



## STUDIES ON THE INTERACTION OF $Mn^{II}$ , $Co^{II}$ , $Ni^{II}$ , $Cu^{II}$ and $Zn^{II}$ WITH TETRADENTATE- $N_6$ -MACROCYCLIC LIGAND

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### ABSTRACT

Complexes of tetradentate- $N_6$ -macrocyclic ligand (L) with  $Mn^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$  and  $Zn^{II}$  have been synthesized and characterised by elemental analysis, molecular mass determination, conductance and magnetic susceptibility measurements and the spectral studies like electronic, ir and proton-nmr studies. The spectral data suggest that the complexes of metal chlorides have octahedral geometry and that of metal perchlorates have tetrahedral geometry. No evidence is found for the participation of nitrogen atoms of pyrimidine and amino group of the amino acid in the coordination. Thus, the ligand coordinates through the macrocyclic ring imine and amine nitrogen atoms.

**Key words :**  $Mn^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$  and  $Zn^{II}$  with tetradentate –  $N_6$ -Macrocyclic ligand.

### INTRODUCTION

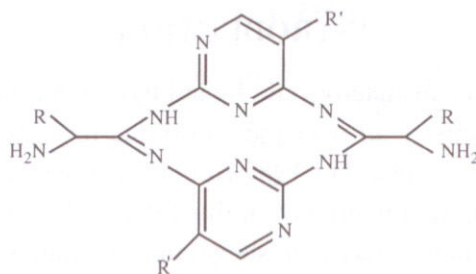
Coordination Chemistry of macrocyclic ligand has been a fascinating area of current research in inorganic chemistry all over the world due to its wider applications and the unusual binding abilities. The award of 1987 Nobel Prize in Chemistry to Pedersen, Lehn and Cram is a testimony to the importance of this field<sup>1-4</sup>. From the literature survey, it is found that a great deal of interest has been shown in pyrimidines and its derivatives due to their biological importance as constituents of nucleic acids<sup>5</sup>. In this work, the incorporation of pyrimidine moiety into the macrocyclic framework is found to enhance the rigidity and binding ability of the ligands towards the transition metal ions<sup>6</sup>. A novel synthesis of  $N_8$ -macrocyclic ligand of pyrimidine based trimethoprim has been reported<sup>7</sup>. The present work also deals with the interaction of  $Mn^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$  and  $Zn^{II}$  metal ions with the ligand (Figure 1). The study of stereochemistry and chemical reactivity of the coordination compounds of the macrocycles will help us to understand the relationship between chemical structure and biological activity of the macrocycle.

## EXPERIMENTAL

Polyphosphoric acid (E-Merck), 2,6-diaminopyridine (Fulka) and adipic acid were used as such. Methanol was dried using  $\text{CaCl}_2$  and then distilled (b.p.  $65^\circ\text{C}$ ). Other solvents used were of BDH/AR grade. The microelemental analysis was carried out using Heraeus CHN-Rapid Analyser. The electronic spectra (Methanol) were on the Beckmann Model 25 Spectrometer. IR Spectra (KBr) on a Bruker IFS-66 VFT-IR Spectrometer. The proton-NMR spectra were recorded on a EM-390-90MHz NMR Spectrometer in DMSO at RSIC, IIT Chennai. The metal ions were estimated by volumetric methods and the chloride was estimated by Volhard's method. The conductivity was measured on a Toshniwal's conductivity bridge at  $25^\circ\text{C}$  using dip type platinised platinum electrode. The magnetic moments were measured out using Gouy method.

### Synthesis of the complex

The macrocyclic ligand (L) was synthesized by the reported method<sup>8</sup>. The 50.0 mL methanolic solution of the metal chloride (0.01 M) was added to the RB flask containing a hot 50.0 mL methanolic solution (say,  $60^\circ\text{C}$ ) of macrocyclic ligand (0.01 M). The contents of the RB flask were refluxed for six to eight hours. When the content was concentrated to half of its volume, it was set aside for two days. The microcrystalline compound got separated out. It was washed with methanol-petether solvent mixture (1 : 1) and dried in vacuum over anhydrous  $\text{CaCl}_2$ . The complexes  $[\text{M}(\text{L})\text{Cl}_2]$  (where  $\text{M} = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$ ) were synthesized by the aforesaid method.



Macrocyclic ligand (L)

R = H, Me,  $\text{CH}_2\text{Ph}$ ,  $\text{HO-C}_6\text{H}_4\text{CH}_2$  and  $\text{C}_8\text{H}_6\text{NCH}_2$   
 R' = 3,4,5-trimethoxy benzyl

Fig. 1. Structure of the macrocyclic ligand (L)

## RESULTS AND DISCUSSION

The macrocyclic complexes were found to be thermodynamically stable upto  $290^\circ\text{C}$ . The complexes were soluble in water, methanol, acetonitrile and dimethyl sulfoxide. From the analytical data (Table 1 and 2), the complexes can be represented  $[\text{M}(\text{C}_{34}\text{H}_{42}\text{N}_{10}\text{O}_6)\text{Cl}_2]$  and  $[\text{M}(\text{C}_{34}\text{H}_{42}\text{N}_{10}\text{O}_6)(\text{ClO}_4)_2]$  where  $\text{M} = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$ . The molecular mass and

the analytical results were in good agreement with the proposed compositions of the complexes. The molar conductivities of the metal perchlorate complexes of the ligand (L) in acetonitrile were in the range 198–283  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  indicating the 1 : 2 electrolytic nature. The metal chloride complexes were non-electrolytic with the conductivity values in the range 12–48  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ . The presence of chloride ions is evident only after the decomposition of the complex, probable due to their presence in the coordination sphere.

**Table 1. Yield, colour and analytical data of the complexes of L**

S. No.	Ligand/Complex	Yield (%)	Colour	Analysis % Found (Calculated)				
				C	H	N	X	M
1.	L2(C <sub>34</sub> H <sub>42</sub> N <sub>10</sub> O <sub>6</sub> )	90	Pale brown	59.42 (59.47)	6.44 (6.12)	20.39 (20.48)	–	–
2.	[Mn(L <sub>2</sub> )Cl <sub>2</sub> ]	80	Pale brown	50.25 (50.49)	5.21 (5.19)	17.26 (17.32)	8.72 (8.48)	6.76 (6.82)
3.	[Mn(L <sub>2</sub> )](ClO <sub>4</sub> ) <sub>2</sub>	82	Pale brown	43.58 (43.43)	4.67 (4.50)	14.83 (14.91)	21.27 (21.10)	5.92 (5.80)
4.	[Co(L <sub>2</sub> )Cl <sub>2</sub> ]	85	Pink	50.18 (50.01)	5.03 (5.19)	17.25 (17.17)	8.77 (8.71)	7.25 (7.19)
5.	[Co(L <sub>2</sub> )](ClO <sub>4</sub> ) <sub>2</sub>	84	Blue	43.32 (43.26)	4.53 (4.49)	14.92 (14.85)	21.10 (21.02)	6.28 (6.22)
6.	[Ni(L <sub>2</sub> )Cl <sub>2</sub> ]	84	Brown	50.02 (50.00)	5.19 (5.28)	17.18 (17.06)	8.73 (8.68)	7.26 (7.11)
7.	[Ni(L <sub>2</sub> )](ClO <sub>4</sub> ) <sub>2</sub>	80	Green	43.27 (43.15)	4.43 (4.58)	14.88 (14.72)	21.09 (21.20)	6.27 (6.24)
8.	[Cu(L <sub>2</sub> )Cl <sub>2</sub> ]	78	Green	49.63 (49.72)	5.12 (5.36)	17.08 (17.15)	8.65 (8.55)	7.76 (7.52)
9.	[Cu(L <sub>2</sub> )](ClO <sub>4</sub> ) <sub>2</sub>	75	Red	43.01 (43.20)	4.46 (4.48)	14.72 (14.80)	20.93 (20.72)	6.69 (6.55)
10.	[Zn(L <sub>2</sub> )Cl <sub>2</sub> ]	65	Grey	49.58 (49.60)	5.16 (5.22)	17.11 (17.32)	8.58 (8.61)	7.92 (7.98)
11.	[Zn(L <sub>2</sub> )](ClO <sub>4</sub> ) <sub>2</sub>	60	Grey	42.90 (42.96)	4.48 (4.54)	14.71 (14.95)	20.89 (20.71)	6.83 (6.88)

### Magnetic properties

The magnetic moments ( $\mu_{\text{eff}}$ ) of the complexes (Table 2) reveal that they are all high-spin type. The manganese (II) chloride complex with the magnetic moment value 6.1 BM supported an octahedral geometry around the Mn<sup>II</sup> ion. The  $\mu_{\text{eff}}$  value 5.95 BM of the manganese (II) perchlorate complex was a high-spin complex. This value was close to the spin only value 5.92 BM. It is independent of the configuration of the manganese (II) around it and therefore, it

**Table 2. Electrical conductance, magnetic moments and electronic spectral data of the macrocyclic complexes of L**

S. No.	Complex	$\chi_M \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at 30°C	$\mu_{\text{eff}}$ B.M. (per mole of metal ion)	Energy Max $\text{cm}^{-1}$	Electronic Spectra Assignments	Stereo-chemistry
1.	[Mn(L2)Cl <sub>2</sub> ]	4.50	6.10	–	–	Octahedral (O <sub>h</sub> )
2.	[Mn(L2)](ClO <sub>4</sub> ) <sub>2</sub>	272.60	5.95	–	–	Tetrahedral (T <sub>d</sub> )
3.	[Co(L2)Cl <sub>2</sub> ]	60.00	4.70	20100	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)	Octahedral (O <sub>h</sub> )
4.	[Co(L2)](ClO <sub>4</sub> ) <sub>2</sub>	215.20	4.20	14950	<sup>4</sup> A <sub>2</sub> (F) → <sup>4</sup> T <sub>1</sub> (P)	Tetrahedral (T <sub>d</sub> )
5.	[Ni(L2)Cl <sub>2</sub> ]	25.50	3.25	25000	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)	Octahedral (O <sub>h</sub> )
6.	[Ni(L2)](ClO <sub>4</sub> ) <sub>2</sub>	206.30	3.75	14800 26000	<sup>3</sup> T <sub>1</sub> (F) → <sup>3</sup> T <sub>1</sub> (P) Charge Transfer Transition	Tetrahedral (T <sub>d</sub> )
7.	[Cu(L2)Cl <sub>2</sub> ]	46.70	1.56	15250	<sup>2</sup> E <sub>g</sub> → 2T <sub>2g</sub>	Octahedral (O <sub>h</sub> )
8.	[Cu(L2)](ClO <sub>4</sub> ) <sub>2</sub>	191.00	1.30	–	Charge Transfer Transition	Tetrahedral (T <sub>d</sub> )
9.	[Zn(L2)Cl <sub>2</sub> ]	43.00	Dia	–	–	Octahedral (O <sub>h</sub> )
10.	[Zn(L2)](ClO <sub>4</sub> ) <sub>2</sub>	242.00	Dia	–	–	Tetrahedral (T <sub>d</sub> )

is difficult to assign the configuration from this determination<sup>9</sup>. The magnetic moments suggested that the cobalt (II) chloride complexes were octahedral in coordination and the cobalt (II) perchlorate complexes were tetrahedral. The  $\mu_{\text{eff}}$  of the chloride complex was slightly lower than the expected as there would be distorted geometry. The nickel (II) chloride complex with the magnetic moment 3.25 BM was suggestive of the distorted octahedral geometry. The nickel (II) perchlorate complex has the magnetic moment (3.75 BM) slightly higher than that of the spin only value. It was in agreement with the tetrahedral geometry. The low magnetic moment value than the spin only value for the copper (II) chloride complex was significant of the distorted octahedral geometry. The copper (II) perchlorate complex with the magnetic moment 1.30 BM indicated the presence of one paramagnetic electron and tetrahedral geometry<sup>10</sup>. The zinc (II) chloride and perchlorate complexes were found to be diamagnetic.

### Electronic spectra

The electronic spectral data of the complexes are given in Table 2. The weak d–d transitions were overshadowed by the stronger charge transfer transitions in the manganese (II) complexes<sup>11</sup>. The band at 14950  $\text{cm}^{-1}$  for the cobalt (II) perchlorate complex was assigned to <sup>4</sup>A<sub>2</sub>(F) → <sup>4</sup>T<sub>1</sub>(P) transition of tetrahedral geometry<sup>12</sup>. The cobalt (II) chloride complex gave a band at 20100  $\text{cm}^{-1}$ . It was for the <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P) transition of octahedral geometry. The nickel (II) chloride showed a band at 25000  $\text{cm}^{-1}$  due to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(P) transition of

octahedral geometry<sup>13</sup>. The band at 14800 cm<sup>-1</sup> for the nickel (II) perchlorate complex was assigned to <sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>T<sub>1</sub>(P) transition of tetrahedral geometry. The other band at 26000 cm<sup>-1</sup> for the same complex was attributed to the charge transfer transition. The copper (II) chloride complex exhibited <sup>2</sup>E<sub>g</sub> → 2T<sub>2g</sub> transition through a band at 15250 cm<sup>-1</sup>. Copper (II) perchlorate complex was observed to show a stronger charge transfer transition than the d-d transition.

### Infrared spectra

The IR spectral data for the ligand (L) and the macrocyclic complexes are given in Table 3. From the data, it was understood that the trimethoprim and the L-analine moieties were present.

**Table 3. Some characteristic infrared absorption bands (cm<sup>-1</sup>) of the macrocyclic complexes of L**

S. No.	Ligand/Complex	Macrocyclic					Non-ligand bands			
		γNH <sub>2</sub>	γNH	γC=N	γ as C-C-N	Pyrimidine ring vib.	γM-N	γM-Cl	γCl-O of ClO <sub>4</sub> <sup>-</sup>	
1.	L2(C <sub>34</sub> H <sub>42</sub> N <sub>10</sub> O <sub>6</sub> )	3506	3310	1634	1152	1565	995	-	-	-
2.	[Mn(L2)Cl <sub>2</sub> ]	3510	3280	1608	1152	1565	1000	529	320	-
3.	[Mn(L2)](ClO <sub>4</sub> ) <sub>2</sub>	3505	3250	1610	1150	1560	965	513	-	1131
4.	[Co(L2)Cl <sub>2</sub> ]	3506	3265	1610	1152	1562	990	540	310	-
5.	[Co(L2)](ClO <sub>4</sub> ) <sub>2</sub>	3505	3270	1590	1150	1560	995	547	-	1100
6.	[Ni(L2)Cl <sub>2</sub> ]	3505	3260	1590	1155	1565	1000	525	345	-
7.	[Ni(L2)](ClO <sub>4</sub> ) <sub>2</sub>	3502	3260	1605	1150	1560	995	540	-	1120
8.	[Cu(L2)Cl <sub>2</sub> ]	3505	3260	1600	1155	1565	990	510	300	-
9.	[Cu(L2)](ClO <sub>4</sub> ) <sub>2</sub>	3505	3270	1600	1150	1565	995	505	-	1110
10.	[Zn(L2)Cl <sub>2</sub> ]	3506	3250	1600	1155	1560	1000	507	325	-
11.	[Zn(L2)](ClO <sub>4</sub> ) <sub>2</sub>	3510	3250	1580	1160	1565	990	540	-	1080

The stretching and bending vibrations of the -NH<sub>2</sub> group of amino acid were observed at 3506 and 850 cm<sup>-1</sup>, respectively in the ir spectrum of the free macrocyclic ligand as well as in the macrocyclic complexes of Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> chlorides and perchlorates. This clearly indicated that the amino group did not take part in coordination<sup>14</sup>. The bands at 3310 and 1634 cm<sup>-1</sup>, observed for the N-H and C=N vibrations of the free ligand were found to have a negative shift of 40-70 cm<sup>-1</sup> and 20-30 cm<sup>-1</sup>, respectively<sup>15-18</sup> in all the complexes of Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup>. The band at 543-506 cm<sup>-1</sup> was assigned to M-N stretching in the complexes as there was a coordination through nitrogen. The M-Cl vibrations were identified through the bands appeared around 380-320 cm<sup>-1</sup> for those complexes that were involved in the chloride coordination<sup>19</sup>. In the perchlorate complexes, a strong and broad band appeared near 1100 cm<sup>-1</sup>, which was indicative of the noncoordinating perchlorate species, keeping away

from the coordination sphere<sup>20</sup>. The bands at 660 and 741  $\text{cm}^{-1}$  were assigned to the in-plane and out-of-plane bending motions of aromatic ring indicating the non-coordination of the nitrogens in the pyrimidine ring. Thus, it might be quadridentate and macrocyclic compound that was formed having coordination through two imine and two secondary amine nitrogens of the macrocyclic ring, not involving the nitrogen atoms of the pyrimidine. It was in accordance with the fact that quadridentate macrocycles could be formed more readily than the hexa- or quinquidentate ligands<sup>21</sup>. It was very interesting to note that the imine and amine nitrogens were equally active and excluded the weak and less stable coordination by the pyrimidine nitrogen<sup>22,23</sup>.

Thus, from the aforesaid observations, the following structures (Figure 2) were proposed for the macrocyclic complexes of the ligand (L).

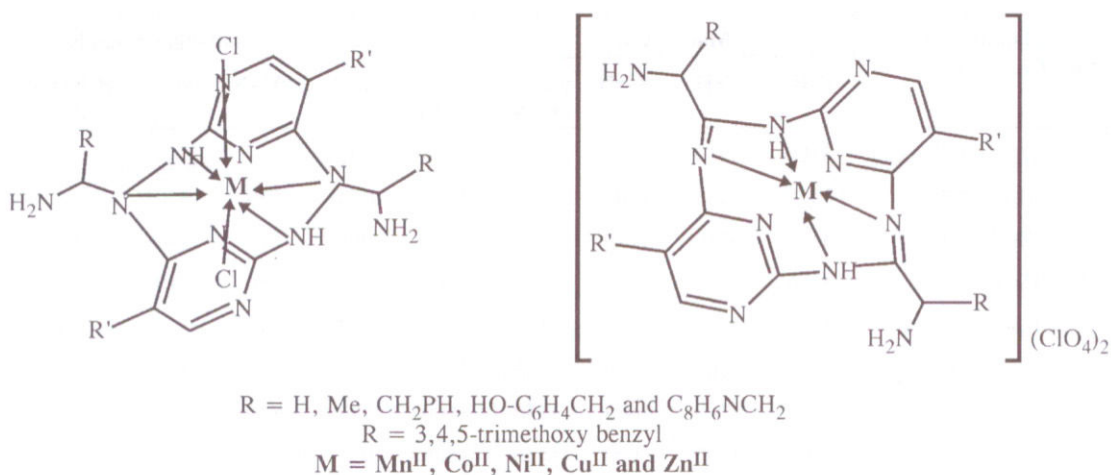


Fig. 2. Structure of the metal (II) chloride and perchlorate complexes

### ACKNOWLEDGEMENT

The authors Dr. M. Amaladasan and Dr. V. Alex Ramani thank the authorities of St. Joseph's College (Autonomous), Tiruchirappalli 620 002, for the facilities and support. They also gratefully acknowledge the UGC for financial support for this project.

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Accepted : 22.1.2005