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# Synthesis and Characterization of Macrocyclic Complexes of Mn(II), Co(II) and Cu(II)

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**Abstract :** The 12- membered $N_6$macrocyclic complexes with Mn(II),Co(II) and Cu(II) have been synthesized By Schiff base process. The ligand and the metal complexes were characterized by elemental analysis, conductance, magnetic susceptibility measurements and the spectral studies. Thus, the macrocyclic ligand coordinates through imine and secondary amine nitrogens of the macrocyclicring. The spectral data suggest that the complexes of metal chlorides have octahedral and that of metal sulphates have tetrahedral geometry.

**Keywords :** Synthesis, Characterization, L-phenylalanine, Macrocyclic Complexes.

## Introduction

Macrocyclis chemistry has gain more attention in the development of both inorganic and bioinorganic chemistry in view of its biological significance[1,2].Anumberof nitrogen donor macrocyclic derivatives have been used in analytical, industrial and medical applications[3]. Macrocyclic compounds and their derivatives are interesting ligand system because they are good hosts for metal anions,neutral molecules and organic cation guests[4]. The macrocyclic complexes show remarkable stability[5]compared to its closed chain analogues and the metal ion is firmly held in the cavity of macrocycles.

In the present study, the synthesis and characterization of Mn(II),Co(II)and Cu(II)Complexes of tetradentate$N_6$-macrocyclic ligand are discussed. Complexes were characterized using various physico-chemical techniques, such as IR and UV/Vis spectroscopy, elemental Analysis, magnetic susceptibility and conductivity measurements.

## Experimental

### Materials and methods

All the chemicals used for the preparation of the ligands were of BDH quality, AR grade. Themicroelemental analysis was carried out using CHN-Rapid Analyzer. Conductivity was measured on aToshniwals conductivity bridge using dip type platinised platinum electrode. Molecular weights were determined by the Rast Camphor method. The magnetic susceptibilities were measured out by using Guoybalance.Proton NMR spectra were recorded on an EM 300-30MHZ NMR spectrometer in DMSO. IR spectra (KBr) of the samples were recorded on a shimadzce FTIR-8400s Spectro-Photometer. The electronic spectra (chloroform) were recorded on the Lamda 35 spectrometer.

### Synthesis of ligand

The condensation reaction was carried out as follows anmethanolic solution (50ml) of the trimethoprim (0.02mol) was added to a hot solution of the L- phenylalanine (0.02 mol) in methanol. The mixture was stirred well and refluxed on a water bath. Then, concentrated hydrochloric acid(1 ml) was added and further refluxed for 6-8hrs.It was then concentrated to half of the volume and set aside for 2 days the resulting pale brown crystals were washed with methanol and ether and dried at 600C.The crude product was recrystallized from alcohol. The desired condensation product was obtained more readily 80-85% yield by the method.

{$C_{46}H_{50}N_{10}O_6$}

Yield: 95 %; color: pale brown .Anal. Calc. for $C_{46}H_{50}N_{10}O_6$ (Mw:838); C,65.78; H,6.12; N,16.36. Found: C,65.86; H,6.01; N,16.69. IR (KBr,cm$^{-1):}$ 3404γ(NH2),3322γ(NH), 1675(C= N),1128γas(C-C-N),1589,990 (pyrimidine ring).$^1$HNMR ( DMSO, ppm) δ= 2.0(4H,s,free-$NH_2$); δ= 3.1(2H,s,ring NH); δ= 3.3(2H,t,-CH); δ= 3.7 (18H,s,-$OCH_3$); δ= 3.9 (4H,d,Ph-$CH_2$); δ= 6.6 (4H,s,pyrimidine –$CH_2$-Ar); δ= 7.4 (5H:5H;d:d;phenyl-H);δ= 7.8 (2H,d,pyrimidine-H).δ= 8.1 (4H,d,Ar-H).

### Synthesis of the metal complexes

To a solution of the metal chloride (or) sulphate(0.01 mol) in methanol were added and refluxed for 5hrs. The resultant solution was cooled two days and the crystals which separated out were filtered washed with methanol-ether mixture (1:1) and dried in vacuum$^{6-8}$ over anhydrous $CaCl_2$.

{Mn ($L_2$)$Cl_2$}

Yield: 80 %; color: Cream White.Anal. Calc. for [Mn($C_{46}H_{50}N_{10}O_6$)$Cl_2$]: C,57.26; H,5.20; N,14.62. Found: C,57.27; H,5.22; N,14.52. IR (KBr,cm$^{-1}$): 3404γ($NH_2$),3326γ(NH), 1675(C= N),1128γas(C-C-N),1502,990 (pyrimidine ring),525(M-N),$\Lambda_m/\Omega^{-1}$ cm$^2$ mol$^{-1}$(in $CH_3CN$): 23.06;$\mu_{eff}$ (300K): 5.8 B.M.

{Mn ($L_2$)$SO_4$}

Yield: 81 % ; color: pale yellow. Anal. Calc. for [Mn($C_{46}H_{50}$ $N_{10}O_6$)$SO_4$] : C,55.72; H,5.00; N,14.20. Found: C,55.80; H,5.09; N,14.15. IR (KBr,cm$^{-1}$): 3401 γ($NH_2$), 3321γ(NH), 1666 (C= N),1128γas(C-C-N),1499, 992 (pyrimidine ring), 511 (M-N), 991($SO_4$). $\Lambda_m/\Omega^{-1}$cm$^2$ mol$^{-1}$(in $CH_3CN$):105.15.$\mu_{eff}$ (300K): 5.95 B.M.

{Co ($L_2$)$Cl_2$}

Yield: 85 % ; color: pink , Anal. Calc. for [Co($C_{46}H_{50}N_{10}O_6$)$Cl_2$] : C, 57.23; H, 5.26; N,14.60. Found: C,57.04; H,5.20; N,14.46. IR (KBr,cm$^{-1}$): 3403 γ($NH_2$), 3323γ(NH), 1670 (C= N), 1129γas(C-C-N), 1499, 991 (pyrimidine ring), 512 (M-N), $\Lambda_m/\Omega^{-1}$ cm$^2$ mol$^{-1}$(in $CH_3CN$): 40.00. $\mu_{eff}$ (300K): 4.62 B.M.

{Co ($L_2$)$SO_4$}

Yield: 84 %; color: Brown. Anal. Calc. for [Co($C_{46}H_{50}N_{10}O_6$)$SO_4$] : C,55.80; H,5.02; N,14.01. Found: C,55.59; H,5.07; N,14.09. IR (KBr,cm$^{-1}$): 3405 γ($NH_2$), 3322γ(NH), 1673 (C= N), 1129γas(C-C-N), 1501, 991 (pyrimidine ring), 510 (M-N), 904 ($SO_4$). $\Lambda_m/\Omega^{-1}$ cm$^2$ mol$^{-1}$(in $CH_3CN$): 153.00. $\mu_{eff}$ (300K): 4.89 B.M.

{Cu ($L_2$)$Cl_2$}

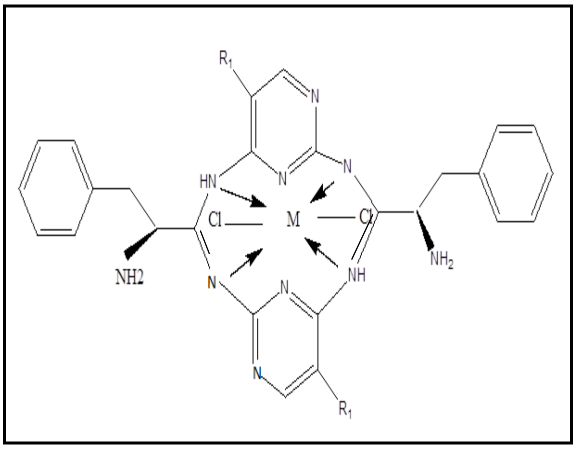
Yield: 75 %; color: green , Anal. Calc. for [Cu($C_{46}H_{50}N_{10}O_6$)$Cl_2$] : C, 56.11; H, 5.36; N,14.40. Found: C,56.77; H,5.18; N,14.39. IR (KBr,cm$^{-1}$): 3321 γ($NH_2$), 3163γ(NH), 1614 (C= N), 1117γas(C-C-N), 1599, 990 (pyrimidine ring), 558 (M-N). $\Lambda_m/\Omega^{-1}$ cm$^2$ mol$^{-1}$(in $CH_3CN$): 60.00. $\mu_{eff}$ (300K): 1.16 B.M.

{Cu ($L_2$) $SO_4$}

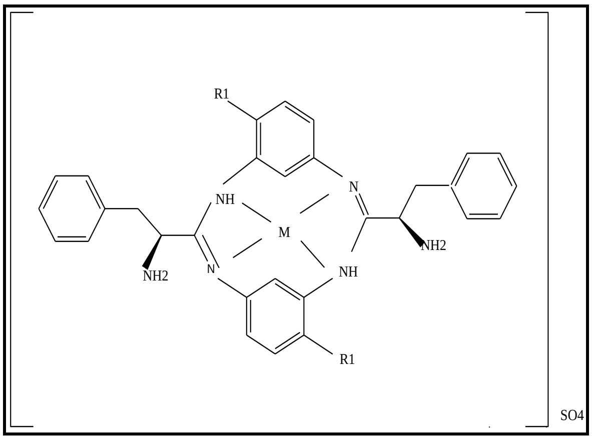
Yield: 80 %; color: red orange. Anal. Calc. for [Mn($C_{46}H_{50}N_{10}O_6$)$SO_4$] : C,55.35; H,5.20; N,14.10. Found: C,55.33; H,5.05; N,14.03. IR (KBr,cm$^{-1}$): 3403 γ($NH_2$), 3322γ(NH), 1672 (C= N), 1129γas(C-C-N), 1500, 907 (pyrimidine ring), 511 (M-N), 992($SO_4$). $\Lambda_m/\Omega^{-1}$ cm$^2$ mol$^{-1}$(in $CH_3CN$): 180.30$\mu_{eff}$ (300K): 1.16 B.M.

## Results and discussion

The Schiff base macrocyclic complexes were prepared from $C_{46}H_{50}N_{10}O_6$ in the presence of MX (where M= Mn(II),Co(II),and Cu(II),X=$Cl^-$,$SO_4^{2-}$) produced a new series of 12-membered tetradentatemacrocyclic metal complexes of the type $M(L_2)Cl_2$ and $M(L_2)\ SO_4$ as shown in Fig(1& 2).



$R^1$= 3,4,5-trimethoxy benzyl
M=Mn (II),Co(II) and Cu(II)
**Fig (1): Proposed structure of metal(II) chloride macrocyclic complexes of $L_2$**



$R^1$= 3,4,5-trimethoxy benzyl
M=Mn(II),Co(II) and Cu(II)
**Fig (2): Proposed structure of metal(II) sulphatemacrocyclic complexes of $L_2$**

The resulting metal derivatives are colored solids which are stable at room temperature and are non-hygroscopic. The monomeric nature of these complexes is confirmed by molecular weight determination. All the complexes are slightly soluble in methanol or ethanol but soluble in DMF and DMSO. The analytical data of the complexes are in good agreement with the calculated values, thus confirming the proposed composition for all the complexes.

### Molar conductance

The molar conductance of these macrocyclic complexes of ($L_2$) in acetonotrile were measured and the calculated molar conductance values.

The molar conductivities of the sulphate complexes ($L_2$) in acetonitrile are in the range of 90-185 $ohm^{-1}\ cm^2\ mol^{-1}$ which is characteristic of 1:1 electrolytes, indicating that the sulphate groups are ionic in nature. The conductivities of the metal chloride complexes are in the range of 23-60 $ohm^{-1}\ cm^2\ mol^{-1}$ suggest that all of them are non-electrolytes[9]. The presence of chloride ions is evident only after decomposition of the complexes, probably due to their presence in the coordination sphere.

## IR spectra

The infrared spectra of the ligand are compared with those of the complexes to determine the bonding mode of the ligand to the metal in the complexes. The IR spectrum of the macrocyclic complexes of ligand indicates that the trimethoprim and L- phenylalanine moieties are present. Thesecondary amine stretching mode of the free ligand occurring at 3322 $cm^{-1}$has been shifted to around 3250$cm^{-1}$ in the above complexes. The C=N of macrocyclic ring in the complexes are lowered by10-30$cm^{-1}$. These shifts confirm the secondary amine and imine nitrogens of the cyclic ring as donating sites.

A broad band occurring 3404 $cm^{-1}$ and 2731$cm^{-1}$ region of the spectra of the ligand as well as the complexes is assigned to $–NH_2$ group of L-phenyalanine C-H stretch of the pyrimidine ring, benzyl aromatic ring and methoxy groups are appearing in the above region may be indication of non- involvement of these groups in coordination.

In the sulphate complexes a band of strong intensity is observed near 1043$cm^{-1}$to 632$cm^{-1}$ which is characteristic of uncooridinated $SO_4^{2-}$ion and confirms its presence in a outer sphere of the complex ion. The appearance of new band in the region 560-510$cm^{-1}$assignable to (M-N) further confirms the involvement of nitrogen in coordination[10-12]. The (M-Cl) stretches could not be identified due to poor resolution.

## Magnetic measurements and Electronic spectra

Manganese complex: The magnetic moment of the complexes show that they are all of high spin type. Divalent manganese sulphate complex have a magnetic moment about 5.8 B.M. This moment is independent of the configuration of the manganese (II) around it. It is therefore difficult to have magnetic moment of 5.95 B.M which suggest octahedral configuration around the metalion[13-15].The electronic spectra of the manganese(II)chloride complexes of divalent metals have been assigned octahedral configuration on the basis of their magnetic moments and electronic spectra. In a high spin octahedrally coordinated manganese (II) the lowest configuration $t^2geg^2$ gives rise to the ground state $^6A_1g$. Since this is the only sextet level present, all of the absorption bands must be spin forbidden transitions.

Cobalt complex: The magnetic moment of the cobalt(II) sulphate is 4.62 B.M suggesting tetrahedral. The slightly higher value 4.89 B.M suggests octahedral geometry for the cobalt(II) chloride complex. The electronic spectra of the Cobalt(II)sulphate complex exhibits a band at 19379 $Cm^{-1}$ due to $^4T_1g(F) \rightarrow {}^4A_2g(F)$ transition of tetrahedral geometry. The cobalt(II) chloride displays a band at 15284$Cm^{-1}$ which is assigned to $^4T_1g(F) \rightarrow {}^4T_1g(P)$ transition of octahedral geometry.

Copper complex: The magnetic moment of the copper (II) chloride complex 1.55 B.M suggesting distorted octahedral geometry. The copper(II) sulphate complex exhibits magnetic moment value of 1.16 B.M which indicates tetrahedral geometry.The electronic spectrum of the copper(II) chloride complex displays a band at 11442$Cm^{-1}$ which is due to$^2Eg – {}^2T_2g$ transition of octahedral geometry. The electronic spectrum of copper(II) sulphate shows a low energy band around geometry[16,17].

## NMR spectra

The proton magnetic resonance[18, 19]spectra of the ligand $C_{46}H_{50}N_{10}O_6$are recorded in DMSO solvent using TMS as internal standard. The spectral data give some important information to conclude the formation of ligand. The spectrum shows nine signals which are observed at nine different regions from the TMS.$^1$H-NMR spectrum of the macrocyclic ligand display peaks at δ= 2.0(4H,s,free-$NH_2$); δ= 3.1(2H,s,ring NH); δ= 3.3(2H,t,-CH); δ= 3.7 (18H,s,-$OCH_3$); δ= 3.9 (4H,d,Ph-CH2); δ= 6.6 (4H,s,pyrimidine –$CH_2$-Ar); δ=7.4 (5H:5H;d:d;phenyl-H);δ=7.8 (2H,d,pyrimidine-H).δ= 8.1 (4H,d,Ar-H) and thus the $^1$H-NMR spectrum confirms the presence of trimethoprim and L-phenylalanine moieties in the macrocyclic condensed product. From the ratio of the intensities of the peak the number of protons can be calculated as 50.

## Conclusion

The electronic spectral data reveal that all the chloride complexes are in octahedral and sulphate complexes are in tetrahedral geometry. The IR spectral data suggest that the coordination is through four nitrogens of the macrocyclicring. This is based on analytical and spectral data, in all these complexes the ligand is supposed to be in the shaddleshapped so that they can function in tetradentatefashion. These complexes are useful to study the electronic and physic-chemical properties of 3d-metal ions in identical ligand frame works. These studies are essential for the development of critical ligand design parameters and synthetic procedures of macrocycles for various applications.

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