

Antimicrobial Activity of Binuclear Macrocyclic Mn(II) and Fe(II) Complexes with Polydentate ligands.

Dr. Raman kumar

Department of Chemistry P.N.College, Parsa, Saran,
Jai prakash University, Chapra. 841301.

ABSTRACT

The Mn (II) and Fe (II) 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 Mn(II) and Fe(II) have been synthesized. 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 outer d-orbital octahedral paramagnetic hydrogen bonded macrocyclic stable ring structure of the metal complexes. Spectroscopic studies indicate that the coordination occurs through two oxime-amine chelating ligands by neutral polydentate donor utilizing all its azomethine nitrogen for coordination with two halides ions in facial and axial mode with Mn (II) and Fe (II) formed stable ring structure complexes. The Mn (II) and Fe (II) complexes and ligands have been screened for antibacterial, antimicrobial activity and in the applied medicinal chemistry with other area of industries.

Keyword- Macrocyclic complexes, Diacetylmonoxime, intramolecular hydrogenbonding, azomethine nitrogen.

INTRODUCTION

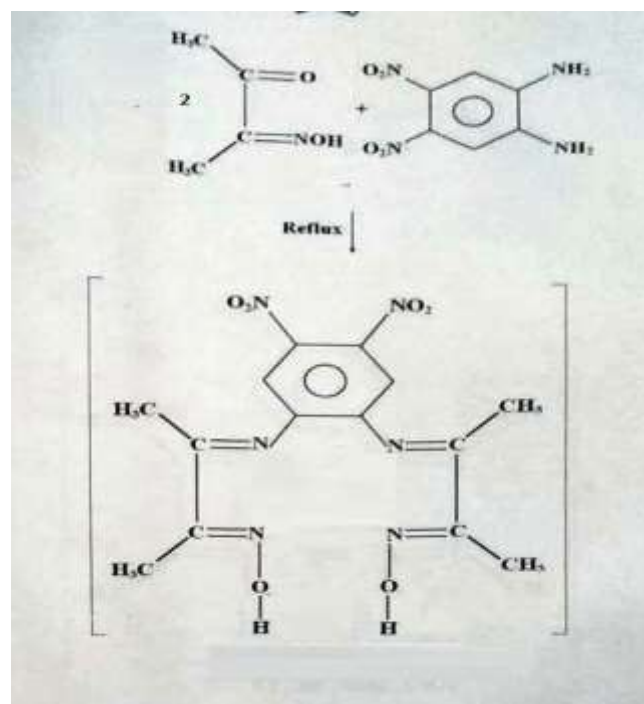
Coordination compounds have received great attention in the field of inorganic chemistry during recent years¹⁻⁴. The reasons for this interest are the fundamental importance in exchange interaction with theory of bonding in new magnetic materials research and in understanding their important roles they 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 ethyl alcohol 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 $[Mn(H_2L)X_2]$ and $[Fe(H_2L)X_2]$. The chelating of ligand with Mn (II) and Fe (II) are expected to form complexes with different geometry. It may enhance their biological activity after chelation also. Which may find their importance in the applied medicinal chemistry with antibacterial, antimicrobial activity and other area of industries¹⁴⁻¹⁷

Materials and method

The salts of the metal are used for synthetic and analytical works were of reagent grade solvent and purified by standard method and dry before use.

Ligand synthesis

The polydentate 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 them is as in Figure - 1



The chemical reaction of synthesis of Ligands (H_2L)

Figure - 1

Preparation of complexes.

1. $[Mn(H_2L)Cl_2]$

0.01 mole of ethanolic solution of manganous 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. $[Mn(H_2L)Br_2]$

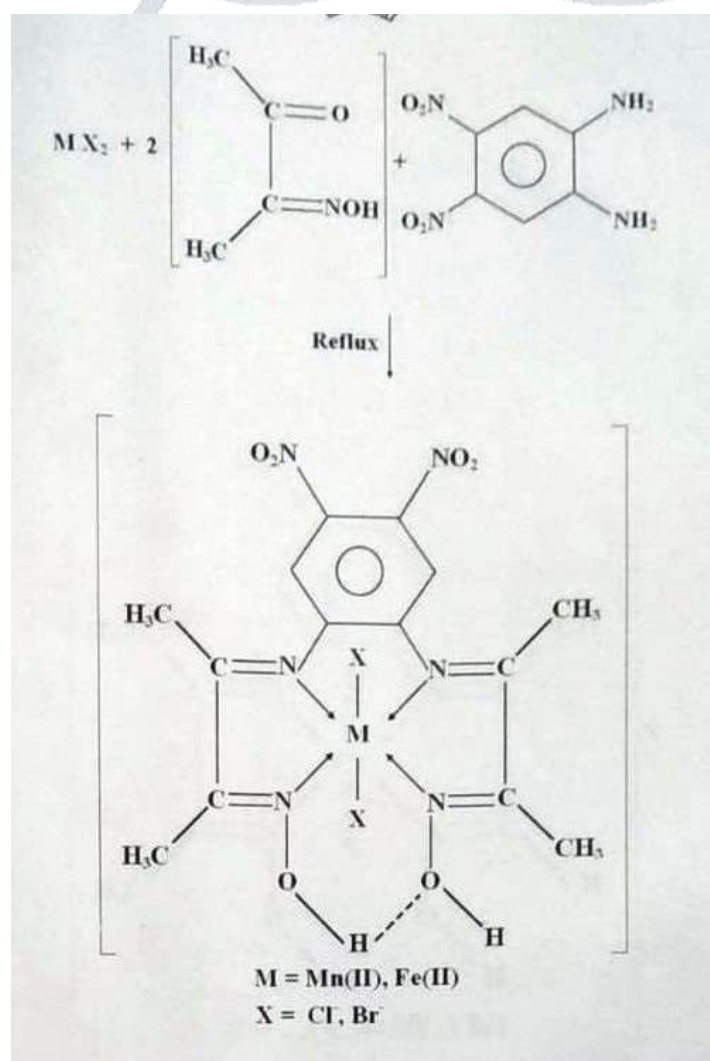
0.01mole of ethanolic solution of manganous bromide and 0.02 mole of diacetylmonoxime was add to 0.1 mole of 1,2-Diamino-4,5-dinitrobenzene and the resulting mixture was continuously and vigorously were refluxed for 4 hour in water bath. A brown colour of solid complex separated out. The synthetic reaction taking place during the synthesis can be shown below.

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

The preparation of Fe (II) complexes, the ethanolic 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 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 solid complex separated out. The reaction between them is shown below.

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

The preparation of Fe (II) complexes, the ethanolic 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 solid complex separated out. The reaction between them is shown below as Figure -2



The chemical reaction of preparation of Complexes of $[\text{Mn}(\text{H}_2\text{L})\text{X}_2]$

Figure- 2

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 Mn(II) and Fe(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. 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 (Table –2) show that Mn (II) and Fe (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%
[Mn(H ₂ L)Cl ₂]	Brown	65	12.91(12.90)	19.72(19.71)	39.44(39.43)	3.76(3.75)
[Mn(H ₂ L)Br ₂]	Brown	60	10.68(10.67)	16.31(16.30)	32.62(32.61)	3.11(3.10)
[Fe(H ₂ L)Cl ₂]	Red	95	13.11(13.10)	19.67(19.66)	39.34(39.33)	3.75(3.74)
[Fe(H ₂ L)Br ₂]	Red	90	10.85(10.84)	16.28(16.27)	32.56(32.55)	3.10(3.09)

Table – 1

I.R Spectral data for the complexes.

Complexes	$\nu_{C=N}$ (Oxime)	$\nu_{C=N}$	$\nu_{M=N}$	$\nu_{M=O}$
[Mn(H ₂ L)Cl ₂]	1505	1590	590	410
[Mn(H ₂ L)Br ₂]	1500	1600	595	415
[Fe(H ₂ L)Cl ₂]	1490	1610	480	405
[Fe(H ₂ L)Br ₂]	1505	1595	490	410

Table-2

Infrared spectra.

Table-2. Lists 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 NH₂ groups. The I.R. spectra of diacetylmonoxime exhibits $\nu_{C=O}$ and $\nu_{C=N}$. In the spectra of the complexes ν_{NH_2} 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 halo complexes, a band in region 295-350 cm^{-1} may be attributed to ν_{M-X} (X= Cl, Br)

Electronic spectra and magnetic moment studies

The UV-visible spectra of the complexes were recorded for their solutions in ethanol and DMSO on solvents in the range (200-1000) nm. The Mn (II) complexes shows slight low value where compared to spin-only value (5.92 B.M). The low value may be due to the presence of Mn (III) species or spin exchange in the solid phase¹⁸. Electronic spectra and magnetic moment data of Fe (II) and Mn (II) complexes support paramagnetic high spin octahedral stereochemistry. These Schiff base ligands and their metal complexes have been investigated as potential antibacterial and antimicrobial agents in long history of medical application. Up to now, a great variety of these ligands and their complexes containing hetero atoms represent good antimicrobial activity.

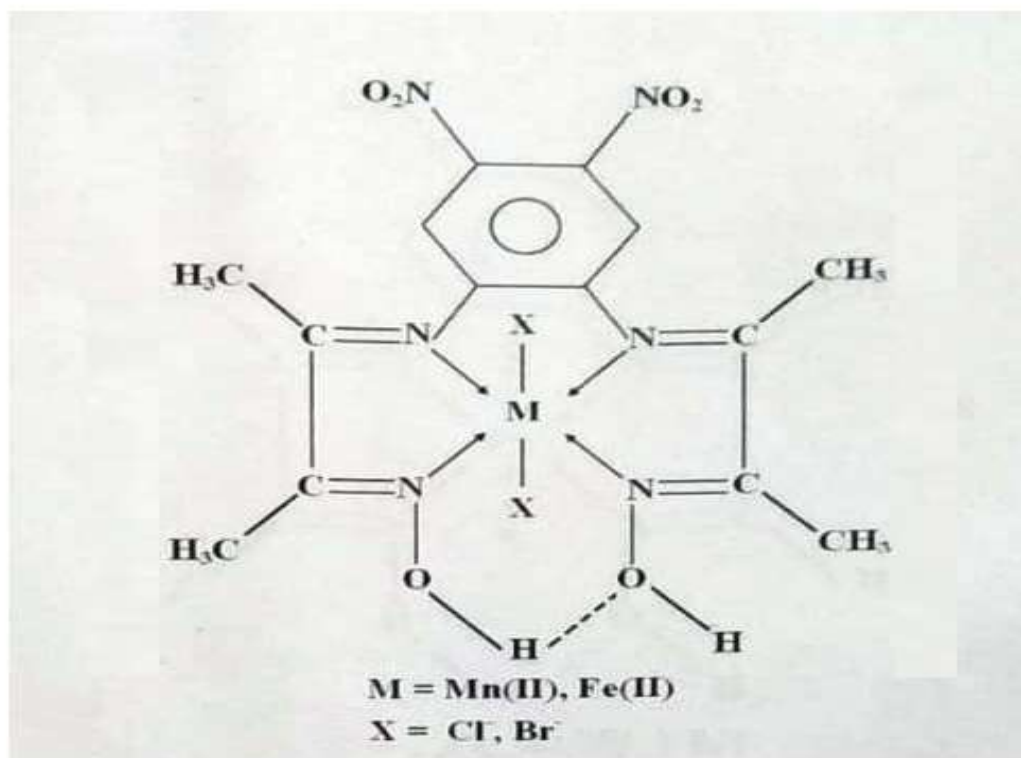
Biological activity.

On the basis of experiment the Mn (II) and Fe (II) complexes have more active as compared to free ligands. The antibacterial and antimicrobial activity of the synthesized Mn (II) and Fe (II) complexes was tested against both Gram-negative and Gram-positive bacteria. The tested solutions were prepared in suitable organic solvent. It seems that enhanced biological activity for the compound of Mn (II) and Fe (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 lipophilic and absorbing nature. The complexes are more active due 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. Therefore the results indicated that chelation improved the antibacterial and antimicrobial activity compared to the ligand and known as antibiotic drugs.¹⁹⁻²⁰

CONCLUSION.

Thus on the basis of above studies it is concluded that the Schiff base ligands (H_2L) acts as a polydentate manner and coordination is proposed through oxime N moiety with central metal ion of complexes while two halogen atoms are capsulated in facial and axial mode with Mn (II) and Fe (II) metal ion and proposed stable two 5-membered capsulated cyclic ring structure while intramolecular 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 Mn (II) and Fe (II) metal ion complexes are monomeric high spin octahedral paramagnetic hydrogen bonded macrocyclic stable ring structure of the metal complexes.

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



Octahedral paramagnetic structure of the metal complexes

Figure- 3

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