Synthesis and Spectral Studies of Fe(II) and Cu(II) Complexes with Schiff base ligands.

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ABSTRACT

On the basis of worldwide intersection which provide to comparative studies on macrocyclic metal Fe(II) and Cu(II) complexes with macrocyclic ligands. Very recently there has been a phenomenal growth in studies of Fe(II) and Cu(II) complexes**.** The complexes of the chelating ligands were synthesized using metal halides. The complexes of a new hydrogen bonded macrocyclic ligand derived from metal ion catalysed template synthesis of 1,2-Diamino-4,5-dinitrobenzene and diacetylmonoxime with Fe(II) and Cu(II) have been synthesized. Analyses with characterizations have been done on the basis of their elemental analyses, conductivity, magnetic moment in addition to spectral data and UV- visible. On the basis of electronic spectra and magnetic moment data suggest that the metal complexes have high spin octahedral paramagnetic extra hydrogen bonded more stable macrocyclic ring structure. The Fe(II) and Cu(II) complexes and ligands have been screened for antibacterial, antimicrobial activity and in the applied medicinal chemistry with other area of industries.

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Keyword- Medicinal chemistry, Conductivity, Hydrogen bond, Axial mode, Cyclic ring structure.

INTRODUCTION

Coordination chemistry has provided great attention in the area of inorganic chemistry during present time in all over the world.[1-4] The reasons due to this interest are the fundamental importance in exchange interaction reaction with theory of bonding in new magnetic materials research and in understanding their important roles which play in large number of widely different processes of technological and biological importance[5-9].The metal complexes were prepared by refluxing hot ethyl alcohol solution of metal halide salts with the components of the ligand namely 1,2-Diamino-4,5-dinitrobenzene and diacetylmonoxime.[10-14] The stoichiometry of the complexes have been found to be $[Fe(H_2L)X_2]$ and $[Cu(H_2L)X_2]$. The chelating of ligand with Fe(II) and Cu(II) are expected to form complexes with different three dimensional cyclic ring structure.[15-18] It may enhance their biological activity as antibacterial and antimicrobial activity after chelating. Which may be finds their importance in the applied medicinal chemistry with antibacterial and antimicrobial activity and other area of chemical industries.

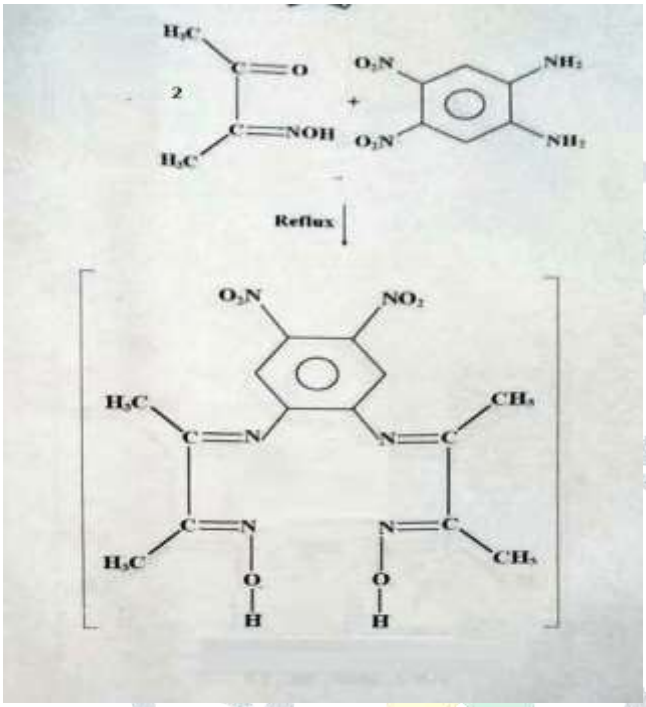
Materials and method

The salts of metal halides are used for synthetic and analytical work in experiment were of reagent grade solvent and purified by standard suitable method and dry before use in laboratory. The solid complexes 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.[11-12] 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 Schiff base ligands (H_2L) was synthesized by the condensation of two reactant molecules of diacetylmonoxime with 1,2-Diamino-4,5-dinitrobenzene under suitable condition in alcoholic medium. The reaction between the reactant molecules is occurs as in Figure - 1



The chemical reaction of synthesis of Ligands (H_2L)

Figure - 1

Preparation of complexes

1. $[Cu(H_2L)Cl_2]Cl$

0.01 mole of alcoholic solution of cupric chloride with 0.02 mole of diacetymonoxime 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.

2.$[Cu(H_2L)Br_2]Br$

0.01 mole of alcoholic solution of cupric 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.

3. $[Cu(H_2L)\ (NO_3)_2]NO_3$

0.01 mole of alcoholic solution of cupric nitrate with 0.02 mole of diacetylmonoxime and 0.1 mole of dinitroortophenylenediamine were refluxed for 4 hours in water bath. The green coloured solid complexes are separated out.

4. $[Cu(H_2L)ClO_4]ClO_4$

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

5. $[Fe(H_2L)cl_2]$

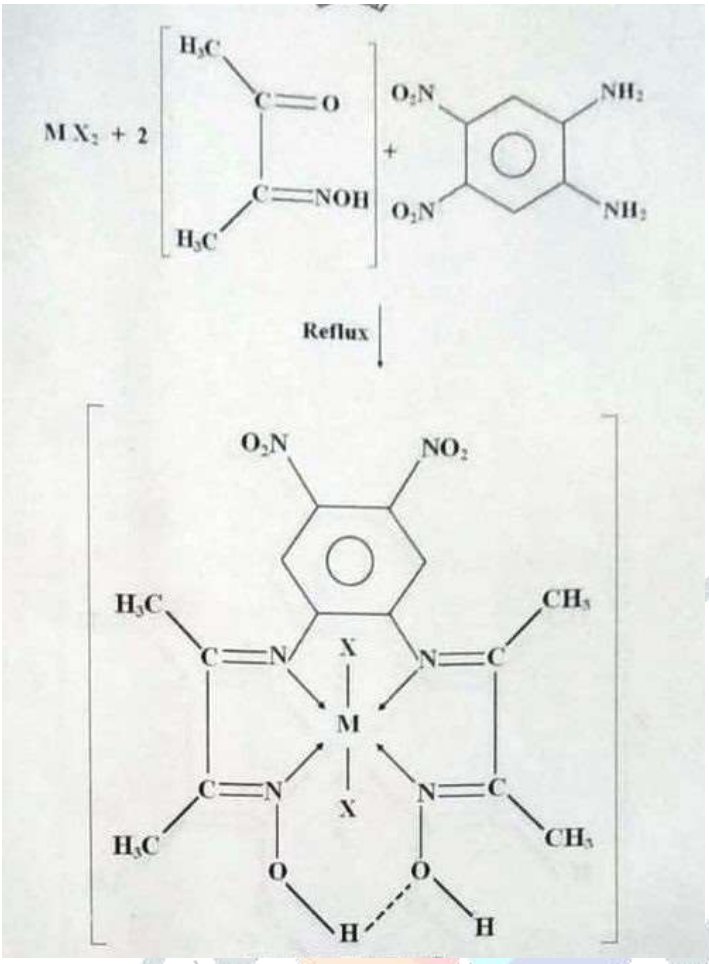
The synthesis of Fe (II) complexes with the alcoholic solution of ferric chloride was kept in bright sunlight for six hours. When intense yellow colour of ferric chloride changed to faint green, almost colourless. The components of the ligand were added to it in inert atmosphere. On refluxing dark red colour of solid complexes are separated out.

6. $[Fe(H_2L)Br_2]$

The synthesis of Fe (II) complexes with the alcoholic solution of ferric bromide was kept in bright sunlight for six hours. When intense brown colour of ferric bromide changed to faint green, almost colourless due to reduction of Fe (III) to Fe (II). The components of the ligand were added to it in inert atmosphere. On refluxing dark red colour of solid complexes are separated out.

7. $[Fe(H_2L)(NO_3)_2]$

The synthesis of Fe(II) complexes with alcoholic solution of ferric chloride was kept in bright sunlight for six hours. When intense brown colour of ferric nitrate changed to faint green almost coloured due to reduction of Fe (III) to Fe(II).The components of the ligand were added to it in inert atmosphere. On refluxing dark red colour of solid complexes are separated out. The reaction between them is shown below as Figure -2



M = Fe (II), Cu (II)

X = Cl^-, Br^-, NO_3^-, ClO_4^-

The chemical reaction of preparation of Complexes of $[M(H_2L)X_2]$

Figure- 2

Results and discussion

The complexes with intra-molecular hydrogen bonded macrocyclic ligand derived from metal ion catalysed template synthesis of 1,2-Diamino-4,5-dinitrobenzene and diacetylmonoxime with Fe(II) and Cu(II) have been synthesized. Characterizations have been done on the basis of their elemental analyses, conductivity, Magnetic moment with spectral data of I.R and UV-visible.

Elemental analysis

The physical and analytical data of the related complexes are given in table – 1. This 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 Fe(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%
$[Cu(H_2L)Cl_2]Cl$	Green	79	12.75(11.74)	19.27(19.26)	37.56(36.54)	3.58(3.57)
$[Cu(H_2L)Br_2]Br$	Green	78	9.08(9.07)	14.13(14.12)	28.27(28.26)	2.81(2.78)
$[Cu(H_2L)(NO_3)_2]NO_3$	Green	72	9.839.82)	23.90(23.89)	31.53(30.52)	2.90(2.89)
$[Cu(H_2L)ClO_4]ClO_4$	Green	79	8.29(8.28)	12.87(14.86)	25.74(25.74)	2.56(2.55)
$[Fe(H_2L)cl_2]$	Red	96	14.12(13.10)	20.68(19.66)	39.32(39.32)	3.74(3.83)
$[Fe(H_2L)Br_2]$	Red	91	10.86(10.83)	16.27(16.26)	32.55(32.54)	3.12(3.11)
$[Fe(H_2L)(NO_3)_2]$	Red	92	11.68(11.65)	23.32(23.31)	35.05(34.01)	3.32(3.31)

Table – 1

I.R Spectral data for the complexes

Complexes	$\nu_{C=N\ (Oxime)}$	$\nu_{C=N}$	$\nu_{M=N}$	$\nu_{M=O}$
$[Cu(H_2L)Cl_2]Cl$	1591	1591	445	397
$[Cu(H_2L)Br_2]Br$	1694	1696	465	401
$[Cu(H_2L)(NO_3)_2]NO_3$	1601	1601	464	406
$[Cu(H_2L)ClO_4]ClO_4$	1504	1606	475	400
$[Fe(H_2L)cl_2]$	1591	1611	480	407
$[Fe(H_2L)Br_2]$	1603	1594	495	410
$[Fe(H_2L)(NO_3)_2]$	1502	1591	474	407

Table-2

Infrared spectra

The most useful infrared assignments for those bands most diagnostic of the mode of coordination of ligand. The most important band in the infrared spectra of 1,2-diamino-4,5-dinitrobenzene is due to ν_s and ν_{as} of $-NH_2$ groups. The I.R. spectra of diacetylmonoxime exhibits $\nu_{c=o}$ and $\nu_{c=N}$. In the spectra of the complexes V_{NH2} of 1,2-diamino-4,5-dinitrobenzene and $\nu_{c=o}$ of diacetylmonoxime is significantly absent indicating Schiff base condensation during macrocyclization. The $\nu_{c=N}$ oxime shows a downward shift indicating its involvement in coordination. In the far I.R. region two bands one in the region 440-610 cm^{-1} and another in the region 395-415 cm^{-1} may be assigned to ν_{M-N} and ν_{M-O} respectively. In the halogen complexes, a band in region 295-350 cm^{-1} may be attributed to ν_{M-}

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 Cu(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 Cu(II) complexes. Electronic spectra and magnetic moment data of Fe(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.

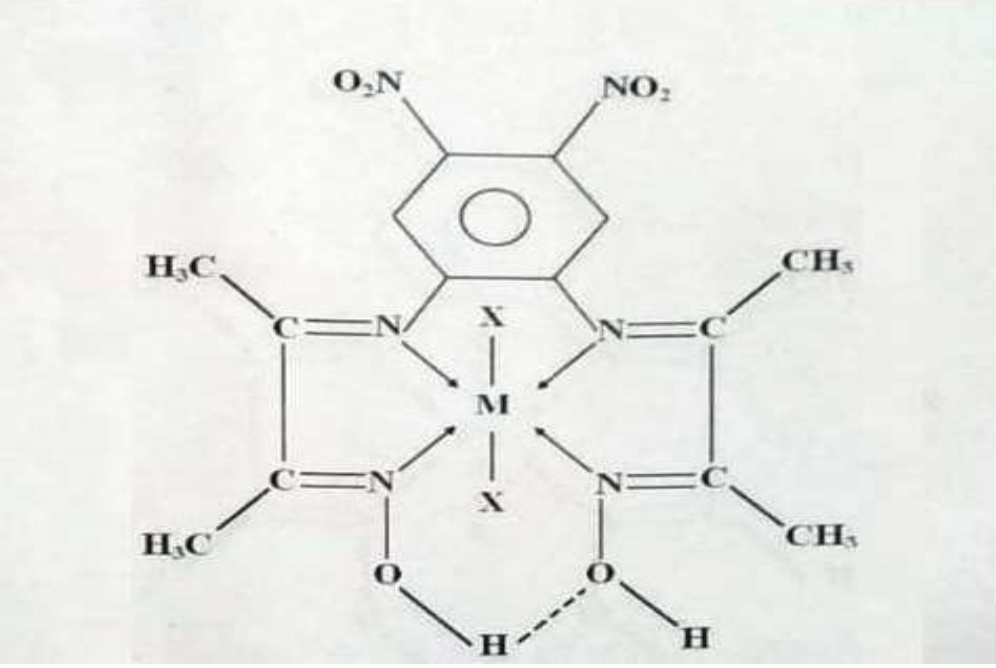
Biological activity

On the basis of latest experimental data the Fe(II) and Cu(II) complexes have work more effective action as compared to free ligands and its metal ions.. The antibacterial and antimicrobial activity of the synthesized Fe(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 Fe(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 chelating improved the effect of antibacterial and antimicrobial activity compared to the ligand and free metal ions, known as antibiotic drugs.[19-21]

CONCLUSION

On the basis of above 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 Fe(II) and Cu(II) 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 Fe(II) and Cu(II) metal ion complexes are unimeric 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 = Fe(II) and Cu(II)

X = Cl^-, Br^-, NO_3^-, ClO_4^-

Octahedral paramagnetic structure of the metal complexes

Figure- 3

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