

Chapter-3

Synthesis and physico-chemical studies of polyazamacrocyclic complexes of few first row transition metal divalent ions.

3.1 SYNTHESIS AND PHYSICO-CHEMICAL STUDIES ON 18-MEMBERED OCTAAZAMACROCYCLIC COMPLEXES OF Mn(II), Co(II), Ni(II), Cu(II) AND Zn(II) IONS

3.1.1 INTRODUCTION

The coordination chemistry of macrocyclic ligands is a fascinating research area. The synthetic, kinetic and structural aspects¹ of polyazamacrocyclic complexes have received considerable attention. A variety of polyazamacrocyclic systems have been synthesized by various workers.^{2,3} Macrocyclic complexes are best prepared with the aid of metal ions as templates to direct the steric course of the condensation reaction, ultimately resulting in ring closure.⁴

Macrocyclic complexes are of great importance in enhancing various industrial applications⁵ and in a number of biological processes such as photosynthesis and dioxygen transport⁶, catalytic properties⁷, potential applications as metal extractants, radio-therapeutic⁸ and medical imaging agents⁹.

The polyazamacrocyclic complexes, particularly the tetraazamacrocyclic complexes have been widely studied along with pentaaza and higher polyazamacrocycles, which have also appeared frequently, particularly in view of their potential for binding more than one metal ion.¹⁰ Several macrocyclic complexes incorporating the hydrazine moiety in the macrocyclic framework recently have been reported.^{4,11} This part of the thesis presents the template

synthesis and characterization of octaazamacrocyclic complexes $[ML^1X_2]$ and $[ML^2X_2]$ ($M = Mn(II), Co(II), Ni(II), Cu(II)$ and $Zn(II)$; $X = Cl$ or NO_3) derived from hydrazine hydrate, *o*-phthalaldehyde and formaldehyde or acetaldehyde.

3.1.2 MATERIALS AND METHODS

The metal salts $MnX_2 \cdot 4H_2O$, $CoX_2 \cdot 6H_2O$, $NiX_2 \cdot 6H_2O$, $CuX_2 \cdot 2H_2O$, $ZnCl_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ ($X = Cl$ or NO_3) (all **BDH**) were commercially pure samples. *o*-Phthalaldehyde, hydrazine hydrate (**BDH**), HCHO (37% aq.solution) and CH_3CHO (**E. Merck**) were used as received.

Synthesis of Dichloro/nitrato (1:2, 10:11 – Diphenyl - 4, 5, 7, 8, 13, 14, 16, 17 – octaazacyclooctadecane - 3, 8, 12, 17 - tetraene) metal(II), $[ML^1X_2]$ [$M = Mn(II), Co(II), Ni(II), Cu(II)$ and $Zn(II)$; $X = Cl$ or NO_3].

To a stirred solution of the respective metal salt (**10 mmol**) dissolved in MeOH (**20 mL**) in three-necked round-bottomed flask, solutions of hydrazine hydrate (**40 mmol, 1.96mL**) and *o*-phthalaldehyde (**20 mmol, 2.68g**) dissolved in MeOH (**20 mL**) were added simultaneously over a period of two hours. Stirring was continued for an additional hour followed by the addition of formaldehyde (37% aq.solution) (**20 mmol, 1.50mL**) solution in MeOH (**20 mL**). The resultant mixture was refluxed over night leading to the formation of a microcrystalline solid product, which was filtered, washed several times with MeOH and dried in vacuo.

[NiL ² (NO ₃) ₂]	559.18	Pale green	300	60	10.5 (10.4)	-	42.4 (42.9)	4.2 (4.3)	25.4 (25.0)	22
[CuL ¹ Cl ₂]	482.86	Light blue	325	45	13.4 (13.1)	14.5 (14.6)	44.4 (44.7)	4.5 (4.1)	23.6 (23.2)	19
[CuL ¹ (NO ₃) ₂]	535.96	Grey blue	310	30	11.3 (11.8)	-	40.4 (40.3)	3.6 (3.7)	26.2 (26.1)	17
[CuL ² Cl ₂]	510.91	Bluish green	290	34	12.5 (12.4)	13.4 (13.8)	47.5 (47.0)	4.5 (4.7)	21.6 (21.9)	15
[CuL ² (NO ₃) ₂]	564.01	Dark green	320	38	11.6 (11.2)	-	42.4 (42.5)	4.1 (4.2)	24.4 (24.8)	19
[ZnL ¹ Cl ₂]	484.69	Off-white	290	42	13.2 (13.4)	14.5 (14.6)	44.2 (44.6)	4.5 (4.1)	23.5 (23.1)	20
[ZnL ¹ (NO ₃) ₂]	537.80	Off-white	295	46	12.4 (12.1)	-	40.6 (40.2)	3.6 (3.7)	26.5 (26.0)	25
[ZnL ² Cl ₂]	512.75	Dirty white	240	45	12.5 (12.7)	13.6 (13.8)	46.4 (46.8)	4.6 (4.7)	21.4 (21.8)	22
[ZnL ² (NO ₃) ₂]	565.85	Light cream	250	40	11.2 (11.5)	-	42.2 (42.4)	4.3 (4.2)	24.6 (24.7)	17

Table 2. IR vibration frequencies (cm^{-1}) of the compounds.

Compound	$\nu(\text{C-H})$	$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-Cl})$	$\nu(\text{N-N})$	Ring vibration	
$[\text{MnL}^1\text{Cl}_2]$	2870 s	3220 s	1590 s	440 m	-	280 m	980 m	1430 s	1080 s 750 s
$[\text{MnL}^1(\text{NO}_3)_2]$	2890 s	3230 s	1590 s	450 m	240 m	-	985 m	1420 s	1070 s 720 s
$[\text{MnL}^2\text{Cl}_2]$	2900 s	3225 s	1610 s	455 m	-	290 m	950 m	1430 s	1075 s 740 s
$[\text{MnL}^2(\text{NO}_3)_2]$	2880 s	3240 s	1620 s	450 m	245 m	-	970 m	1440 s	1080 s 760 s
$[\text{CoL}^1\text{Cl}_2]$	2900 s	3230 s	1590 s	420 m	-	310 m	940 m	1410 s	1090 s 750 s
$[\text{CoL}^1(\text{NO}_3)_2]$	2900 s	3220 s	1595 s	425 m	230 m	-	950 m	1445 s	1080 s 755 s
$[\text{CoL}^2\text{Cl}_2]$	2920 s	3225 s	1590 s	430 m	-	320 m	945 m	1425 s	1090 s 760 s
$[\text{CoL}^2(\text{NO}_3)_2]$	2910 s	3230 s	1660 s	460 m	250 m	-	950 m	1430 s	1100 s 755 s
$[\text{NiL}^1\text{Cl}_2]$	2890 s	3235 s	1630 s	435 m	-	300 m	970 m	1455 s	1095 s 740 s
$[\text{NiL}^1(\text{NO}_3)_2]$	2910 s	3240 s	1570 s	450 m	240 m	-	980 m	1425 s	1090 s 730 s

[NiL ² Cl ₂]	2905 s	3200 s	1600 s	425 m	-	270 m	950 m	1420 s	1075 s	710 s
[NiL ² (NO ₃) ₂]	2890 s	3210 s	1610 s	420 m	250 m	-	970 m	1430 s	1080 s	760 s
[CuL ¹ Cl ₂]	2920 s	3290 s	1590 s	435 m	-	320 m	975 m	1445 s	1100 s	745 s
[CuL ¹ (NO ₃) ₂]	2900 s	3200 s	1630 s	445 m	255 m	-	955 m	1425 s	1080 s	750 s
[CuL ² Cl ₂]	2910 s	3280 s	1610 s	460 m	-	305 m	930 m	1450 s	1075 s	755 s
[CuL ² (NO ₃) ₂]	2890 s	3210 s	1640 s	455 m	235 m	-	960 m	1420 s	1090 s	740 s
[ZnL ¹ Cl ₂]	2910 s	3230 s	1580 s	450 m	-	290 m	980 m	1430 s	1085 s	720 s
[ZnL ¹ (NO ₃) ₂]	2910 s	3240 s	1590 s	430 m	250 m	-	960 m	1425 s	1070 s	730 s
[ZnL ² Cl ₂]	2920 s	3225 s	1595 s	420 m	-	280 m	970 m	1450 s	1090 s	710 s
[ZnL ² (NO ₃) ₂]	2870 s	3240 s	1600 s	450 m	240 m	-	950 m	1460 s	1080 s	750 s

Table 3. ¹H NMR Spectroscopic data of the compounds.

Compound	CH=N	N-CH ₂ -N	-CH ₃	C-NH-	Ring proton
[ZnL ¹ Cl ₂]	8.35 s	3.10 m	-	6.96 m	7.30 m
[ZnL ¹ (NO ₃) ₂]	8.32 s	2.98 m	-	6.70 m	7.18 m
[ZnL ² Cl ₂]	8.38 s	2.96 m	2.30 s	6.90 m	7.28 m
[ZnL ² (NO ₃) ₂]	8.33 s	3.05 m	2.32 s	6.75 m	7.25 m

*Chemical Shifts (δ/ppm) with multiplicities in parenthesis
s = singlet and m = multiplet

Table 4. Magnetic moment value, electronic Spectra data, their Assignments and EPR data of the compounds.

Compound	μ_{eff} (B.M)	Band position/ ϵ $\text{cm}^{-1}/\text{M}^{-1}\text{cm}^{-1}$	Assignments	EPR data		
				g_{\parallel}	g_{\perp}	G
[MnL ¹ Cl ₂]	5.80	22,400/17.00 18,700/18.00	⁶ A _{1g} → ⁴ T _{2g} ⁶ A _{1g} → ⁴ T _{1g}	-	-	-
[MnL ¹ (NO ₃) ₂]	5.78	22,450/16.00 18,650/15.00	⁶ A _{1g} → ⁴ T _{2g} ⁶ A _{1g} → ⁴ T _{1g}	-	-	-
[MnL ² Cl ₂]	5.79	22,500/16.32 18,550/18.10	⁶ A _{1g} → ⁴ T _{2g} ⁶ A _{1g} → ⁴ T _{1g}	-	-	-
[MnL ² (NO ₃) ₂]	5.76	22,500/16.00 18,700/17.27	⁶ A _{1g} → ⁴ T _{2g} ⁶ A _{1g} → ⁴ T _{1g}	-	-	-
[CoL ¹ Cl ₂]	4.55	16,100/14.00 21,700/16.00	⁴ T _{1g} (F) → ⁴ A _{2g} (F) ⁴ T _{1g} (F) → ⁴ T _{1g} (P)	-	-	-
[CoL ¹ (NO ₃) ₂]	4.51	15,900/14.25 21,400/16.30	⁴ T _{1g} (F) → ⁴ A _{2g} (F) ⁴ T _{1g} (F) → ⁴ T _{1g} (P)	-	-	-
[CoL ² Cl ₂]	4.53	16,500/13.00 21,850/16.50	⁴ T _{1g} (F) → ⁴ A _{2g} (F) ⁴ T _{1g} (F) → ⁴ T _{1g} (P)	-	-	-

[CoL ² (NO ₃) ₂]	4.52	16,000/13.10	⁴ T _{1g} (F) → ⁴ A _{2g} (F)	-	-	-
		21,450/15.15	⁴ T _{1g} (F) → ⁴ T _{1g} (P)	-	-	-
[NiL ¹ Cl ₂]	3.15	17,500/13.30	³ A _{2g} (F) → ³ T _{1g} (P)	-	-	-
		11,400/19.20	³ A _{2g} (F) → ³ T _{1g} (F)	-	-	-
[NiL ¹ (NO ₃) ₂]	3.10	17,600/18.00	³ A _{2g} (F) → ³ T _{1g} (P)	-	-	-
		11,200/19.10	³ A _{2g} (F) → ³ T _{1g} (F)	-	-	-
[NiL ² Cl ₂]	3.14	17,500/15.70	³ A _{2g} (F) → ³ T _{1g} (P)	-	-	-
		11,450/19.00	³ A _{2g} (F) → ³ T _{1g} (F)	-	-	-
[NiL ² (NO ₃) ₂]	3.12	17,700/16.00	³ A _{2g} (F) → ³ T _{1g} (P)	-	-	-
		11,450/17.00	³ A _{2g} (F) → ³ T _{1g} (F)	-	-	-
[CuL ¹ Cl ₂]	1.75	18,600/42.00	² B _{1g} → ² E _g	2.252	2.052	4.84
		16,400/45.00	² B _{1g} → ² B _{2g}			
[CuL ¹ (NO ₃) ₂]	1.74	19,000/43.10	² B _{1g} → ² E _g	2.210	2.040	5.25
		15,200/40.15	² B _{1g} → ² B _{2g}			
[CuL ² Cl ₂]	1.79	18,500/44.00	² B _{1g} → ² E _g	2.190	2.059	3.22
		15,300/41.00	² B _{1g} → ² B _{2g}			
[CuL ² (NO ₃) ₂]	1.80	18,700/42.05	² B _{1g} → ² E _g	2.230	2.058	3.96
		16,600/45.00	² B _{1g} → ² B _{2g}			

$\nu(\text{C-H})$. The spectra of nitrate complexes gave additional bands around 1210, 1050, and 860 cm^{-1} regions consistent with the monodentate bonding of this group¹⁶. Bands observed in the 230-255 and 270-320 cm^{-1} regions reasonably may be assigned¹⁶ to $\nu(\text{M-O})$ and $\nu(\text{M-Cl})$, respectively. All the complexes show bands in the 1410-1460, 1070-1100, and 710-760 cm^{-1} regions corresponding to phenyl ring vibrations¹⁷. However, a medium-intensity band around 930-985 cm^{-1} may be ascribed to the $\nu(\text{N-N})$ stretching mode of the hydrazine moiety.

The ^1H NMR data (**Table 3**) for all mononuclear zinc(II) complexes show a multiplet in the 6.70-6.96 ppm region which can be assigned¹⁸ to the secondary amino (C-NH ; 4H) protons of the hydrazine moiety. A multiplet in the 2.96-3.10 ppm region may be assigned¹⁹ to the methylene protons [$\text{N-CH}_2\text{-N}$; 4H]. However, a multiplet in the region 7.18 - 7.30 ppm, (49.52-49.61), arguably may be assigned to aromatic ring protons. A singlet in the region 8.32-8.38 ppm may be assigned¹⁴ to the four equivalent carboximine protons (CH=N ; 4H), while a singlet at ca. 2.30-2.32 ppm may be ascribed to the methyl protons of the acetaldehyde moiety [$-\text{CH}_3$; 6H] for complexes derived from acetaldehyde.

The EPR spectra of the polycrystalline copper(II) macrocyclic complexes were recorded at room temperature. No hyperfine splitting has been noticed and may be due to the fact that the paramagnetic centers are not diluted in a $d_{x^2-y^2}$ ground state²⁰. The calculated g_{\parallel} and g_{\perp} values of the copper complexes fall in the 2.190-2.252 and 2.040-2.059 ranges, respectively, which

suggest that $d_{x^2-y^2}$ may be the ground state in axial symmetry. The g values are related²¹ by the expression $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, which measures the exchange interaction between copper centres in a polycrystalline solid. The calculated G values for these complexes appear in the range 3.22-5.25, which suggests that the exchange interaction is negligible. It should be noted²² that for an ionic environment $g_{\parallel} > 2.3$, while for a covalent environment $g_{\parallel} < 2.3$. The copper complexes show $g_{\parallel} < 2.3$ indicating their considerable covalent character.

The electronic spectral and magnetic moment data of the complexes (Table 4) are consistent with the proposed structures. The manganese(II) complexes exhibit two bands in the 22,400-22,500 and 18,550-18,700 cm^{-1} regions assignable²³ to ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transitions, respectively, corresponding to an octahedral geometry for the manganese ion. The cobalt complexes show two bands appearing at 15,900-16,500 and 21,400-21,850 cm^{-1} assignable²³ to the transitions ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively. The electronic spectra of nickel(II) complexes show two bands in the 17,500-17,700 and 11,200-11,450 cm^{-1} regions which may be assigned²³ 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 Ni(II) ion. The electronic spectra of the macrocyclic copper(II) complexes show a broad band with maxima in the regions 18,500-19,000 and 15,200-16,600 cm^{-1} and may be ascribed²³ to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, corresponding to a distorted octahedral geometry around the copper(II) ion. The high-intensity band

observed at ca. 36, 000 cm^{-1} for all the complexes in the UV region may be assigned to a ligand to metal charge transfer excitation and a broad absorption maximum at ca. 29, 600 cm^{-1} may be due to the $n \rightarrow \pi^*$ ligand transition. The observed magnetic moments for all complexes (**Table 4**) are consistent with the high-spin octahedral geometry around the metal ions which further corroborates the electronic spectral findings.

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