

# *Chapter-4*

**Template synthesis of polyazamacrocyclic complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) derived from pyridine-2,6-dicarboxylic acid and their characterization.**

## 4.1 TEMPLATE SYNTHESIS OF 20-MEMBERED DECAAZAMACROCYCLIC COMPLEXES OF Mn(II), Co(II), Ni(II), Cu(II) AND Zn(II) AND THEIR CHARACTERIZATION

### 4.1.1 INTRODUCTION

The chemistry of macrocyclic compounds is a rapidly developing area in view of their various applications<sup>1-3</sup>, for example their use as models for protein metal binding sites in biological systems<sup>2,4</sup>, in medicine and catalysis etc. Thus, there has been a continued interest to design and develop new macrocyclic ligands having various industrial applications.<sup>5-8</sup>

Metal-ion coordination by pyridine-containing polyaza macrocycles has been investigated extensively in the last few years.<sup>9</sup> The presence of the pyridine groups in the multidentate macrocyclic framework offers the opportunity to obtain highly stable metal complexes due to the fact that there has been an interest in the geometrical and chemical consequences of the interplay of metal and ligand bonding requirements<sup>10-12</sup> for their importance in nature. Polyazamacrocycles exhibit interesting coordination properties and are capable of forming both mononuclear and binuclear complexes.<sup>13</sup>

Polyamide macrocycles are of particular interest in view of their two possible potential donor atoms, nitrogen and oxygen. Their complexes are also of special interest because they can function as catalysts in many organic oxidation reactions.<sup>5,8</sup> Macrocyclic polyamides of different ring sizes have been prepared by convenient methods.<sup>14-17</sup> The metal template synthesis is

found to direct the steric course of the condensation reaction resulting in ring closure.<sup>18,19</sup> Here, we wish to report the synthesis and characterization of tetraoxodecaaza macrocyclic complexes obtained from pyridine-2,6-dicarboxylic acid, hydrazine hydrate and formaldehyde in the mole ratio 2:4:2 in the presence of metal ions.

#### 4.1.2 MATERIALS AND METHODS

The chemicals, pyridine-2,6-dicarboxylic acid (**Fluka**), hydrazine hydrate (**BDH**) and formaldehyde (37% aq. solution) (**E. Merck**), were used as received. The metal salts,  $MnX_2 \cdot 4H_2O$ ,  $CoX_2 \cdot 6H_2O$ ,  $NiX_2 \cdot 6H_2O$ ,  $CuX_2 \cdot 2H_2O$  ( $X = Cl$  or  $NO_3$ )  $ZnCl_2$  and  $Zn(NO_3)_2 \cdot 6H_2O$  (**all BDH**) were commercially available pure samples.

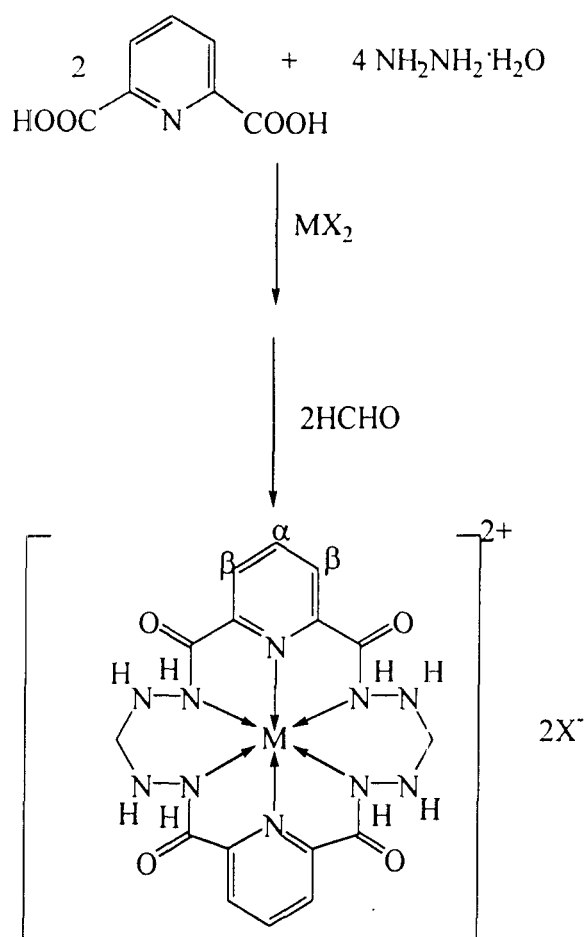
**Synthesis of Dichloride/nitrate (2:20,10:12-dipyridyl-3,9,13,19-tetraoxo-1,4,5,7,8,11,14,15,17,18-decaazacycloeicosane)metal(II),  $[ML]X_2$  [ $M = Mn(II)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$  and  $Zn(II)$ ;  $X = Cl$  or  $NO_3$ ].**

A mixture of pyridine-2,6-dicarboxylic acid (**20 mmol, 3.34 g**) and hydrazine hydrate (**40 mmol, 1.96 mL**) in methanol (**20 mL**) was placed in a 250 mL round bottomed flask and refluxed for 3-4 h. A methanolic solution (**20 mL**) of the metal salt (**10 mmol**) was added dropwise followed by the addition of 37% aqueous formaldehyde (**20 mmol, 1.50 mL**). The resultant reaction mixture was refluxed at 80 °C for further 7-8 h. After cooling to room temperature the solid product obtained, was filtered and washed several times with methanol and dried in vacuo.

### 4.1.3 RESULTS AND DISCUSSION

A new series of tetraamide decaazamacrocyclic complexes,  $[ML]X_2$  [ $M = Mn(II), Co(II), Ni(II), Cu(II), \text{ and } Zn(II), X = Cl \text{ or } NO_3$ ], have been synthesized by the template reaction of pyridine-2,6-dicarboxylic acid, hydrazine hydrate and formaldehyde in 2:4:2 molar ratio (**Scheme 12**). The analytical results (**Table 5**) suggest that the proposed macrocyclic complexes have 1:1 metal to ligand stoichiometry. All the efforts to grow single crystal suitable for X-ray crystallography failed exhausting all procedures known in this regard. The observed molar conductance values are indicative of the 1:2 electrolytic<sup>20</sup> nature of these complexes (**Table 5**).

The IR spectra of all the complexes (**Table 6**) show bands mainly in the regions 1670-1720, 1450-1520, 1240-1285 and 640-675  $cm^{-1}$  which may be assigned to amide I [ $\nu(C=O)$ ], amide II [ $\nu(C-N) + \delta(N-H)$ ], amide III [ $\delta(N-H)$ ] and amide IV, wagging [ $\rho(C=O)$ ] vibrations, respectively.<sup>14,21</sup> The amide I band appeared in the region expected for a free amide<sup>22,23,24</sup> suggesting that the amide oxygen is not involved in coordination. All complexes exhibit a single sharp band at ca. 3220-3260  $cm^{-1}$ , ascribed<sup>21</sup> to the coordinated secondary amino group whose position was found to be shifted to lower energy, suggesting<sup>21</sup> that the nitrogen of the amide group is involved in coordination to the metal ions. Further confirmation regarding formation of polyamide macrocycle complexes has been deduced from the appearance of a medium-



Scheme 12

Table 5. Formula weight (calcd.), colour, melting point (°C), yield%, elemental analyses and molar conductance value of the compounds.

Compounds	F.W. (Calcd.)	Colour	M.p. (°C)	Yield %	Analyses Found (Calcd.) %						Molar Conductance (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
					M	Cl	C	H	N		
[MnL]Cl <sub>2</sub>	540.22	Yellow	290	64	10.4 (10.1)	13.4 (13.1)	35.2 (35.5)	3.5 (3.3)	25.4 (25.9)	169	
[MnL](NO <sub>3</sub> ) <sub>2</sub>	593.33	Yellow	300	68	9.6 (9.2)	-	32.1 (32.3)	3.4 (3.0)	28.1 (28.3)	176	
[CoL]Cl <sub>2</sub>	544.22	Orange	250	62	10.2 (10.8)	13.5 (13.0)	35.5 (35.3)	3.2 (3.3)	25.3 (25.7)	167	
[CoL](NO <sub>3</sub> ) <sub>2</sub>	597.32	Brown	280	76	9.4 (9.8)	-	32.4 (32.1)	3.5 (3.0)	28.5 (28.1)	158	
[NiL]Cl <sub>2</sub>	544.00	Violet	315	71	10.2 (10.7)	13.2 (13.0)	35.5 (35.3)	3.7 (3.3)	25.2 (25.7)	175	
[NiL](NO <sub>3</sub> ) <sub>2</sub>	597.10	Violet	310	69	9.3 (9.8)	-	32.6 (32.1)	3.6 (3.0)	28.6 (28.1)	183	
[CuL]Cl <sub>2</sub>	548.83	Blue	270	69	11.1 (11.5)	12.4 (12.9)	35.4 (35.0)	3.7 (3.3)	25.2 (25.5)	158	
[CuL](NO <sub>3</sub> ) <sub>2</sub>	601.93	Blue	280	72	10.8 (10.5)	-	31.4 (31.9)	3.4 (3.0)	27.4 (27.9)	170	
[ZnL]Cl <sub>2</sub>	550.67	White	230	74	11.4 (11.8)	12.3 (12.8)	34.3 (34.8)	3.5 (3.2)	25.8 (25.4)	182	
[ZnL](NO <sub>3</sub> ) <sub>2</sub>	603.77	White	260	75	10.5 (10.8)	-	31.5 (31.8)	3.2 (3.0)	27.5 (27.8)	167	

Table 6. IR vibration frequencies ( $\text{cm}^{-1}$ ) of compounds.

Compounds	Amide Bands							Pyridine ring					
	$\nu(\text{N-H})$	$\nu(\text{C-H})$	$\nu(\text{C-N})$	I	II	III	IV	$\nu(\text{N-N})$	$\nu(\text{M-N})$	$\nu(\text{M-N})_{\text{py}}$	In-plane ring deformations (6a)	Out-of-plane ring deformations (16b)	In-plane ring deformations (8a)
[MnL]Cl <sub>2</sub>	3260 s	2890 s	1170 s	1675 s	1520 s	1240 w	650 m	950 s	380 m	250 m	640 s	430 m	1600 s
[MnL](NO <sub>3</sub> ) <sub>2</sub>	3240 s	2910 s	1200 s	1720 s	1450 s	1285 w	675 m	980 s	330 m	230 m	650 s	420 m	1610 s
[CoL]Cl <sub>2</sub>	3250 s	2940 s	1180 s	1680 s	1460 s	1265 w	660 m	960 s	340 m	245 m	645 s	435 m	1590 s
[CoL](NO <sub>3</sub> ) <sub>2</sub>	3230 s	2895 s	1175 s	1695 s	1510 s	1280 w	670 m	955 s	365 m	240 m	630 s	425 m	1595 s
[NiL]Cl <sub>2</sub>	3245 s	2935 s	1200 s	1710 s	1490 s	1260 w	675 m	985 s	370 m	260 m	655 s	440 m	1620 s
[NiL](NO <sub>3</sub> ) <sub>2</sub>	3220 s	2920 s	1160 s	1685 s	1500 s	1280 w	655 m	945 s	350 m	250 m	650 s	425 m	1590 s
[CuL]Cl <sub>2</sub>	3250 s	2905 s	1175 s	1670 s	1510 s	1250 w	670 m	950 s	380 m	235 m	660 s	430 m	1605 s
[CuL](NO <sub>3</sub> ) <sub>2</sub>	3260 s	2900 s	1195 s	1715 s	1520 s	1285 w	660 m	940 s	350 m	240 m	630 s	435 m	1630 s
[ZnL]Cl <sub>2</sub>	3235 s	2890 s	1190 s	1720 s	1450 s	1260 w	650 m	970 s	330 m	230 m	635 s	445 m	1620 s
[ZnL](NO <sub>3</sub> ) <sub>2</sub>	3225 s	2920 s	1200 s	1700 s	1480 s	1275 w	640 m	990 s	345 m	255 m	650 s	450 m	1600 s

Table 7.  $^1\text{H}$  NMR Spectroscopic data of the compounds.

Compound	N-(CH <sub>2</sub> )-N	CO-NH	-NH	Pyridine ring proton	
				H <sub>α</sub>	H <sub>β</sub>
[ZnL]Cl <sub>2</sub>	2.85 (m)	8.40 (s)	6.84 (s)	8.44 (t, J = 7.8)	7.83 (d, J = 7.7)
[ZnL](NO <sub>3</sub> ) <sub>2</sub>	2.96 (m)	8.38 (s)	6.88 (s)	8.42 (t, J = 7.8)	7.86 (d, J = 7.8)

Chemical Shift ( $\delta$ /ppm) with multiplicities in parenthesis and J values in Hertz; m = multiplets;

s = singlet; d = doublet; t = triplet;



Table 8. Magnetic moment value, electronic Spectra data, their Assignments and EPR data of the compounds.

Compounds	$\mu_{\text{eff}}$ (B.M.)	UV Bands Position ( $\text{cm}^{-1}$ )/ $\lambda_{\text{max}}$ ( $\text{cm}^{-1}$ )/ $\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	Assignments	EPR data	
				$g_{\parallel}$	$g_{\perp}$
[MnL]Cl <sub>2</sub>	5.79	22,500/444.44/12.00 18,550/539.08/14.00	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub>	-	-
[MnL](NO <sub>3</sub> ) <sub>2</sub>	5.76	22,400/446.42/13.84 18,600/537.63/15.16	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub>	-	-
[CoL]Cl <sub>2</sub>	4.80	15,750/634.92/18.00 21,800/458.71/17.73	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F) <sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)	-	-
[CoL](NO <sub>3</sub> ) <sub>2</sub>	4.82	16,200/617.28/14.08 21,700/460.82/16.00	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F) <sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)	-	-
[NiL]Cl <sub>2</sub>	3.25	17,500/571.42/15.01 11,700/854.70/18.07	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P) <sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F)	-	-
[NiL](NO <sub>3</sub> ) <sub>2</sub>	3.20	17,400/574.71/19.00 11,450/873.36/17.57	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P) <sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F)	-	-
[CuL]Cl <sub>2</sub>	1.80	19,600/510.20/43.10 17,000/588.23/42.07	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub>	2.35	2.09
[CuL](NO <sub>3</sub> ) <sub>2</sub>	1.75	18,700/534.75/44.25 16,500/606.06/42.14	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub>	2.37	2.10

intensity band at  $330\text{-}380\text{ cm}^{-1}$  assigned<sup>21,22</sup> to  $\nu(\text{M-N})$ . However, bands corresponding to  $\nu(\text{C-H})$  and  $\nu(\text{N-N})$  appeared at their expected positions.

A shift of pyridine ring vibrations<sup>25,26</sup> to higher energy as compared to that of free pyridine (**Table 6**) is suggesting that the nitrogen atom of pyridine-2,6-dicarboxylic acid is involved in coordination to the metal ion. The involvement of the pyridine nitrogen in coordination has been further confirmed by the appearance of a medium-intensity band in the region  $230\text{-}260\text{ cm}^{-1}$  corresponding<sup>26</sup> to  $\nu(\text{M-N})_{\text{py}}$ .

The  $^1\text{H}$  NMR spectra of both zinc complexes were studied showing a broad singlet at  $8.38\text{-}8.40\text{ ppm}$  which may reasonably be assigned<sup>27,28</sup> to the amide  $[\text{CO-NH (4H)}]$  protons. The spectra show two multiplets in the regions  $6.84\text{-}6.88$  and  $2.85\text{-}2.96\text{ ppm}$  which correspond to the secondary amino protons,  $(-\text{NH}, 4\text{H})$ , and methylene protons,  $(\text{N-CH}_2\text{-N}, 4\text{H})$ , of the aldehydic moiety<sup>29,30</sup>, respectively. A triplet at  $8.42\text{-}8.44\text{ ppm}$  and a doublet at  $7.83\text{-}7.86\text{ ppm}$  may reasonably be assigned<sup>31,32</sup> to the coordinated pyridine moiety of the pyridine-2,6-dicarboxylic acid molecule corresponding to  $\text{H}_\alpha$  and  $\text{H}_\beta$  of the pyridine ring (**Scheme 12**), (**Table 7**).

The EPR spectra (**Table 8**) of the copper complexes have been recorded at room temperature and exhibit an axial-type signal with two  $g$  values. All the complexes exhibit similar patterns of absorption with a single broad signal. However, no complex was found to give hyperfine splitting which may be due to the strong dipolar and exchange interactions between copper(II) ions in the unit

cell.<sup>33</sup> In the  $d_{x^2-y^2}$  ground state, the  $g_{\parallel} > g_{\perp} > 2.02$  in most cases while a  $dz^2$  ground state usually<sup>34</sup> gives a spectrum with  $g_{\perp} > g_{\parallel} > 2.02$ . From the spectra the  $g_{\parallel}$  and  $g_{\perp}$  values have been calculated (**Table 8**) and were found to be in the range 2.35-2.37 and 2.09-2.10, respectively, which indicates essentially a  $d_{x^2-y^2}$  ground state for the copper(II) ion. The axial spectrum with  $g_{\parallel} > g_{\perp} > 2.04$  is consistent<sup>35</sup> with a distorted octahedral structure around the Cu(II) ion. It has been reported<sup>36</sup> that the  $g_{\parallel}$  value in a copper(II) complex can be used as a measure of the covalent character of the metal-ligand bond. If  $g_{\parallel}$  exceeds 2.3 the environment is essentially ionic while for  $g_{\parallel}$  less than 2.3 indicates a covalent environment. The  $g_{\parallel}$  values calculated for these complexes exhibit considerable ionic character. In an axial symmetry the  $g$  values are related<sup>37</sup> by the expression  $G = (g_{\parallel}-2)/(g_{\perp}-2)$  which measures the exchange of interaction between copper centres in the polycrystalline solid. If  $G > 4$  the exchange interaction is negligible and if  $G < 4$ , it indicates considerable exchange interaction in the solid complexes. The calculated  $G$  values appeared in the range 3.7-3.8, suggesting that there is a considerable exchange interaction between copper(II) centres ( $G < 4$ ).<sup>38</sup>

The spectral and magnetic moment data (**Table 8**) recorded at room temperature of all the complexes are consistent with the proposed structures. The Mn(II) complexes have magnetic moments of 5.76 and 5.79 BM., which are typical for high-spin octahedral complexes.<sup>39</sup> The electronic spectra of both Mn(II) complexes showed two bands appearing in the 18,550-18,600 and 22,400-22,500  $\text{cm}^{-1}$  regions which may reasonably correspond to the  ${}^6A_{1g} \rightarrow {}^4T_{1g}$

and  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  transitions, respectively, consistent with the presence of an octahedral coordination geometry<sup>40</sup> around the Mn(II) ion. The observed magnetic moments of the Co(II) complexes correspond to typical high-spin octahedral complexes.<sup>39</sup> However, the values are slightly higher than the expected spin-only values due to spin-orbit coupling contribution. The cobalt(II) complexes exhibit two bands in the 15,750-16,200 and 21,700-21,800  $\text{cm}^{-1}$  regions, assignable to  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  transitions, respectively, consistent with the presence of an octahedral coordination geometry<sup>40</sup> around the cobalt(II) ion. The observed magnetic moments<sup>39</sup> and the bands observed in the electronic spectra<sup>40</sup> of the Ni(II) complexes (**Table 8**) compliment each other and justify the octahedral geometry around the Ni(II) ion.

However, the magnetic moments of the copper(II) complexes are consistent with a distorted octahedral geometry around the Cu(II) ion.<sup>32,39,41</sup> The copper complexes exhibit two discernable bands centered in the 16,500-17,000 and 18,700-19,600  $\text{cm}^{-1}$  regions, assignable to  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions, respectively, corresponding to distorted octahedral geometry<sup>40</sup> around the copper(II) ion. The octahedral geometry in all these complexes may be compared with the complexes formed by similar type of ligand systems.<sup>23,42</sup> The distortion in the octahedral geometry would be possibly due to rigidity imposed by pyridine rings leading to a meridional configuration due to the twist around the metal. All the macrocyclic complexes exhibit a high-intensity band around 33,400  $\text{cm}^{-1}$  which is characteristic of L $\rightarrow$ M charge transfer excitation.

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