

Synthesis and antifungal studies of Macrocyclic Co(II), Ni (II) and Cu(II) Complexes with Bidentate Schiff base ligands.

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Abstract

The synthesis and characterization with antifungal studies of the complexes of MH_2L where $M = Co(II), Ni(II), Cu(II)$ and $H_2L =$ Tetradentate macrocyclic ligand. Complexes were characterized on the basis of elemental analysis, magnetic moment, electrochemical study and conductance, Infra red with electronic spectral data. The IR studies show that the ligand has contained equatorial four mono-dentate nitrogen donor atoms. Complexes have been found to have low conductance values which indicate that the complexes act as non-electrolytic in nature. On the basis of all over the study the complexes are expected to have three-dimensional layer lattice structure involving coordination with four donor nitrogen atoms with central metal ions while the remain position of central metal ion is coordinated with halides ions in axial mode, which to give paramagnetic octahedral structure as evidenced by electronic spectral studies with magnetic moment data.

Keyword- Antifungal, Donor nitrogen atom, Non-electrolytic nature, Ligand, Layer lattice structure.

INTRODUCTION

Coordination compounds have received great attention in the field of inorganic chemistry during recent years¹⁻⁴. The reasons for this interest are the fundamental importance in exchange interaction with theory of bonding in new magnetic materials research and in understanding their important roles they play in large number of widely differing processes of technological and biological importance⁵⁻⁹. Consequently in the present communication in continuation of our earlier interest in the field¹⁰⁻¹³. The metal complexes were prepared by refluxing hot ethanolic solution of metal salts with the components of the ligand namely 1,2-Diamino-4,5-dinitrobenzene and diacetylmonoxime. The stoichiometry of the complex have been found to be of the type $[Co(H_2L)X_2]$, $[Ni(H_2L)X_2]$ and $[Cu(H_2L)X_2]$. The chelating of ligand with Co(II), Ni(II) and Cu(II) are expected to form complex with different geometry. It may enhance their antifungal activity after chelating also. Which may find their importance in the applied medicinal chemistry and other area of industries.¹⁴⁻¹⁷

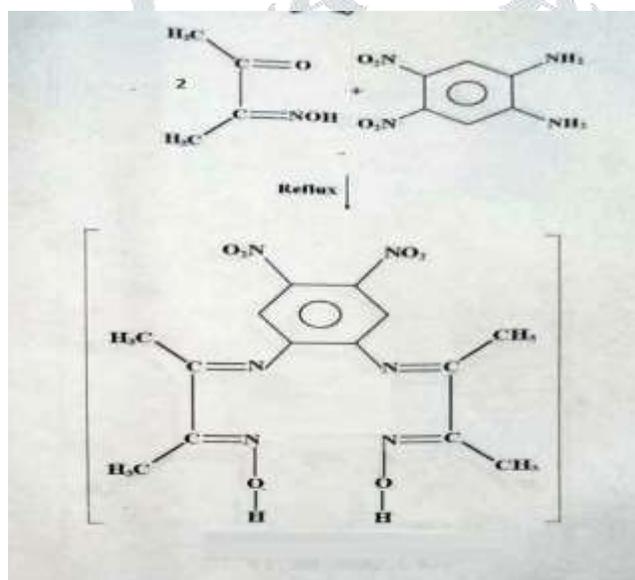
Materials and method

All the chemicals were of AR grade and distilled then dried before use in laboratory. While metal salts were of BDH quality. The tetradentate Schiff base ligands (H_2L) was synthesized by condensation of two molecules of diacetylmonoxime with 1,2-Diamino-4,5-dinitrobenzene in alcoholic medium. The solid which separated at the end of the refluxing period was filtered then dissolved in boiling water and purified to give colourless solid. H, C and N were estimated by semi-micro combustion method on a Carbo-Erba 1106 elemental analyzer. Metal were estimated using standard procedure. Conductivity measurement were taken using conductivity meter model 303 using DMF as a solvent. Magnetic moment was determined using Guoy balance. The IR spectra were recorded with Backmann IR-20 spectrophotometer in KBr disc.

Ligand synthesis

The bidentate Schiff base ligands (H_2L) was synthesized by condensation of two molecules of diacetylmonoxime with 1,2-Diamino-4,5-dinitrobenzene in alcoholic

Medium. The reaction between the reactant molecules is occurs as in Figure – 1



The chemical reaction of synthesis of Ligand (H_2L)

Figure - 1

Preparation of complexes

1. $[Co(H_2L)Cl_2]$

0.01 mole of ethanolic solution of Cobalt chloride and 0.02 mole of diacetylmonoxime was add to 0.1 mole of 1,2-Diamino-4,5-dinitrobenzene and the resulting mixture was continuously and vigorously were refluxed for 4 hours in water bath. A brown colour of solid

complex separated out. The synthetic reaction taking place during the synthesis can be shown below.

2. $[\text{Co}(\text{H}_2\text{L})\text{Br}_2]$ 0.01mole of
ethanolic solution of Cobalt bromide and 0.02 mole of diacetylmonoxime was add to 0.1 mole of 1,2-Diamino-4,5-dinitrobenzene and the resulting mixture was continuously and vigorously were refluxed for 4 hour in water bath. A brown colour of solid complex separated out. The synthetic reaction taking place during the synthesis can be shown below.

3. $[\text{Ni}(\text{H}_2\text{L})\text{Cl}_2]$

The preparation of Ni(II) complexes, the ethanolic solution of Nickel chloride was kept in bright sunlight for six hours. When intense yellow colour of Nical chloride changed to faint green, almost colourless due to reduction of Ni(III) to Ni (II). The components of the ligand were add to it in inert atmosphere. On refluxing dark red colour solid complex separated out. The reaction between them is shown below.

4. $[\text{Ni}(\text{H}_2\text{L})\text{Br}_2]$

The preparation of Ni (II) complexes, the ethanolic solution of Nickel bromide was kept in bright sunlight for six hours. When intense brown colour of ferric bromide changed to faint green, almost colourless. The components of the ligand were added to it in inert atmosphere. On refluxing dark red colour solid complex separated out. The reaction between them is shown below.

5. $[\text{Cu}(\text{H}_2\text{L})\text{Cl}_2]$

0.01 mole of alcoholic solution of copper chloride with 0.02 mole of diacetylmonoxime and 0.1 mole of dinitroorthophenylenediamine were refluxed for 4 hour in a water bath. The green coloured of solid complexes are separated out. It was filtered, washed dried and analysed. The synthesis chemical reaction is given below.

6. $[\text{Cu}(\text{H}_2\text{L})\text{Br}_2]$

0.01 mole of alcoholic solution of copper bromide with 0.02 mole of diacetylmonoxime and 0.1 mole dinitroorthophenylenediamine were refluxed for 4 hour in water bath. The green coloured of solid complexes are separated out.

Results and discussion.

The complexes of a new intramolecular hydrogen bonded macrocyclic ligand derived from metal ion catalysed template synthesis of 1,2-Diamino-4,5-dinitrobenzene and

diacetylmonoxime with Co(II), N(II) and Cu(II) have been synthesized. Characterizations have been done on the basis of their elemental analyses, conductivity. Magnetic moment in addition to spectral data of I.R and UV-visible.

Elemental analysis

The physical and analytical data of the complexes are given in table – 1. Which is in satisfactory agreement with the calculated values. The suggested molecular formula are supported by the subsequent spectral as well as magnetic moment, molar conductivity in 10^{-3} M solution of DMSO, the value of λ_m show that Co(II), N(II) and Cu(II) complexes are non-electrolytic in nature.

Physical and analytical data for the complexes

Complexes	Colour	Yield %	Elemental analysis Calculation. (Found)			
			M%	N%	C%	H%
[Co(H ₂ L)Cl ₂]	Brown	65	12.91(12.90)	19.72(19.71)	39.44(39.43)	3.76(3.75)
[Co(H ₂ L)Br ₂]	Brown	60	10.68(10.67)	16.31(16.30)	32.62(32.61)	3.11(3.10)
[Ni(H ₂ L)Cl ₂]	Red	95	13.11(13.10)	19.67(19.66)	39.34(39.33)	3.75(3.74)
[Ni(H ₂ L)Br ₂]	Red	90	10.85(10.84)	16.28(16.27)	32.56(32.55)	3.10(3.09)
[Cu(H ₂ L)Cl ₂]	Blue	85	14.11(13.20)	18.67(19.77)	38.34(39.33)	3.76(3.64)
[Cu(H ₂ L)Br ₂]	Blue	75	11.85(10.86)	17.38(16.47)	33.56(32.65)	3.20(3.10)

Table - 1

Infrared spectra.

There are several features of the spectra which highly attracts attention and reflects on the synthesis and the structure of the macrocyclic complexes of particular significance is the spectral pattern in the ranges of $3500-3200\text{ cm}^{-1}$ and $1700-1500\text{ cm}^{-1}$. The pair of band are observed in the region $2400-3200\text{ cm}^{-1}$. The structure of the macrocycles show mainly two kinds of N-H groups a pair involving co-ordination with the metal ion and a couple of N-H group on the main frame of the macrocyclic structure but without being involved in coordination.¹³⁻¹⁵ It appears that these N-H groups differ in their respective vibration energies as reflected in the infrared spectra of the macrocyclic complexes.

The group of these bonds are obtained in the region $1700-1500\text{ cm}^{-1}$ These bands are located near 1650 , 1580 and 1545 cm^{-1} and their energies sharply differ from the energies of group of three bands observed for the free ligand in the same region. Another significant feature of these bands is the strength and they are almost of equal intensity which implies presence of energetically different amide. The IR band near 1650 and 1580 cm^{-1} and appear consistent with the proposed structure with chelate rings.

The properties of the spectra of the macrocyclic complexes in the region 1350 to 550 cm^{-1} are rich in vibration bands but their energies are significantly different from the free ligand. A pair of strong bands appear in the spectra of macrocycles which are absent in the spectrum of the free ligand. They appear in the region 480 to 460 cm^{-1} and 580 to 530 cm^{-1} are tentatively assigned to $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$. These bands in all the complexes shift to the higher wave number side confirming involvement of one of its N-atom in bonding with the metal ions whereas IR data have been present in Table -2

I.R Spectral data for the complexes.

Complexes	$\nu_{\text{C=N (Oxime)}}$	$\nu_{\text{C=N}}$	$\nu_{\text{M=N}}$	$\nu_{\text{M=O}}$
[Co(H ₂ L)Cl ₂]	1505	1590	590	410
[Co(H ₂ L)Br ₂]	1500	1600	595	415
[Ni(H ₂ L)Cl ₂]	1490	1610	480	405
[Ni(H ₂ L)Br ₂]	1505	1595	490	410
[Cu(H ₂ L)Cl ₂]	1460	1660	490	415
[Cu(H ₂ L)Br ₂]	1535	1565	480	418

Table- 2

Electronic spectra and magnetic moment studies

The UV-visible spectra of the complexes were recorded for their solutions in ethyl alcohol and DMSO solvents in the range (200-1000) nm. The ligand field spectra of Co(II) complexes exhibit two bands in the region 624 and 455 nm which are assignable to ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transition the ν_2/ν_1 ratio is 1.35 which is very close of value of 1.42 obtained for pure octahedral Co(II) complexes. Electronic spectra and magnetic moment data of Co(II), Ni(II) and Cu(II) complexes support paramagnetic high spin octahedral geometry. These Schiff base ligands and their metal complexes have been investigated as potential antibacterial and antimicrobial agents in long history of medical application. Recently greater variety of these ligand and their complexes containing hetero atoms represent good antifungal activity.

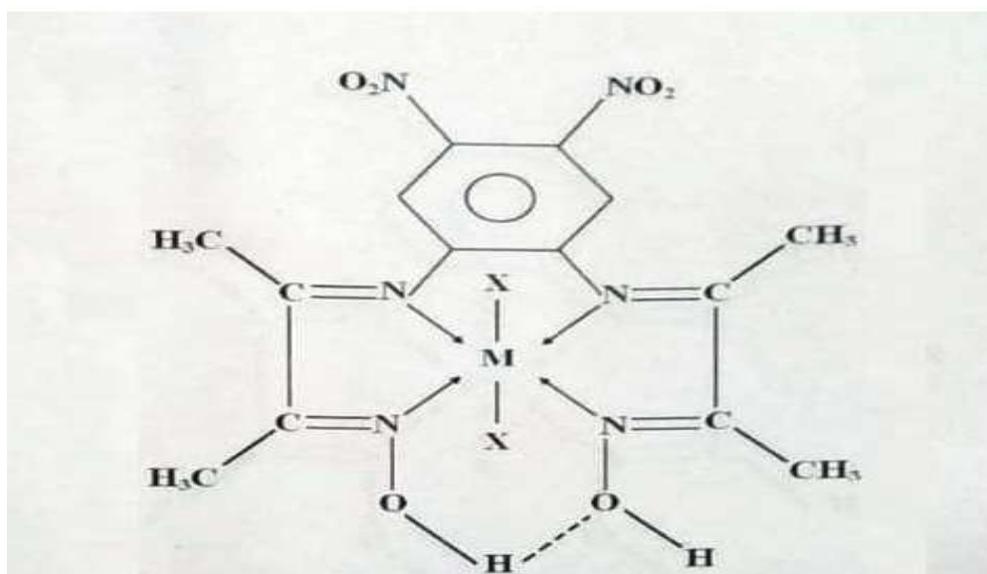
Antifungal activity

On the basis of experimental proofs the Co(II), Ni(II) and Cu(II) complexes have work more effective action as compared to free ligands and its metal ions.. The antifungal activity of the synthesized Co(II), Ni(II) and Cu(II) complexes was tested against both Gram-negative and Gram-positive bacteria and other microorganism.. The tested solutions of complexes were prepared in suitable solvent. It seems that enhanced biological activity for the complex compound of Co(II), Ni(II) and Cu(II) is due to its electron donating group and the poly-conjugated nature of the compound. On the basis of conjugation compounds provide large surface areas which enhance greater extent of lipophilic and absorbing nature. The complexes are more active as compared to the greater dissolving ability in fats, oils, lipids and non-polar suitable organic solvent with more absorbing nature of the complexes as a result which controls the growth or increases the ratio of death of the bacteria and other microorganism.. Therefore the results indicated that chelation improved the effect of antifungal compared to the ligand and free metal ions, known as antibiotic drugs.¹⁸⁻²¹

CONCLUSION

On the basis of above experimental studies it is concluded that the Schiff base ligands (H_2L) acts as a tetradentate manner and coordination is proposed through equatorial oxime N moiety with central metal ion of complexes while two halogen atoms are capsulated in facial and axial mode with metal ion and proposed stable two 5-membered capsulated cyclic ring structure while intra-molecular hydrogen between two stable five members cyclic ring structure enhance their extra stability of complexes. On the basis of physicochemical and spectroscopic observation it is proposed that the geometry of the type Co(II), Ni(II) and Cu(II) metal ion complexes are monomeric high spin octahedral paramagnetic intra-molecular hydrogen bonded macrocyclic stable ring structure of the metal complexes. Which provide the extra stability of complexes.

On the basis of electronic spectra and magnetic moment data suggest that the high spin octahedral paramagnetic hydrogen bonded macrocyclic stable ring structure of the metal complexes can be proposed to have the following structures.



M = Co(II), Ni(II) and Cu(II)

X = Cl^{-1} , Br^{-1}

Figure-2

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