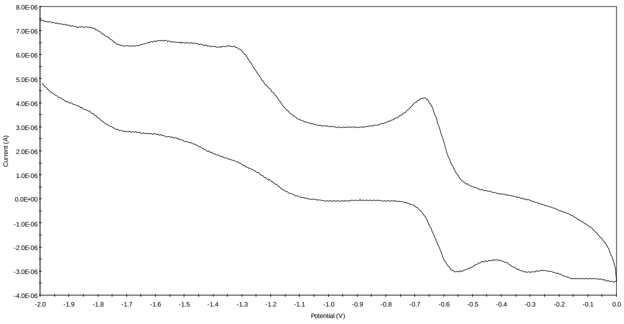


Fig.2. Cyclic voltammogram of $[Ni(L)_2(NO_3)_2].xH_2O$ Mass spectra

The mass spectrum of the complexes was recorded by JEOL GC mate Mass Spectrophotometer. The mass spectrum of the nickel(II) complex are shown in Fig.3 and the fragments observed in the mass spectrum of the same complex are shown in Fig.6. It shows the base peak is seen at the m/z 785 which is confirmed of the complex. In this complex two ligands one metal are bind. The next intense peak observed at m/z 1206. In this complex which bind three ligands and two metal ions.

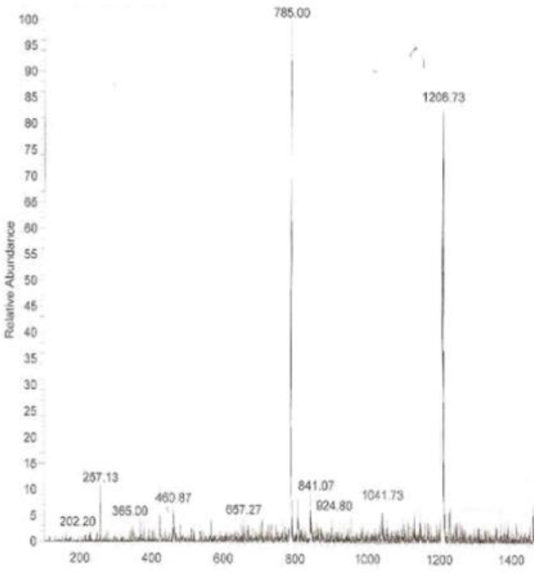


Fig.3. The Mass spectrum of the Ni(II) complex

IV. CONCLUSIONS

A new macrocyclic ligand (H_2L) has been synthesized. The position and the number of donor atoms together with the flexibility of H_2L make it a versatile molecule which can bind the metal through different Oxygen donor atoms. Macrocyclic ligands form stable complexes and the luminescence and electrochemical behaviors will be explored more for better electron transfer and energy transfer process. As the complexes are very stable, a lot of application in the field of analytical chemistry and applied chemistry could be provided.

V. REFERENCES

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