

A Study on the Anti-microbial Activity and Luminescence Characteristics of Some Novel Cobalt, Nickel, Copper and Zinc Co-ordinated Macrocyclic Schiff Base Complexes

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Abstract:

Metal complexes of the transition metal ions Co(II), Ni(II), Cu(II) and Zn(II) derived from the Schiff base, which is formed as a result of acenaphthoquinone and 1,8-diaminonaphthalene, have been synthesized by microwave method. The elemental analysis for carbon, hydrogen and nitrogen were performed by micro-analytical methods. The molecular weight of the Schiff base ligand was determined using Rast method in naphthalene solvent. The molar conductance measurements of the metal complexes in the solvent dimethyl sulfoxide reveal the non-electrolytic nature of the complexes. The structures of the synthesized metal complexes have been further elucidated based on ¹H-NMR, FTIR and electronic absorption and emission spectroscopic analyses. All the metal complexes, but copper complex, were observed to adopt octahedral geometry whereas copper complex exhibits distorted octahedral geometry. The metal complexes were assessed for anti-microbial activity against selected bacterial and fungal strains and are found to show fairly good results.

Keywords: Acenaphthoquinone, 1,8-diaminonaphthalene, Schiff base, metals complexes, luminescence characteristics, anti-microbial activity.

Introduction:

Metal complexes of Schiff bases have gained lot of attention in recent years due to their extensive applications in analytical chemistry, therapeutic chemistry and utility in synthetic chemistry. The efficient design of macrocyclic ligand is crucial to realize application-specific properties as dictated by structure-function relationship especially in areas related to biological systems. Such macrocyclic Schiff base ligands find varied applications in bioinorganic coordination and catalysis^[1]. Moreover, macrocyclic Schiff base nitrogen donor ligands have gained special attention because of their versatile coordination behaviour and mixed hard-soft donor character^[2] and resulting therapeutic effects such as anti-bacterial^[3], anti-tumour^[4], and other pharmacological activities^[5]. Charge transfer plays a pivotal role in energy conversion, especially in biological systems, employed by nature in photosynthesis for energy harvesting, and in the assay of

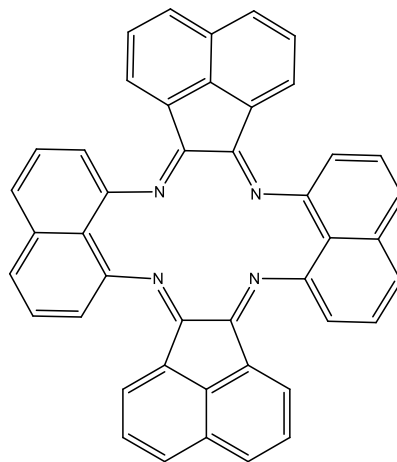
different biochemical related analyses. Therefore, charge transfer complexes are of special interest for technological applications. Therefore, we, in the present study, have endeavoured to synthesize the charge transfer complexes from the Schiff base formed by the condensation of acenaphthoquinone, 1,8-diaminonaphthalene. Macrocyclic ligands, of the present form, are known to be very versatile due to their capability of forming stable complexes.^[6] Moreover, the biologically important 3d transition metal ions such as cobalt, nickel, copper and zinc ions were chosen for the present investigation. Bearing the above said fact, we are presenting the synthesis, characterisation and biological evaluation of macrocyclic Schiff base with cobalt, nickel, copper and zinc metal complexes for potent anti-microbial activity in the present study.

Experimental:

Acenaphthoquinone and 1,8-Diaminonaphthalene were purchased from Loba Chemie and used as such without further purification. Co(II), Ni(II), Cu(II) and Zn(II) metal chlorides were of analytical grade chemicals from BDH chemicals. All other reagents and solvents were purchased from commercial sources and were of analytical grade. For elemental analysis, the percentage of carbon, hydrogen and nitrogen in the samples were analysed using Carlo Erba 1108 model elemental analyser using sulphanilamide as a reference standard. The EI-Mass spectrum of the Ligand was recorded using JEOL GcMate II. The ¹H NMR was recorded on a JEOL GSX-400 spectrometer employing DMSO as solvent at ambient temperature. The IR Spectra was recorded for all the samples using JASCO FT-IR/4100 spectrometer in the wavelength range of 400-4000cm⁻¹. UV-visible spectra of the samples were recorded using Perkin Elmer Lambda-25 UV-Visible Spectrometer using methanol as solvent in the range of 200-1100 nm. Molar conductance of the ligand and complexes were measured using Elico conductivity meter. Wet chemical analyses for chloride ions were performed using standard methods. The ligand and metal complexes were screened for anti-microbial activity by disc diffusion method against the bacterial strains *Escherichia coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia* and *Staphylococcus aureus* as well as the fungal strains *Candida albicans* and *Aspergillus niger* grown in appropriate culture media.

Synthesis of Schiff base ligand:

In a typical synthesis, 5 mmol of acenaphthoquinone and 5 mmol of 1,8-diaminonaphthalene were taken in a semi-micro boiling tube. The tube was sealed with cotton and placed inside a conical flask. It was placed inside the microwave oven and heated for 5 minutes. The Schiff base ligand formed was washed with ethanol and then with ether and dried. The yield was found to be 95%. The proposed structure of the ligand is given by Scheme 1.



Scheme 1 The proposed structure of the macrocyclic Schiff base ligand

Synthesis of Schiff base Complex:

To synthesize metal complexes, 10 mmol of the macrocyclic Schiff base ligand and 5 mmol of metal(II) chloride were mixed in a semi-micro boiling tube. It is sealed with cotton, placed inside a conical flask and heated in the microwave oven for 5 minutes. The Schiff base complex formed was washed thoroughly with ethanol and then dried in vacuum. Similarly, the Schiff base Complexes of Cobalt(II), Nickel(II), Copper(II) and Zinc(II) complexes were prepared by microwave heating of the respective metal(II) chlorides with the Schiff base ligand.

Results and Discussions:

1. Elemental Composition Analysis:

The elemental composition of the ligand and the metal complexes has been confirmed by the analytical data which is furnished in Table 1.

Table 1. Analytical data of the Schiff base ligand and its complexes

Compounds/ Complexes	Molecular Weight (g mol ⁻¹)	Calculated (%)						
		Co	Ni	Cu	Zn	C	N	H
C ₄₄ H ₂₄ N ₄ (Ligand)	608.20 (608.69)	-	-	-	-	86.82	9.20	3.97
[Co(C ₄₄ H ₂₄ N ₄)Cl ₂]	737.07(738.53)	7.98	-	-	-	71.56	7.59	3.28
[Ni(C ₄₄ H ₂₄ Cl ₂ N ₄)Cl ₂]	736.07(738.2)	-	7.95	-	-	71.58	7.59	3.28
[Cu(C ₄₄ H ₂₄ Cl ₂ N ₄)Cl ₂]	741.07 (743.14)	-	-	8.55	-	71.11	7.54	3.26
[Zn(C ₄₄ H ₂₄ Cl ₂ N ₄)Cl ₂]	742.07(744.9)	-	-	-	8.78	70.94	7.52	3.25

2. Electrolytic Conductivity Studies:

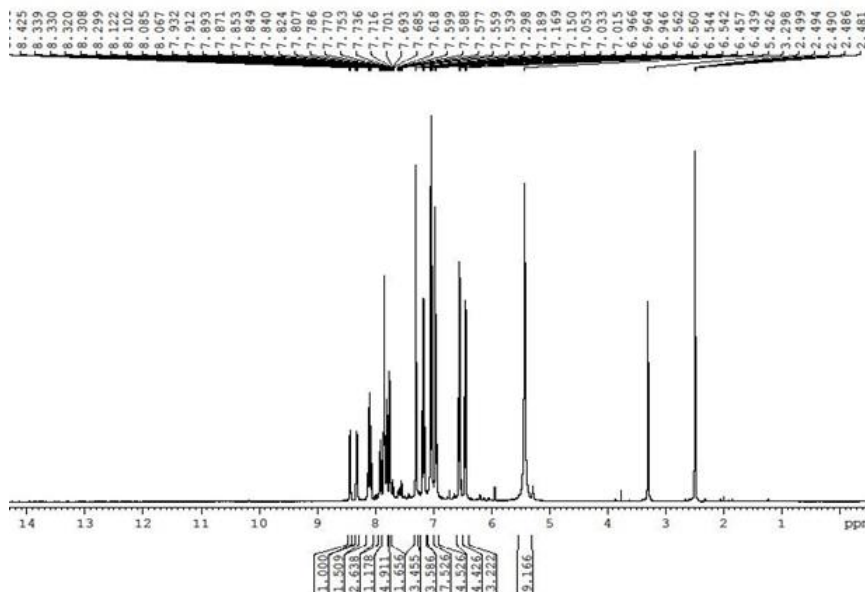
The molar conductance of all the complexes was measured in DMSO for 10^{-3} M solutions at room temperature. From the conductance data (Table 2), it can be concluded that all the complexes are non-electrolytic in nature. Hence, it is confirmed that the two chloride ions are coordinated to the central metal ion and are present inside the coordination sphere.

Table 2. Molar Conductance data in 0.001M solution of ligand /metal complexes in DMSO

Sl. No.	Ligand/Complex	Specific conductance (10^{-6} S/m)	Molar conductance ($S\ m^2\ mol^{-1}$)
1.	$C_{44}H_{24}N_4$ (L)	0.7	7.0×10^{-2}
2.	$[Co(L)Cl_2]$	2.9	2.9×10^{-1}
3.	$[Ni(L)Cl_2]$	4.7	4.7×10^{-1}
4.	$[Cu(L)Cl_2]$	2.1	2.1×10^{-1}
5.	$[Zn(L)Cl_2]$	1.6	1.6×10^{-1}

3. Proton NMR Spectral Studies:

The 1H NMR spectrum of the Schiff base ligand (L) in deuterated chloroform ($CDCl_3$) is given in the Fig. 1. The spectrum shows signals at 6.560(2 protons), 6.964(2 protons), 7.618(2 protons), 7.685(2 protons) and 7.701 (2 protons). The absence of $-NH_2$ or $-NH$ protons clearly indicate the formation of Schiff base by the condensation of acenaphthaquinone and 1,8-diaminonaphthalene.



4. Mass Spectral Studies:

The Mass spectrum of the ligand is displayed in Fig. 2. The figure shows the well-defined molecular ion peak at $m/z = 608$ corresponding to the molecular weight of the Ligand L. Moreover, the peaks at 320, 278 and 158 correspond to various fragments such as $C_{22}H_{12}N_3$, $C_{20}H_{10}N_2$ and $C_{10}H_6N_2$, respectively. This confirms the molecular formula of the ligand as $C_{44}H_{24}N_4$.

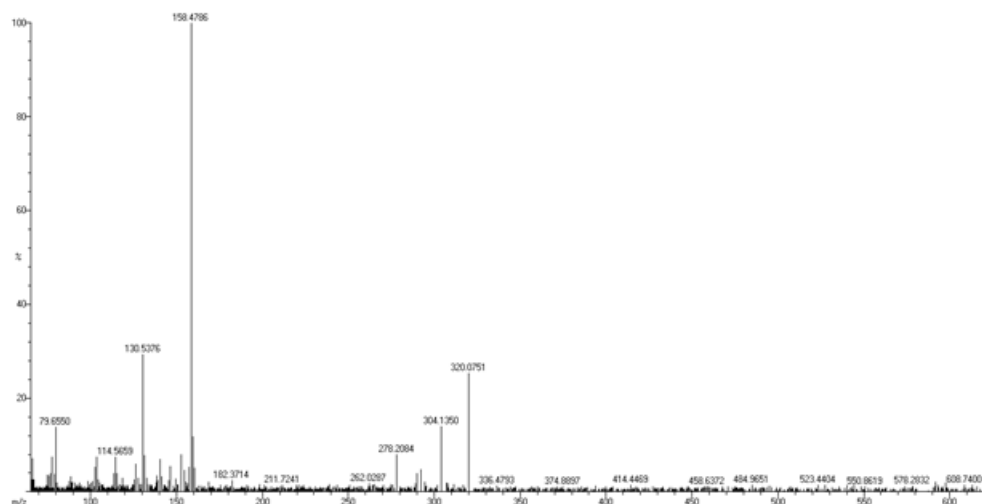


Fig.2 Mass spectra of the synthesized Schiff base Ligand

5. FTIR Spectral Studies:

The FTIR spectrum of the Schiff base complex AB is given in Fig.3. The significant absorption bands of the spectra are: (i) aromatic ring puckering frequency at 765.959 cm^{-1} (ii) aromatic C-C stretching as well as bending vibrations at 3050.21 cm^{-1} and 3364.21 cm^{-1} . The absorption peak observed at 1614 cm^{-1} confirms the presence of $>C=N$ imino group^[7-10] in the ligand.

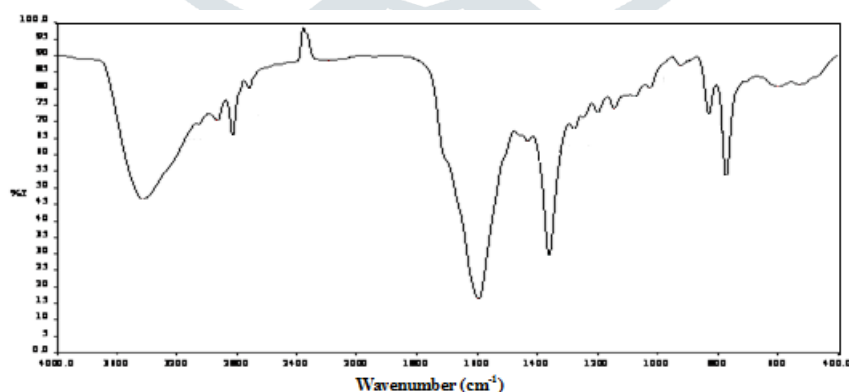


Fig.3 FT-IR spectra of the synthesized Schiff base Ligand

6. Electronic Absorbance Spectral Studies:

The electronic spectra of the Schiff base complexes [Co(L)Cl₂], [Ni(L)Cl₂], [Cu(L)Cl₂] and [Zn(L)Cl₂] were recorded at room temperature in DMSO solution (Fig. 4) and the spectral data are summarized in Table 3. All the metal complexes were observed to adopt octahedral geometry except that the copper complex which was found to exhibit distorted octahedral geometry.

Table 3. Electronic absorbance spectral data of M(II) Schiff base complex

S.No.	Complexes	Wavelength (nm)	Transition	Geometry
1.	[Co(L)Cl ₂]	345, 700	$4T_{1g} \rightarrow 4T_{2g}$, $4T_{1g} \rightarrow 4T_{2g}(P)$	Octahedral
2.	[Ni(L)Cl ₂]	355, 500	$3A_{2g} \rightarrow 3T_{2g}$, $3A_{2g} \rightarrow 3T_{1g}(F)$	Octahedral
3.	[Cu(L)Cl ₂]	347, 650	$2E_g \rightarrow 2T_{2g}$ $2B_{1g} \rightarrow 2A_{1g}$	Distorted octahedral
4.	[Zn(L)Cl ₂]	275, 292	$n \rightarrow n^*$, $n \rightarrow n^*$	Octahedral

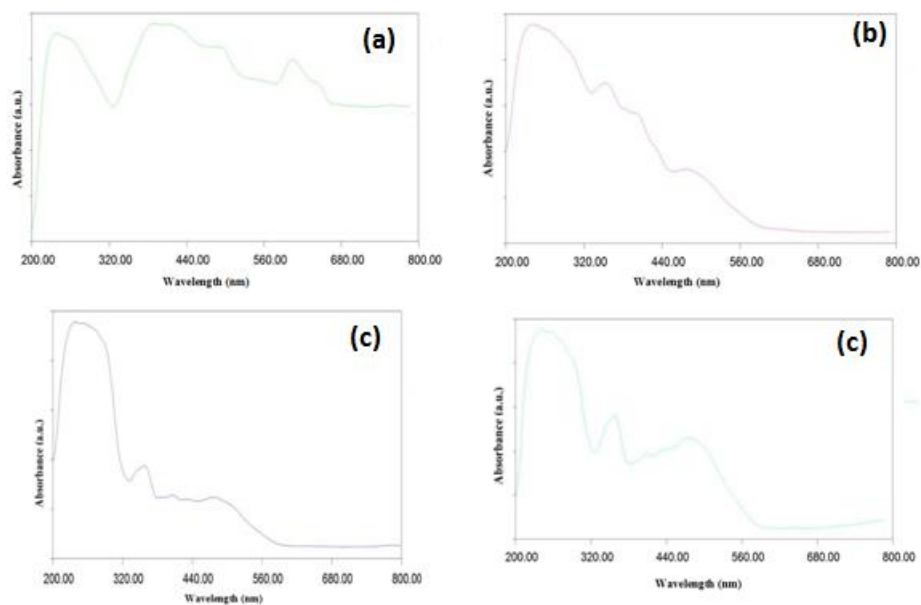


Fig. 4 Electronic absorbance spectra of metal complexes (a) [Co(L)Cl₂] (b) [Zn(L)Cl₂] (c) [Cu(L)Cl₂] (d) [Ni(L)Cl₂]

7. Photoluminescence spectral Analysis:

The photoluminescence behavior of the complexes were investigated at the excitation wavelength of 395 nm and the results are shown in Fig. 5 All the complexes were seen to exhibit a strong luminescence with peak maxima centred on $\lambda_{\text{max}} = 790$ nm. The following trend in fluorescent emission intensity was observed for the complexes.

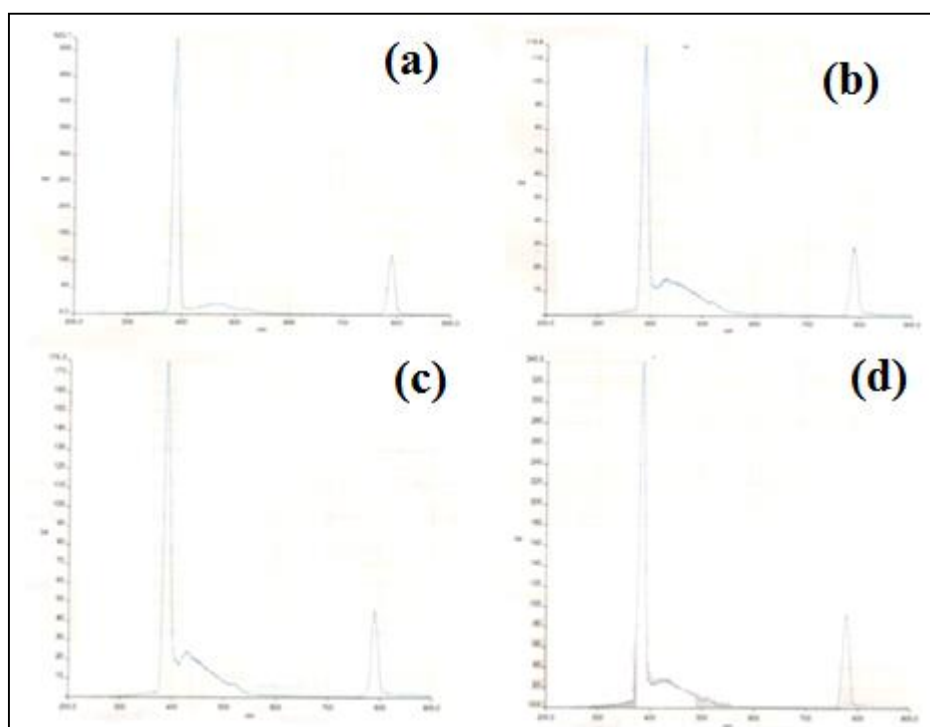
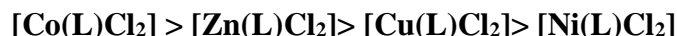


Fig. 5 Photoluminescence spectra of the complexes (a) [CoLCl₂], (b) [ZnLCl₂], (c) [CuLCl₂] and (d) [NiLCl₂]

8. Anti-microbial Studies

The anti-microbial activity of the ligands and the respective metal complexes have been evaluated for the bacterial strains *Escherichia coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia* and *staphylococcus aureus* as well as for fungal strains *Aspergillus niger* and *candida albicans* and the results are summarized in Table 4.

Anti-bacterial activity of the Synthesized Complexes was tested for *in vitro* anti-bacterial activity by the disc diffusion method. The mechanism of higher toxic activity of the complexes compared to those of the ligands can be attributed to the increase in the lipophilic nature of the complexes as a consequence of chelation,^[11] thereby favouring permeation of the complex through the lipid layer of bacterial cell membrane. It is well-known that chelation reduces the polarity of the metal atom due to the partial sharing of positive charge with the donor groups of the ligand and possible delocalization of π electron within the chelate ring.

Table 4. Anti-microbial activity of the ligand and the derived metal complexes

Compounds/ complexes	Zone of Inhibition (mm)					
	Bacterial strain				Fungal strain	
	<i>Escherichia coli</i>	<i>Pseudomonas aeruginosa</i>	<i>Klebsiella pneumonia</i>	<i>Staphylococcus aureus</i>	<i>Aspergillus niger</i>	<i>candida albicans</i>
Ligand (L)	10.3	9.1	10.3	10.1	8.9	11.3
[Co(L)Cl ₂]	10.3	15.4	11.2	11.2	11.2	13.3
[Ni(L)Cl ₂]	11.4	11.4	12.2	13.8	11.3	15.2
[Cu(L)Cl ₂]	12.3	15.3	14.3	13.6	12.4	15.3
[Zn(L)Cl ₂]	11.3	10.1	12.4	10.3	10.3	10.4

Conclusions:

The Schiff base formed by the condensation of acenaphthoquinone and 1,8-diaminonaphthalene and the respective transition metal complexes with Co(II), Ni(II), Cu(II) and Zn(II) ions derived from Schiff base were synthesized. The ligand and the complexes were characterized by the analytical, electrical conductivity and spectral techniques. It is worth noting that all the complexes showed good emission characteristics. The anti-microbial screening of the ligands and their complexes indicate the significant potential of metal complexes against all the tested bacterial and fungal strains.

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