

Chapter-5

Metal template synthesis of diamidediimine macrocycles and their spectrochemical studies.

5.1 TEMPLATE SYNTHESIS OF Mn(II), Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF DIAMIDEDIIMINE MACROCYCLES

5.1.1 INTRODUCTION

The chemistry of macrocyclic dioxotetraamines has received much attention and has been extensively studied in recent years.¹⁻⁶ Such ligands show unique ligating behaviour towards divalent 3d cations with simultaneous dissociation of two amino groups.^{7,8}

They bear dual structural features of macrocyclic tetraamines and oligopeptides and have many interesting properties and important functions. They can stabilize the higher oxidation states of some transition metals.^{9,10} These properties have been applied to superoxide dismutase like catalysts. Furthermore, some of these compounds have been used as metal-ion carriers.^{11,12} Transition metal(II) complexes of macrocyclic dioxotetraamines have interesting properties and can be considered as models for metalloproteins and oxygen carriers.^{13,14} Great effort has been devoted to the incorporation of functionalized pendant groups into a saturated macrocyclic tetraamine structure (e.g. cyclam) to modify its conformational and the redox properties of the metal complex.¹⁵ Polyamide macrocycles are of particular interest in view of their two possible donor atoms i.e amide nitrogen and amide oxygen. However, in most of the polyamide

macrocyclic complexes amide nitrogen is engaged in coordination and not the oxygen.¹⁶⁻¹⁸ Here, we report the synthesis and characterization of dioxotetraamine macrocyclic complexes $[MLX_2]$ ($M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{and Zn(II)}$) and $[\text{CuL}]X_2$ ($X = \text{Cl or NO}_3$) obtained by the template condensation reaction of *o*-aminobenzoic acid with *o*-phenylenediamine and 2,4-pentanedione.

5.1.2 MATERIALS AND METHODS

o-Aminobenzoic acid, *o*-phenylenediamine and 2,4-pentanedione (all **E. Merck**) were used as received. Metal salts, $\text{MnX}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoX}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiX}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuX}_2 \cdot 2\text{H}_2\text{O}$ ($X = \text{Cl or NO}_3$), ZnCl_2 and $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (all **BDH**) were commercially available pure samples.

Synthesis of dichloro/nitrato(1,2:5,6:9,10-tribenzo-3,8-dioxo-12,14-dimethyl-4,7,11,15-tetraazacyclopentadecane-11,14-diene)metal(II), $[MLX_2]$ ($M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}$ and Zn(II)); ($X = \text{Cl or NO}_3$) and (1,2:5,6:9,10-tribenzo-3,8-dioxo-12,14-dimethyl-4,7,11,15-tetraazacyclopentadecane-11,14-diene)copper(II) dichloride/nitrate $[\text{CuL}]X_2$; $X = \text{Cl or NO}_3$.

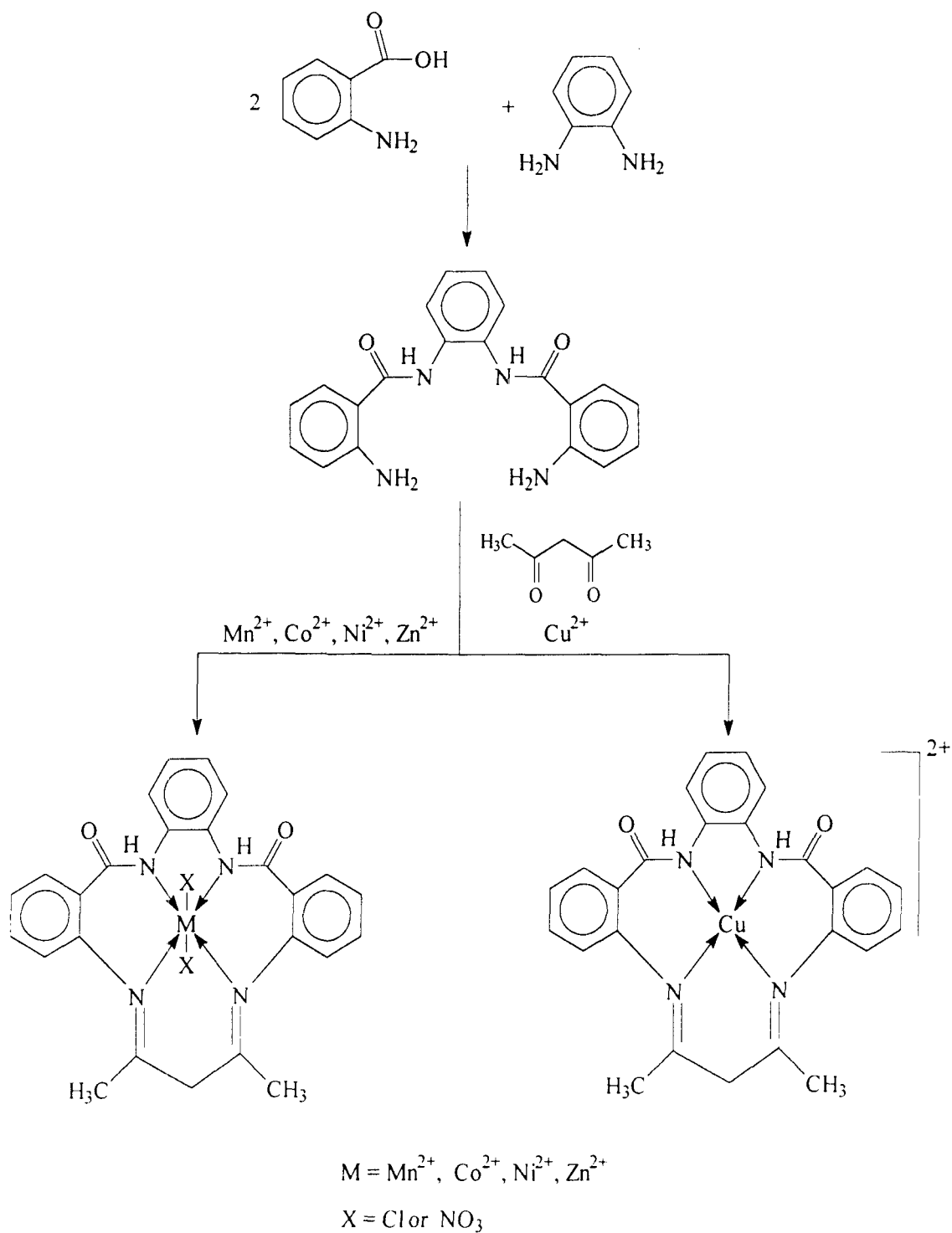
A mixture of *o*-aminobenzoic acid (20 mmol, 0.274g) and *o*-phenylenediamine (10 mmol, 0.108g) dissolved in (20 mL) methanol was refluxed for about 5h. This was followed by addition of a methanolic solution (20 mL) of the metal salts (10 mmol). A methanolic solution (20 mL) of 2,4-pentanedione (10 mmol, 0.103 mL) was then added and the resultant

mixture was refluxed for 10 h . The solid product produced was filtered washed with methanol and dried in vacuo.

5.1.3 RESULTS AND DISCUSSION

The template reaction of *o*-aminobenzoic acid, *o*-phenylenediamine and 2,4-pentanedione in a 2:1:1 molar ratio resulted in the isolation of a new class of dioxotetraamine macrocyclic complexes as shown in (Scheme 13). The elemental analyses results are consistent with the proposed 1:1 metal to ligand stoichiometry (Table 9). All the complexes show non-electrolytic nature¹⁹ in DMSO except copper complexes which show 1:2 electrolytic nature. They are obtained in a 40-58% yield, are air stable and insoluble in most of the organic solvents, except DMSO and DMF.

The IR spectra of all the complexes (Table 10) show bands mainly in the regions 1680-1735, 1480-1530, 1240-1270 and 640-670 cm^{-1} assignable²⁰ to amide I, II, III and IV vibrations, respectively. All exhibit a single sharp band at ca.3240 cm^{-1} which may be ascribed²¹ to coordinated secondary amino groups. Thus the amide nitrogen takes part in coordination to the metal ions. The absence of bands assignable to the primary amino groups also indicate the formation of the proposed macrocyclic moiety. This result has been further confirmed by the appearance of a strong medium intensity band in the 1590-1620 cm^{-1} regions, assigned²¹ to the coordinated imine $\nu(\text{C}=\text{N})$ bands . However, the amide I bands are observed in the region expected for the metal free amide group which rules out



Scheme 13

Table 9. 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 (Calc.) %				Molar Conductance (cm ² ohm ⁻¹ mol ⁻¹)	
					M	Cl	C	H		N
[MnLCl ₂]	536.31	Off white	298	55	10.5 (10.2)	13.0 (13.2)	55.4 (55.9)	4.3 (4.1)	10.7 (10.4)	16
[Mn L(NO ₃) ₂]	589.42	Off white	302	44	9.7 (9.3)	-	50.6 (50.9)	3.4 (3.7)	14.6 (14.2)	21
[Co LCl ₂]	540.31	Pink	300	40	10.4 (10.9)	13.4 (13.1)	55.0 (55.5)	4.5 (4.1)	10.0 (10.3)	19
[Co L(NO ₃) ₂]	593.41	Light pink	305	43	9.8 (9.9)	-	50.9 (50.6)	3.3 (3.7)	14.5 (14.1)	14
[Ni LCl ₂]	540.09	Sky blue	310	52	10.4 (10.8)	13.2 (13.1)	55.1 (55.5)	4.3 (4.1)	10.7 (10.3)	22
[Ni L(NO ₃) ₂]	593.19	Sky blue	300	58	9.5 (9.8)	-	50.3 (50.6)	3.6 (3.7)	14.3 (14.1)	17
[Cu L]Cl ₂	544.92	Lichen green	320	42	11.2 (11.6)	13.5 (13.0)	55.2 (55.1)	4.5 (4.0)	10.7 (10.2)	118
[Cu L](NO ₃) ₂	598.02	Lichen green	315	48	10.9 (10.6)	-	50.4 (50.2)	3.6 (3.7)	14.4 (14.0)	105
[Zn LCl ₂]	546.76	Dirty white	299	44	11.6 (11.9)	12.8 (12.9)	54.3 (54.9)	4.3 (4.0)	10.6 (10.2)	20
[Zn L(NO ₃) ₂]	599.86	Dirty white	285	49	10.9 (10.8)	-	50.2 (50.0)	3.9 (3.6)	14.2 (14.0)	13

Table 10. IR vibration frequencies (cm^{-1}) of Compounds.

Compounds	$\nu(\text{N-H})$ Amide	$\nu(\text{C=N})$	Amide Bands				$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-Cl})$	Ring Vibrations
			I	II	III	IV				
[MnLCl ₂]	3235 s	1610 s	1720 s	1510 s	1270 w	645 m	-	320 m	1440 s, 1090 s, 735 s	
[MnL(NO ₃) ₂]	3254 s	1600 s	1684 s	1530 s	1262 w	665 m	268 m	-	1450 s, 1070 s, 740 s	
[CoLCl ₂]	3250 s	1595 s	1715 s	1500 s	1258 w	650 m	-	300 m	1410 s, 1085 s, 740 s	
[CoL(NO ₃) ₂]	3220 s	1605 s	1695 s	1480 s	1250 w	670 m	250 m	-	1460 s, 1080 s, 720 s	
[Ni LCl ₂]	3260 s	1600 s	1700 s	1525 s	1240 w	650 m	-	310 m	1450 s, 1090 s, 720 s	
[Ni L(NO ₃) ₂]	3240 s	1612 s	1710 s	1505 s	1265 w	660 m	245 m	-	1420 s, 1100 s, 730 s	
[Cu L]Cl ₂	3235 s	1605 s	1680 s	1495 s	1255 w	645 m	-	-	1420, 1075 s, 740 s	
[Cu L](NO ₃) ₂	3245 s	1590 s	1700 s	1500 s	1260 w	665 m	-	-	1430, 1075 s, 735 s	
[ZnLCl ₂]	3260 s	1615 s	1735 s	1520 s	1250 w	640 m	-	315 m	1450, 1095 s, 725 s	
[ZnL(NO ₃) ₂]	3225 s	1620 s	1720 s	1505 s	1240 w	662 m	260 m	-	1460, 1090 s, 740 s	

Table 11. ¹H NMR Spectroscopic data of the Compounds.

Compound	CO-NH	CH ₃ -C=N	C-CH ₂ -C	Ring proton
[ZnLC1 ₂]	8.35 (s)	2.48 (s)	2.08 (s)	7.28 (m)
[ZnL(NO ₃) ₂]	8.32 (s)	2.55 (s)	1.99 (s)	7.32 (m)

Chemical Shift (δ/ppm) with multiplicities in parenthesis . s = singlet; m = multiplets;

Table 12. Magnetic moment value, electronic Spectra data, their Assignments and EPR data of the compounds.

Compounds	μ_{eff} (B.M.)	Band Position (cm^{-1})	Assignments	EPR data		
				g_{\parallel}	g_{\perp}	G
[MnLCl ₂]	5.75	22, 400 19, 700	⁶ A _{1g} → ⁴ T _{2g} ⁶ A _{1g} → ⁴ T _{1g}	-	-	-
[MnL(NO ₃) ₂]	5.78	22, 900 19, 400	⁶ A _{1g} → ⁴ T _{2g} ⁶ A _{1g} → ⁴ T _{1g}	-	-	-
[CoLCl ₂]	4.57	21, 500 15, 700	⁴ T _{1g} (F) → ⁴ T _{1g} (P) ⁴ T _{1g} (F) → ⁴ A _{2g} (F)	-	-	-
[CoL(NO ₃) ₂]	4.53	21, 700 16, 100	⁴ T _{1g} (F) → ⁴ T _{1g} (P) ⁴ T _{1g} (F) → ⁴ A _{2g} (F)	-	-	-
[NiLCl ₂]	3.13	17, 300 11, 250	³ A _{2g} (F) → ³ T _{1g} (P) ³ A _{2g} (F) → ³ T _{1g} (F)	-	-	-
[NiL(NO ₃) ₂]	3.15	17, 500 11, 200	³ A _{2g} (F) → ³ T _{1g} (P) ³ A _{2g} (F) → ³ T _{1g} (F)	-	-	-
[CuL]Cl ₂	1.80	21, 500 16, 300 13, 500	² B _{1g} → ² E _g ² B _{1g} → ² A _{1g} ² B _{1g} → ² B _{2g}	2.13	2.05	2.6
[CuL](NO ₃) ₂	1.79	21, 900 16, 100 12, 800	² B _{1g} → ² E _g ² B _{1g} → ² A _{1g} ² B _{1g} → ² B _{2g}	2.23	2.08	2.8

the possibility of a coordinated amide oxygen. Bands at ca. 2900 and 1460 cm^{-1} for all the complexes correspond to C–H stretching and C–H bending vibrations, respectively. However, the bands corresponding to the phenyl group appeared at their estimated positions. A medium intensity band in the spectra of all the complexes in the 365-420 cm^{-1} region is assigned²² to M–N stretching vibrations. The chloro complexes display bands at ca.300 cm^{-1} which may be attributed²² to the $\nu(\text{M–Cl})$ vibration. The spectra of nitrate complexes gave additional bands at ca. 1260, 1025 and 870 cm^{-1} consistent²² with the nitrate group. The bands in the 245-268 cm^{-1} regions, may be assigned to $\nu(\text{M–O})$ of the coordinated NO_3 group.

The ^1H NMR spectra (**Table 11**) of all the zinc (II) macrocyclic complexes recorded in d_6 -DMSO, exhibited a broad singlet at 8.32-8.35 ppm range, which may reasonably be assigned²³ to the amide protons (CO–NH; 2H). A multiplet in all the complexes in the 7.28-7.32 ppm range corresponds to the phenyl ring protons. Two singlets at 1.99-2.08 and 2.48-2.55 ppm may be assigned to the methylene (C–CH₂–C; 2H) and methyl (CH₃–C=N; 6H) protons of the 2,4-pentanedione moiety, respectively, No compound exhibits the signals corresponding to the carboxylic (–CO₂H) or amino (–NH₂) protons which provide support for the structure shown in (**Scheme13**).

The e.p.r spectra of the copper(II) complexes were recorded at room temperature. 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.²⁴ The g_{\parallel} and g_{\perp} have been calculated and observed in the 2.13-2.23 and 2.05-2.08 regions respectively²⁵, which support that the $d_{x^2-y^2}$ may be the ground state ($g_{\parallel} > g_{\perp} > 2.02$). The g values are related by the expression²⁶, $G = (g_{\parallel}-2)/(g_{\perp}-2)$ which measure the exchange interaction between copper centers in the polycrystalline solid. In the present case the axial symmetry parameter, G lies in the 2.6-2.8 range which indicate²⁷ exchange interaction in the solid complexes.

The electronic spectra (**Table 12**) show appearance of two bands in the 22,400-22,900 and 19,400-19,700 cm^{-1} regions in the Mn(II) complexes which may reasonably be assigned²⁸ to ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transitions, respectively, consistent with an octahedral geometry around the Mn(II) ion. The magnetic moment²⁹ values in the range 5.75-5.78 B.M. (**Table 12**) further correspond to high spin octahedral complexes. The electronic spectra of the Co(II) complexes show two bands in the 21,500-21,700 and 15,700-16,100 cm^{-1} regions which may be assigned²⁸ to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions, respectively consistent with an octahedral geometry around the Co(II) ion. The observed²⁹ magnetic moment in the 4.53-4.57 B.M. range is in support of high spin octahedral geometry. The electronic spectra of the Ni(II) complexes show two main bands in the 17,300-17,500 cm^{-1} and 11,200-11,250 cm^{-1} regions which may be ascribed²⁸ to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transitions, respectively, consistent with an octahedral geometry around the nickel(II) ion. The observed

magnetic moment values²⁹ (3.13-3.15 B.M.) also support octahedral geometry of the Ni(II) ion. The electronic spectra of the copper(II) complexes show a broad band in the 16,100-16,300 cm^{-1} region assignable to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions. However, two weak shoulders appearing in the regions 21,500-21,900 and 12,800-13,500 cm^{-1} may be ascribed²⁸ to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, suggesting a square planar geometry around the copper(II) ions.

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