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PREPARATION AND PROPERTIES OF MACROCYCLIC LIGAND AND ITS COMPLEXES DERIVED FROM TRIMETHOPRIM AND DIETHYL PHTHALATE

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ABSTRACT

Macrocyclic complexes of Mn^{II}, Co^{II}, Ni^{II} and Cu^{II} using a macrocyclic ligand derived by the condensation of Trimethoprim and diethyl phthalate have been prepared and characterized by electronic, IR and NMR spectral studies as well as magnetic moment and conductivity. On the basis of spectral studies, an octahedral geometry has been proposed for all the complexes.

INTRODUCTION: The chemistry of macrocyclic ligands has been known for several decades¹. Generally, macrocyclic polyamides are prepared by reaction of polyamine with either the diester salt of dicarboxylic acid or the dicarboxylic acid dichloride²⁻⁴. Three novel complexes of Cu(II), Co(II) and Zn(II) using macrocyclic ligand derived by the condensation of diethyl phthalate and benzidine have been designed, synthesized and characterised⁵. The Schiff base condensation of 2, 6 -diamino pyridine with 1, 3 diphenyl 1, 3 dipropanedione in the presence Ni(II), Co(II) and Cu(II)chloride in boiling methanol gives the complexes of the 16-membered macrocycle⁶.

New family of 15-membered tetraamide macrocyclic complexes have been synthesized by template condensation reaction of o-aminobenzoic acid with aliphatic or aromatic diamines and diethyl malonate⁷. Macrocyclic ligands are defined as cyclic molecules generally consisting of organic frames, either aliphatic or aromatic units into which the donor atoms are

interspersed⁸ the macrocyclic ligands have been synthesized by the condensation reaction of diethyl phthalate with o-phenylene diamine⁹. The present work deals synthesis and physicochemical studies of a new series of macrocyclic complexes bearing tetra amide groups derived from trimethoprim with diethyl phthalate in the presence of transition metal ions as template.

MATERIALS AND METHODS: All the chemical reagents used in the preparation of macrocyclic Ligands and their metal complexes were of reagent grade (Merck). The solvents used for the synthesis of macrocyclic ligands and metal complexes were distilled before use. All other chemicals were of AR grade and used without further purification. Proton NMR spectra were recorded on a EM 300-30 MHz NMR spectrometer in DMSO. IR spectra of the samples were recorded on a shimadze FTIR-8400s spectro-photometer in 4000-400 cm⁻¹ range in a KBr pellet. The electronic spectra (ethanol) were recorded on the Lamda 35

spectrometer. The magnetic moments were measured out by using gouy balance. The conductivity was measured on a Toshniwals conductivity bridge using dip type platinised platinum electrode Purity of the compound checked by TLC.

Synthesis of Macrocyclic Ligand: Trimethoprim and Diethyl Phthalate were condensed to give macrocyclic ligand by the reported method^{5, 9-10}. 50 ml ethanolic

solution of Trimethoprim (10mmol) was added to the 50 ml of ethanolic solution of Diethyl Phthalate (10mmol) and refluxed for three hours. Then, the solution was reduced to one third on a water bath. The resulting light brown colour crystals were washed with ethanol and ether then dried. The crude product were recrystallised from ethanol, the desired products was obtained.

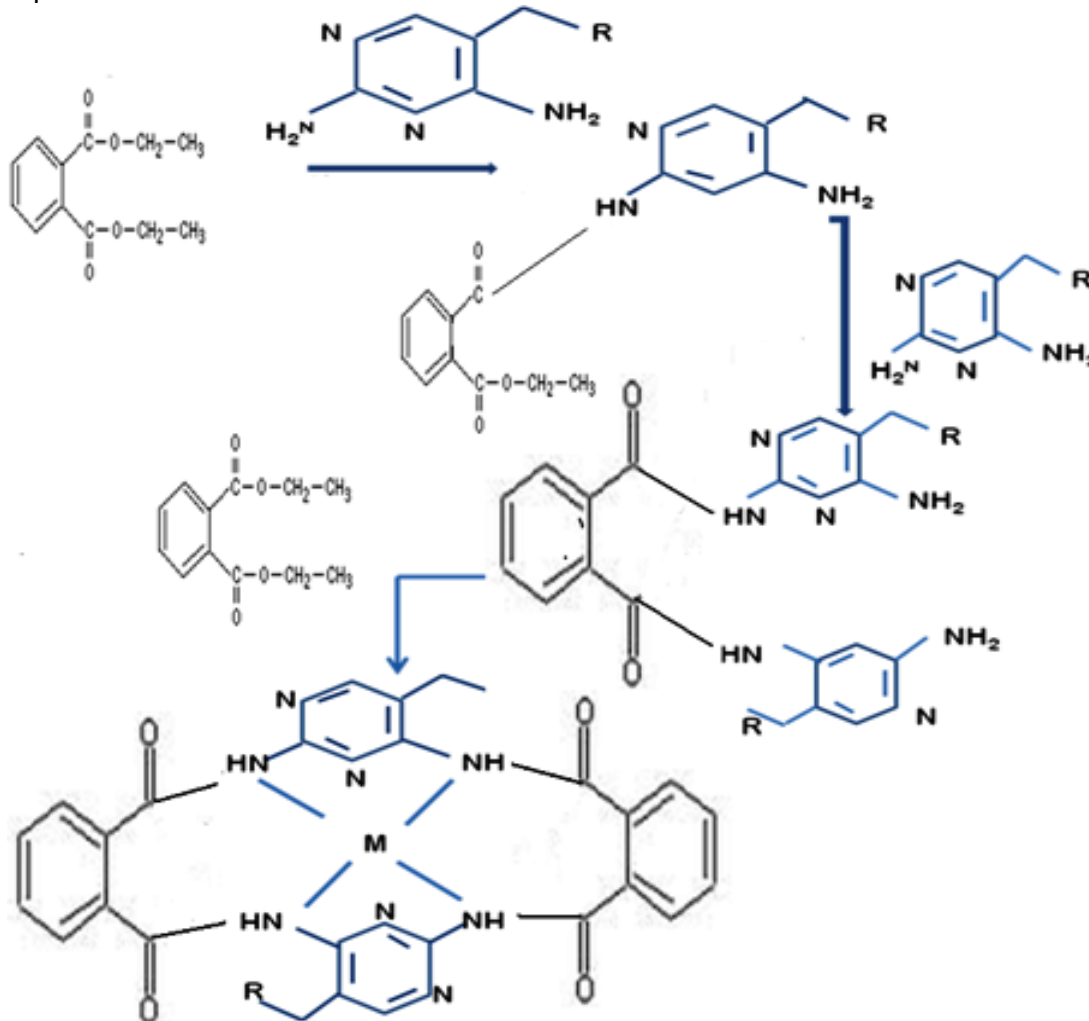


FIG. 1: MACROCYCLIC LIGAND, R=3, 4, 5-TRIMETHOXY BENZYL

Synthesis of Macrocyclic complexes: A solution of macrocyclic ligand (5mmol) in ethanol (20ml) was added to a solution of metal chloride(5mmol) in ethanol (10ml) and the mixture was refluxed for three hour and It was then concentrated to half of the volume and set aside for two days. The microcrystalline compound which separated out was filtered washed with ethanol-ether mixture (1:1) and dried in vacuum over anhydrous calcium

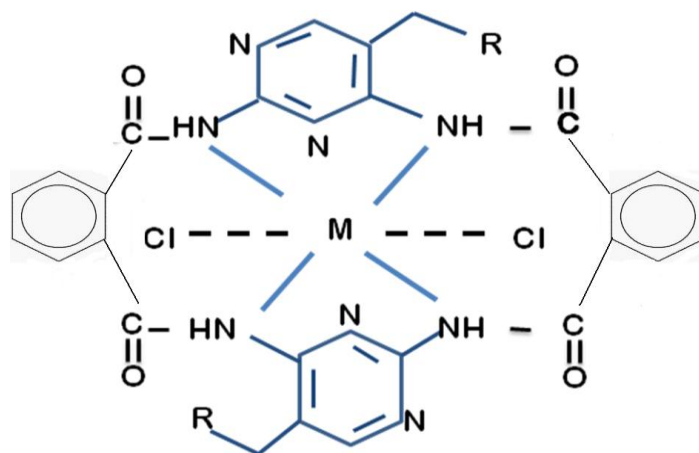


FIG. 2: MACROCYCLIC COMPLEXES

RESULTS AND DISCUSSION: All the complexes were found to be colour and soluble in water, acetonitrile, ethanol and DMSO. They were thermodynamically stable up to 350°C.

Molar conductivities: The molar conductances of these macrocyclic complexes in acetonitrile were measured and then calculated molar conductance value are reported in **Table 1**. The conductivities of the complexes were in the range of 10 – 50 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ¹¹ which is characteristics of 1:0 electrolytes, suggest that all of them are non –electrolytes. The presence of chloride ions is evident only after decomposition of the complexes, probably due to their presence in the coordination sphere. Based on the conductance, metal chloride complexes are assigned the structure $[\text{M}(\text{ML})\text{cl}_2]$. ML-Macrocyclic ligand. M-Metal.

Magnetic moments: The magnetic moments of the complexes (**Table 1**) reveal that they are all high spin type. The manganese (II) chloride complex with the magnetic moment value 5.95 B.M. supported an octahedral geometry around the Mn^{II} ion. The magnetic moments values of Co^{II} and Ni^{II} were 4.92 and 3.26 B.M, respectively suggesting consistency with their octahedral environment ¹². Cu^{II} Complex shows magnetic moment value of 1.68 B.M. expected for one

unpaired electron, which offers possibility of a distorted octahedral geometry ¹².

Electronic spectra: The electronic spectra of the Mn^{II} , Co^{II} , Ni^{II} and Cu^{II} complexes were recorded in ethanol solution and spectral data were presented in table. Mn^{II} complex exhibits two to three very weak bands at 18,515 cm^{-1} , 20,405 cm^{-1} and 26,954 cm^{-1} which are assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{D})$ transition respectively. These observations reveal that the stereochemistry of this complex is consistent with the six coordinated octahedral geometry. The electronic spectral of Co^{II} complexes show bands at 14705 cm^{-1} and 20833 cm^{-1} .

These two bands are assignable to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ transitions respectively in an octahedral environment. The Ni^{II} complex exhibit two absorption bands at 16129 cm^{-1} and 25641 cm^{-1} assignable to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions respectively in an octahedral environment ¹³. Cu^{II} complexes shows a bands in the 21739 cm^{-1} and 20833 cm^{-1} region assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{F}_g$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transitions respectively corresponding to a distorted octahedral geometry. The high intensity bands observed around 34000 cm^{-1} for all the complexes in the U.V. region may be assigned as a metal to ligand charge transfer excitation ⁷.

TABLE 1: COLUR, CONDUCTANCE, MAGNETIC MOMENTS AND ELECTRONIC SPECTRA OF THE MACROCYCLIC COMPLEXES

Complexes	Colour	Molar conductance ($\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	Magnetic moments (B.M.)	Electronic spectra		Stereo chemistry
				Energy (cm^{-1})	Assignment	
$[\text{Mn}(\text{ML})\text{cl}_2]$	red	20.14	5.95	26,954	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{D})$	Octahedral
$[\text{Co}(\text{ML})\text{cl}_2]$	pink	29.25	4.92	14705	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$	Octahedral
$[\text{Ni}(\text{ML})\text{cl}_2]$	Light Green	25.88	3.26	25641	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$	Octahedral
$[\text{Cu}(\text{ML})\text{cl}_2]$	Green	21.03	1.68	20833	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$	Distorted Octahedral

IR Spectra: The Infra Red spectra gave some important information regarding to the skeleton of the complexes. the IR spectra of the macrocyclic ligands show characteristics bands for $\nu(\text{N-H})$ at 3454 cm^{-1} , $\nu(\text{C=O})$ at 1658 cm^{-1} and $\nu(\text{C-N})$ at 1442 cm^{-1} . In all the complexes, $\nu(\text{N-H})$ bands were shifted by 34-51 cm^{-1} to lower frequencies, due to coordination of the NH groups. The $\nu(\text{C-N})$ bands were also shifted by 10-65 cm^{-1} due to participation of the azomethine groups in coordination. On the other hand, the stretching vibrations of $\nu(\text{C=O})$ was not affected in all the complexes, which indicates that the carbonyl groups are not involved in coordination to the metal.

The coordination of nitrogen to the metal atom is supported by the appearance of a new band in the region 543-506 cm^{-1} assignable to $\nu(\text{M-N})$ vibration. ⁹.

¹H NMR spectra: The proton magnetic resonance spectrum of the macrocyclic ligand was taken in DMSO solvent. The spectrum shows four different types of protons. Since signals are observed at four different regions from the TMS (Internal standard).the intensities of the peaks are in the ratio 9:2:2:6. ¹H NMR spectrum of the macrocyclic ligand display peaks at δ 4.2(18H, M, O-CH₃): δ 5.7-6.1(4H, S, Pyridine-H): δ 6.6(2H, S, ring NH): δ 7.5-7.8(12H, M, Ar-H).

Thus, the ^1H NMR spectrum confirms the presence of Trimethoprim and Diethyl phthalate moieties in the macrocyclic product. All the above along with the absence of any band characteristics of NH_2 OR OC_2H_5 protons, support the proposed macrocycle^{7,14}.

CONCLUSION: Conductivity measurement indicates that the metal complexes are non-electrolytes in nature. The magnetic moments of all the complexes reveal that they are all of high spin type with paramagnetic nature. Electronic spectra data support that all the metal complexes have octahedral. The IR spectra data reveal that the macrocyclic ligand coordinated through four amino nitrogen of the macrocyclic ring and there is no indication of pyrimidine nitrogen in coordination.

Based on the various physiochemical studies such as conductivity, magnetic susceptibility, electronic and IR spectral studies octahedral geometry may be proposed for all the complexes

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