

# *Chapter-8*

**Metal ion promoted synthesis of pentaazamacrocyclic complexes derived from 2,6-diaminopyridine.**

## 8.1 METAL ION PROMOTED SYNTHESIS OF PENTAAZAMACROCYCLIC COMPLEXES OF FEW FIRST ROW TRANSITION METAL SERIES DERIVED FROM 2,6-DIAMINOPYRIDINE

### 8.1.1 INTRODUCTION

The coordination chemistry of macrocyclic ligands is a fascinating research area. The synthetic, kinetic and structural aspects<sup>1,2</sup> of polyazamacrocyclic complexes have received considerable attention and a variety of polyazamacrocyclic systems have been synthesized by various workers.<sup>3-7</sup> The polyazamacrocyclic complexes, particularly those of tetraazamacrocyclic along with the pentaaza and higher polyazamacrocyclics have been widely studied in view of their potential for binding more than one metal ion.<sup>8,9</sup> The relationship of electronic properties and reactivities of these synthetic macrocyclic complexes to those of naturally occurring macrocycles, such as porphyrins<sup>10</sup> and corrins continues to promote great interest in their design and preparation. Studies of macrocyclic complexes have shown that some are involved in important biological processes<sup>11,12</sup>, such as photosynthesis and dioxygen transport<sup>13,14</sup> in addition to their catalytic properties<sup>14,15</sup>, which may lead to important industrial applications. Their enhanced kinetic and thermodynamic stabilities led to a widespread study of the features which also influence their potential applications as metal extractants<sup>16,17</sup>, radiotherapeutic<sup>18</sup>, medical imaging agents<sup>19</sup>, MRI contrast agents<sup>20,21</sup> and can also be used as effective

sequestering agents for toxic metals.<sup>22</sup> Cyclic tetraamines have received considerable attention owing to their coordination properties towards various metal cations.<sup>23</sup> The metal template synthesis is found to be an effective method to synthesize macrocyclic complexes. It direct the steric course of the condensation reaction resulting in ring closure.<sup>8,24</sup> Here in we report the synthesis and characterization of pentaazamacrocyclic complexes  $[MLX_2]$   $[M = Mn(II), Co(II), Ni(II), Zn(II)]$  and  $[CuL]X_2$  ( $X = Cl$  or  $NO_3$ ) obtained from the template condensation reaction of 2,6-diaminopyridine with 1,2-diaminoethane and 1,3-dibromopropane.

### 8.1.2 MATERIALS AND METHODS

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. The chemicals 2,6-diaminopyridine (**Aldrich**) and 1,2-diaminoethane, 1,3-dibromopropane (**E.Merck**) were used as received.

**Synthesis of dichloro/nitrato (2:15-pyridyl-1,3,7,10,14-pentaazacyclopentadecane) metal (II),  $[MLX_2]$  ( $M = Mn(II), Co(II), Ni(II), Zn(II)$ ;  $X = Cl$  or  $NO_3$ ) and (2:15 - pyridyl-1, 3, 7, 10, 14-pentaazacyclopentadecane) copper(II), dichloride/nitrate  $[CuL]X_2$ ; ( $X = Cl$  or  $NO_3$ ).**

A mixture of 2,6-diaminopyridine (**10 mmol, 0.109g**) and 1,2-diaminoethane (**10 mmol, 0.067 mL**) in methanol (**20 mL**) was stirred for about 24 hours. Finally a methanolic solution (**20 mL**) of metal salt (**10 mmol**) and 1,3-dibromopropane (**20 mmol, 0.207 mL**) were added simultaneously. The

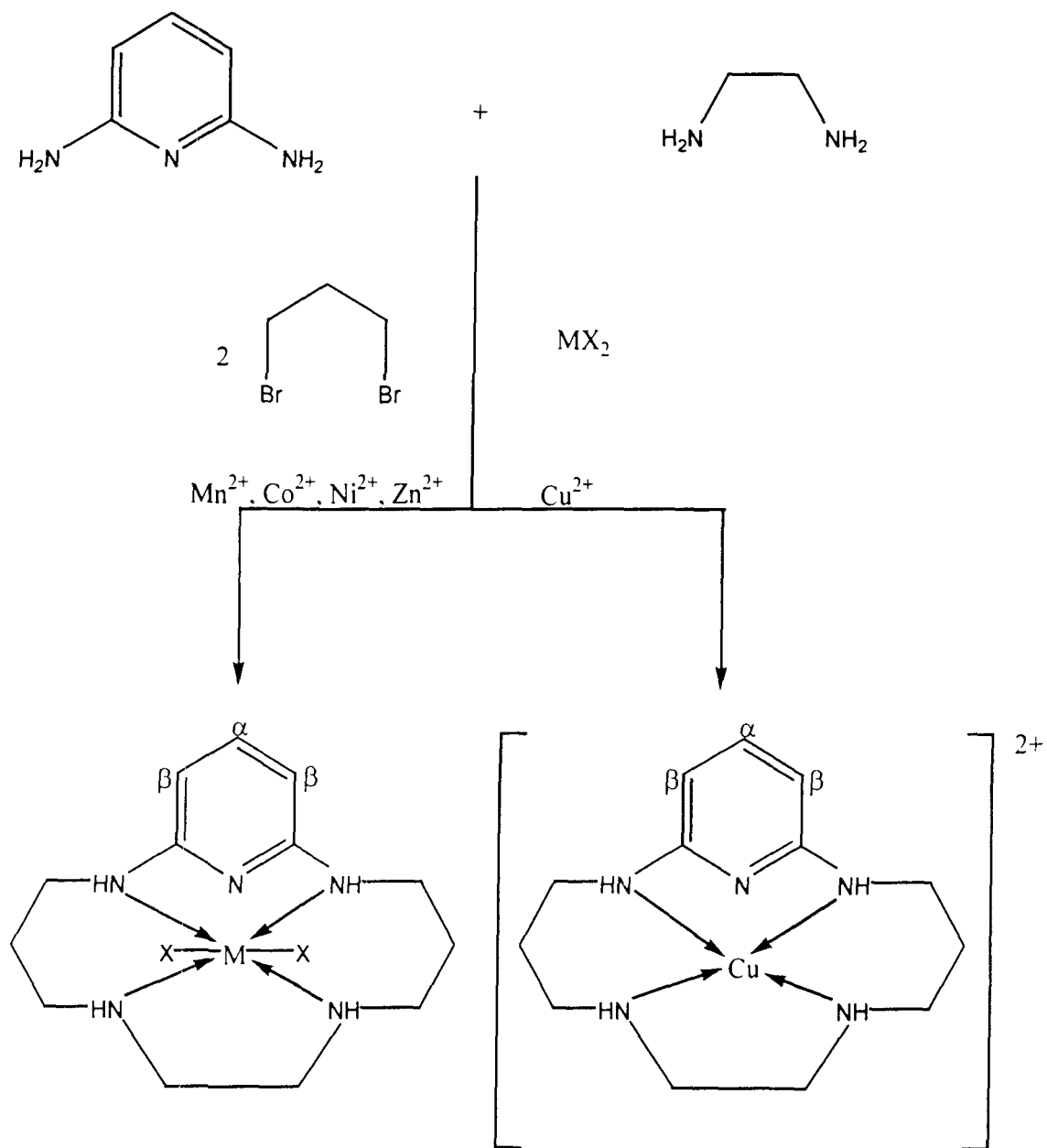
resultant mixture was refluxed for about 8 hours, giving a solid product, which was washed several times with methanol and dried in vacuo.

### 8.1.3 RESULTS AND DISCUSSIONS

The template reaction of metal salts with 2,6-diaminopyridine, 1,2-diaminoethane and 1,3-dibromopropane in a 1:1:1:2 molar ratio resulted in the formation of a new class of pentaazamacrocyclic complexes with stoichiometries  $[MLX_2]$  [ M = Mn(II), Co(II), Ni(II), Zn(II) ]; and  $[CuL]X_2$  ( X= Cl or NO<sub>3</sub>).

The elemental analysis results (**Table 20**) are consistent with the proposed 1:1 metal to ligand stoichiometry (**Scheme 16**) . All the complexes were non electrolytes<sup>25</sup> in DMSO, except the copper complexes which were of 1:2 electrolyte type.

The IR spectra (**Table 21**) of all the complexes showed no bands corresponding to primary amine stretching vibrations. The bands at ca. 3200cm<sup>-1</sup> assignable<sup>26</sup> to the coordinated secondary amino stretching mode indicated that the proposed condensation has occurred. All the complexes show bands in the 1160- 1200 cm<sup>-1</sup> regions, which may be reasonably assigned to  $\nu(C-N)$ . The bands observed in the 2890-2940 and 1430-1480 cm<sup>-1</sup> regions can be ascribed to  $\nu(C-H)$  and  $\delta(C-H)$  respectively. The pyridine moiety exhibits three important ring vibrations<sup>27,28</sup>, i.e 6a and 8a vibrations (in plane ring deformation) appearing at 603-610 and 1580-1600 cm<sup>-1</sup> respectively<sup>27</sup> while the 16b vibration (out of plane ring deformation) is observed at



$M = Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}$   
 $X = Cl \text{ or } NO_3$

Scheme 16

**Table 20: Formula weight (calcd.), colour, melting point (°C), yield %, elemental analyses and molar conductance values of the compounds.**

Compounds	F.W. (Calcd.)	Colour	M.P. (°C)	Yield %	Found (Calc.) %						Molar Conductance cm <sup>2</sup> ohm <sup>-1</sup> mol <sup>-1</sup>
					M	Cl	C	H	N		
[Mn L Cl <sub>2</sub> ]	375.20	Pale grey	250	45	14.2 (14.6)	18.4 (18.8)	41.3 (41.6)	6.5 (6.1)	18.2 (18.6)	24	
[Mn L(NO <sub>3</sub> ) <sub>2</sub> ]	428.30	Pale grey	265	48	12.3 (12.8)	-	36.8 (36.4)	5.2 (5.4)	22.4 (22.8)	19	
[Co L Cl <sub>2</sub> ]	379.19	Bright green	235	42	15.7 (15.5)	18.1 (18.6)	41.6 (41.1)	6.3 (6.1)	18.2 (18.4)	22	
[Co L(NO <sub>3</sub> ) <sub>2</sub> ]	432.30	Bright green	272	50	13.8 (13.6)	-	36.5 (36.1)	5.7 (5.3)	22.9 (22.6)	16	
[Ni L Cl <sub>2</sub> ]	378.97	Light green	198	40	15.2 (15.4)	18.4 (18.7)	41.5 (41.2)	6.4 (6.1)	18.6 (18.4)	25	
[Ni L (NO <sub>3</sub> ) <sub>2</sub> ]	432.07	Light green	187	46	13.1 (13.5)	-	36.6 (36.1)	5.8 (5.3)	22.9 (22.6)	18	
[Cu L]Cl <sub>2</sub>	383.81	Dark green	310	39	16.0 (16.5)	18.6 (18.4)	40.2 (40.6)	6.5 (6.0)	18.6 (18.2)	102	
[Cu L](NO <sub>3</sub> ) <sub>2</sub>	436.91	Dark green	320	43	14.0 (14.5)	-	35.3 (35.7)	5.0 (5.3)	22.8 (22.4)	106	
[Zn L Cl <sub>2</sub> ]	385.64	Olive green	254	49	16.5 (16.9)	18.7 (18.3)	40.0 (40.4)	6.4 (6.0)	18.4 (18.1)	20	
[Zn L(NO <sub>3</sub> ) <sub>2</sub> ]	438.74	Olive green	220	51	14.4 (14.9)	-	35.0 (35.5)	5.6 (5.2)	22.7 (22.3)	23	

**Table 21: IR vibration frequencies ( $\text{cm}^{-1}$ ) of Compounds**

Compounds	$\nu(\text{N-H})$	$\nu(\text{C-H})$	$\nu(\text{C-N})$	$\delta(\text{N-H})$	$\delta(\text{C-H})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-Cl})$	Pyridine ring		
									In-plane ring deformations	Out-of-plane ring deformations	In plane ring deformations
[Mn LCl <sub>2</sub> ]	3190 s	2890 s	1186 s	1630 w	1480 s	425 m	-	300 s	604 s	408 m	1580 s
[Mn L(NO <sub>3</sub> ) <sub>2</sub> ]	3180 s	2935 s	1175 s	1615 w	1452 s	442 m	245 s	-	607 s	405 m	1590 s
[Co LCl <sub>2</sub> ]	3200 s	2900 s	1160 s	1605 w	1430 s	420 m	-	350 s	605 s	410 m	1585 s
[Co L(NO <sub>3</sub> ) <sub>2</sub> ]	3210 s	2940 s	1200 s	1620 w	1435 s	450 m	255 s	-	609 s	412 m	1593 s
[Ni LCl <sub>2</sub> ]	3194 s	2915 s	1180 s	1630 w	1470 s	435 m	-	360 s	610 s	407 m	1595 s
[Ni L(NO <sub>3</sub> ) <sub>2</sub> ]	3205 s	2895 s	1165 s	1625 w	1465 s	445 m	235 s	-	606 s	405 m	1600 s
[Cu L]Cl <sub>2</sub>	3200 s	2900 s	1185 s	1610 w	1450 s	420 m	-	-	603 s	409 m	1590 s
[Cu L](NO <sub>3</sub> ) <sub>2</sub>	3220 s	2920 s	1170 s	1630 w	1480 s	430 m	-	-	608 s	408 m	1594 s
[Zn LCl <sub>2</sub> ]	3180 s	2905 s	1200 s	1620 w	1440 s	440 m	-	355 s	605 s	404 m	1600 s
[Zn L(NO <sub>3</sub> ) <sub>2</sub> ]	3205 s	2898 s	1190 s	1604 w	1458 s	425 m	240 s	-	610 s	407 m	1580 s

Table 22: <sup>1</sup>H NMR Spectroscopic data of the Compounds

Compound	C-NH-C	N-CH <sub>2</sub> -CH <sub>2</sub> -N	C-CH <sub>2</sub> -C	Pyridine ring proton	
				H $\alpha$	H $\beta$
[ZnLCl <sub>2</sub> ]	6.98 (m)	2.52 (m)	1.50 (m)	8.44 (t)	7.55 (d)
[ZnL(NO <sub>3</sub> ) <sub>2</sub> ]	6.94 (m)	2.50 (m)	1.52 (m)	8.39 (t)	7.62 (d)

Chemical Shift ( $\delta$ /ppm) with multiplicities in parenthesis

m = multiplets; d = doublet; t = triplet;



Table 23: Magnetic moment value, electronic Spectra data, their Assignments and EPR data of the compounds.

Compounds	$\mu_{\text{eff}}(\text{B.M.})$	Band position ( $\text{cm}^{-1}$ )	Assignments	EPR data		
				$g_{\parallel}$	$g_{\perp}$	G
[Mn LCl <sub>2</sub> ]	5.78	18, 400 22, 600	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub>	—	—	—
[Mn L(NO <sub>3</sub> ) <sub>2</sub> ]	5.76	18, 750 22, 440	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub>	—	—	—
[Co LCl <sub>2</sub> ]	4.55	14, 600 21, 800	<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)	—	—	—
[Co L(NO <sub>3</sub> ) <sub>2</sub> ]	4.57	14, 800 21, 700	<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)	—	—	—
[Ni LCl <sub>2</sub> ]	3.20	11, 250 17, 640	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F) <sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)	—	—	—
[Ni L(NO <sub>3</sub> ) <sub>2</sub> ]	3.12	11, 400 17, 550	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F) <sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)	—	—	—
[Cu L]Cl <sub>2</sub>	1.80	11, 400 15, 900 21, 500	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>	2.15	2.05	3.00
[Cu L](NO <sub>3</sub> ) <sub>2</sub>	1.95	11, 800 16, 440 20, 800	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>	2.23	2.08	2.87

404-412  $\text{cm}^{-1}$  regions. However, a medium intensity band at 420-450  $\text{cm}^{-1}$  in all the complexes is due to the  $\nu(\text{M}-\text{N})$  vibrations.<sup>29</sup> The spectra of nitrate complexes gave additional bands around 1230, 1020, and 890  $\text{cm}^{-1}$ , which are consistent with the monodentate nature of this group. Bands appearing in the nitro and chloro complexes in the regions 235-255 and 300-360  $\text{cm}^{-1}$  are assignable to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{Cl})$  respectively.<sup>30, 31</sup>

The  $^1\text{H-NMR}$  data (**Table 22**) for all mononuclear zinc (II) complexes show a multiplet in the 6.94-6.98 ppm region which can be assigned<sup>32</sup> to the secondary amino ( $\text{C}-\text{NH}-\text{C}$ ; 4H) protons of the 1,2-diaminoethane and 1,3-dibromopropane moiety. Two multiplets observed in the 2.50-2.52 ppm region may be assigned to the methylene protons of  $[\text{N}-(\text{CH}_2)_2-\text{N}$ ; 4H] of primary amine moiety. The middle methylene protons ( $\text{C}-\text{CH}_2-\text{C}$ ; 4H) of propane chain of the complexes show a multiplet at 1.50-1.52 ppm. A triplet at 8.39-8.44 ppm and a doublet at 7.55-7.62 ppm may reasonably be assigned<sup>33,34</sup> to pyridine moiety of 2,6-diaminopyridine corresponding to  $\text{H}_\alpha$  and  $\text{H}_\beta$  of pyridine ring.

The EPR spectra of the polycrystalline copper(II) complexes were recorded at room temperature. They showed only a single broad signal while the hyperfine splitting signals were absent in all cases. The absence of hyperfine signals may be due to the strong dipolar and exchange interaction between copper (II) ions in the unit cell<sup>35</sup>. The  $g_{\parallel}$  and  $g_{\perp}$  have been calculated and observed in the 2.15- 2.23 and 2.05-2.08 regions, respectively, which

support<sup>36</sup> that the  $d_{x^2-y^2}$  may be the ground state ( $g_{\parallel} > g_{\perp} > 2.02$ ). The  $g$  values are related<sup>37</sup> by the expression,  $G = (g_{\parallel}-2)/(g_{\perp}-2)$  which measure the exchange interaction between copper centres in the polycrystalline solid, if  $G > 4$ , the exchange interaction is negligible and if  $G < 4$ , considerable exchange interaction is present in the solid complexes.<sup>38</sup> In the present case  $G$  appeared in the 2.87-3.00 range suggesting exchange interaction in these complexes. All the copper complexes show considerable covalent character<sup>39</sup> as the  $g_{\parallel}$  values are less than 2.3.

The spectra and magnetic moment data<sup>40,41</sup> of all the complexes (Table 23) are consistent with the proposed structures. The electronic spectra (Table 23) of the manganese complexes exhibit two bands in the 18,400-18,750 and 22,440-22,600  $\text{cm}^{-1}$  regions, assignable<sup>41</sup> to  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  and  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  transitions, respectively, corresponding to an octahedral geometry for the manganese ion. The cobalt complexes exhibit two bands in the 14,600-14,800 and 21,700-21,800  $\text{cm}^{-1}$  regions, characteristic<sup>41</sup> of the  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  transitions, respectively corresponding to an octahedral geometry for the cobalt ion. The nickel complexes showed two bands in the 11,250-11,400 and 17,550-17,640  $\text{cm}^{-1}$  regions, which may be assigned<sup>41</sup> to  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  transitions, respectively, arising from the octahedral geometry of  $\text{Ni}^{2+}$ . The electronic spectra of the copper complexes showed broad band centred at ca. 16000  $\text{cm}^{-1}$  assignable to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  transitions. However, two weak shoulders appearing

in the regions 20,800-21,500 and 11,400-11,800  $\text{cm}^{-1}$  may be ascribed to  ${}^2B_{1g} \rightarrow {}^2E_g$  and  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  transitions respectively, suggesting a square planar geometry around the copper (II) ions.

The magnetic susceptibilities<sup>40</sup> and electronic spectral data<sup>40,41</sup> (**Table 23**) obtained for all the complexes are consistent with an octrahedral geometry for Mn(II), Co(II), Ni(II) and Zn(II) complexes and square planar geometry for Cu(II) complexes.

## REFERENCES

1. V. Alexander, *Chem. Rev.*, **1995**, *95*, 273.
2. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb and J. J. Christensen, *Chem. Rev.*, **1985**, *85*, 271.
3. S. C. Menon, A. Panda, H. B. Singh and R. J. Butcher, *J. Chem. Commu.*, **2000**, 143.
4. T. Clifford, A. M. Danby, P. Lightfoot, D. T. Richens and R. W. Hay, *J. Chem. Soc., Dalton, trans.*, **2001**, 240.
5. B. Song, T. Storr, S. Liu and C. Orvig, *J. Inorg. Chem.*, **2002**, 685.
6. A. K. Mishra and J. F. Chatal, *New. J. Chem.*, **2001**, *25*, 336.
7. M. B. Inoue, C. A. Villegas, K. Asano, M. Nakamura, M. Inoue and Q. Fernando, *Inorg. Chem.*, **1992**, *31*, 2480.
8. M. P. Suh, W. Shin, K. Kim and J. Kim, *Inorg. Chem.*, **1984**, *23*, 618.
9. M. P. Suh and S. G. Kang, *Inorg. Chem.*, **1988**, *27*, 2544.
10. T. Chandra, B. J. Kraft, J. C. Huffman and J. M. Zalesk, *Inorg. Chem.*, **2003**, *42*, 5158.
11. J. J. R. Fraustoda Silva and R. J. P. Williams, "The Biological Chemistry of The Elements," Clarendon Press, Oxford; **1991**.
12. J. Liu, H. Zhang, C. Chen, H. Deng, T. Lu and L. Ji, *Dalton Trans.*, **2003**, 114.
13. D. Utz, F. W. Heinemann, F. Hampel, D. T. Richens and S. Schindler, *Inorg. Chem.*, **2003**, *42*, 1430.
14. J. Reedijk, Ed, "Bioinorganic Catalysis," 2<sup>nd</sup> Ed; Marcel Dekker. New York. **1999**.
15. N. R. Champness, C. S. Frampton, G. Reid and D. A. Tocher, *J. Chem. Soc., Dalton, Trans.*, **1994**, 3031.
16. K. R. Adam, M. Antotovich, D. S. Baldwin, P. A. Duckworth, A. J. Leong, L. F. Lindoy, M. McParlin and P. A. Tasker, *J. Chem. Soc., Dalton. Trans.*, **1993**, 1013.
17. Y. Dong, S. Farquhar, K. Gloe, L. F. Lindoy, B. R. Rumbel, P. Turner and K. Wichmann. *Dalton Trans.*, **2003**, 1558.
18. P. V. Bernhardt and P. C. Sharpe, *Inorg. Chem.*, **2000**, *39*, 4123.
19. J. W. Sibert, A. H. Cory and J. G. Cory, *Chem. Commun.*, **2002**, 154.
20. R. Hovland, C. Glogard, A. J. Aasen and J. Klaveness, *J. Chem. Soc., Perkin. Trans.*, **2001**, *2*, 929.

21. S. J. A. Pope, A. M. Kenwright, V. A. Boote and S. Faulkner. *J. Chem. Soc., Dalton Trans.*, **2003**, 3780.
22. M. N. Hughes, "The Inorganic Chemistry of the Biological Processes Wiley," New York, **1981**.
23. M. Meyer, G. V. Dahaoui, C. Lecomte and R. Guilard, *Coord. Chem. Rev.* **1998**, 178.
24. D. G. McCallum, L. Hall, C. White, R. Ostrander, A. L. Rheingold, J. Whelan and B. Bosnich. *Inorg. Chem.*; **1994**, 33, 924.
25. W. J. Geary, *Coord. Chem. Rev.*; **1971**, 7, 81.
26. M. P. Suh and S. K. Kim, *Inorg. Chem.*; **1993**, 32, 3562.
27. N. S. Gill, R. H. Nuttal, D. E. Scarfe and D.W. A. Sharp, *J. Inorg. Nucl. Chem.*, **1961**, 18, 87.
28. R. J. H. Clark and C. S. Williams. *Inorg. Chem.*, **1965**, 4, 350.
29. M. Shakir and S. P. Varkey. *Transition. Met. Chem.*, **1994**, 19, 606.
30. V. B. Rana, P. Singh, D. P. Singh and M. P. Teotia, *Polyhedron.*, **1982**, 1, 377.
31. M. Shakir, S. P. Varkey and O. S. M. Nasman, *Polyhedron.*, **1995**, 14, 1283.
32. K. Burgess, D. Lim, K. Kantoo and C. Y. Ke, *J. Org. Chem.*, **1994**, 59, 2179.
33. F. A. Bovey, "NMR Data Tables for Organic Compounds Vol 1, Wiley interscience, New York, **1967**.
34. L. Branco, J. Costa, R. Delgado, M. G. B. Drew, V. Felix and B. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, **2002**, 3539.
35. I. S. Ahuja and S. Tripathi, *Indian J. Chem.*, **1991**, 30A, 1060.
36. M. C. Jain, A. K. Srivastava and P. C. Jain, *Inorg. Chim. Acta.*, **1977**, 23, 199.
37. I. M. Proctor, B. J. Hathaway and P. Nicholls. *J. Chem. Soc.*, **1968**, A, 1678.
38. A. K. D. Mazumder, S. C. Das, P. K. Karmakar N. K. Saha and K. D. Banerg, *J. Ind. Chem. Soc.*, **1992**, 69, 761.
39. D. Kivelson and R. R. Neiman. *J. Chem. Phys.*, **1961**, 35, 149.
40. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 5<sup>th</sup> Edn; Wiley, New York, **1988**.
41. A. B. P. Lever, "Inorganic Electronic Spectroscopy," 2<sup>nd</sup> Edn; Elsevier Amsterdam **1984**, 318.