STUDIES ON TRANSITION METAL COMPLEXES OF MACROCYCLIC LIGAND DERIVED FROM 2, 6-DIBENZOYL PYRIDINE DIHYDRAZONE

Deepshikha[1], Mayank[2], Rajpal Tyagi[3], Mamta Gupta[4]
[1,2]*Associate Professor, Department of Chemistry, Multanimal Modi College, Modinagar.*
[3,4]*Assistant Professor, Department of Chemistry Multanimal Modi College, Modinagar.*

Abstract- **Study of macrocyclic compounds and their complexes is becoming a major growth area of research in chemistry. Macrocyclic compounds are the compounds having oxygen, nitrogen, sulphur, etc. atoms in the ring. These rings are of different sizes depending upon the number of atoms involved in the formation of the ring. Macrocyclic compounds are capable of interacting with several metal ions to give metal chelates of novel structure. A new series of 13-membered tetraaza macrocylic complexes has been prepared and characterized on the basis of analytical, IR, ^{1}H-NMR, EPR, UV-visible spectra, magnetic susceptibility and conductivity data.**

Index Terms- **Transition metal complexes, Macrocyclic ligand.**

I. INTRODUCTION

Transition metal complexes of polyamide macrocyclic prepared through metal ion controlled condensation reaction have been reported[1,2]. The metal ions direct the reaction preferentially towards the cyclic rather than oligomeric or polymeric product[3-5]. A new series of 13-membered tetraaza Macrocyclic complexes has been prepared by the template condensation of triethylene tetraamine[6-8] with ethyl aceto acetate or methyl acetoacetate in 1:2 molar ratio. The complex have been characterized on the basis of analytical data i.e. IR, 1H-NMR, EPR, UV- VIS spectra, magnetic susceptibility and conductivity data. In macrocyclic complexes both metal ions and size of the ring play an important role. We report macrocyclic complexes derived from the condensation reaction of 2,6-dibenzoyl pyridine, hydrazine hydrate, formaldehyde and metal ions structure direct agent.

II. EXPERIMENTAL

The metal salts $MX_2.nH_2O$ (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); X=Cl, NO_3 andn=1,3,6), (BDH) were commercially pure samples. The chemicals such as 2,6-dibenzoyl pyridine (Aldrich), hydrazine hydrate 85% (Sigma) and formaldehyde solution 37% (E.Merck) were used as received. Solvents were dried before use.

Preparation of 2, 6-dibenzoyl pyridine dihydrazone, 'L': To a stirring solution of 2,6- dibenzoylpyridine (0.574 g, 2 mmol) in methanol (-20 ml) was added a solution of hydrazine (0.242 ml, 4 mmol) dissolved in methanol (-20 ml). The stirring continued for 6-8 h, resulting in a colourless solution. The resultant reaction mixture was allowed to stand for 48 h resulting in the isolation of microcrystalline solid.

Synthesis of dichloro/nitrato (1,3:11,13-dipyridyl-4,10,14,20-tetra phenyl- 2,5,8,9,12,15,16,18,19-decaaza-4,9,14,19-tetraene cycloeicosane) metal (II), [MLX_2] (M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) and [CuL]X_2 (X=Cl, NO_3): To a stirring methanolic solution (-20 ml) of 2,6-dibenzoylpyridine dihyrzone, 'L' (1.26 g, 4 mmol), solutions of formaldehyde 0.298 ml, 4 mmol) taken in 20 ml methanol and $MX_2.nH_2O$ (X=Cl, NO_3 and n=1,3,6) (2 mmol) dissolved in 20 ml of methanol were added simultaneously. The reaction mixture was further stirred overnight affording the isolation of solid product, which was filtered, washed several times and vacuum dried.

Elemental analyses were obtained from the laboratory. Metals and chloride were determined volumetrically and gravimetrically[9] respectively. The electronic spectra of the compounds in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature. EPR spectra were recorded on a JEOL JES RX2X EPR spectrophotometer. Magnetic susceptibility measurements were carried out using a Faraday Balance at 25°C. The electrical conductivities[11] of 10-3 M solutions in DMSO were obtained on a digital conductivity meter APX 185 equilibrated at 25°C±0.05. 1H NMR spectra were recorded in DMSO-d6 using a Jeol, Eclipse 400 with the

Me4Si as an internal standard. The IR spectra (4000-200 cm-1) were recorded as KBr discs on a Perkin-Elmer 2400 spectrophotometer.

III. RESULT AND DISCUSSION

A new series of decaazamacrocyclic complexes $[ML_1X_2]$ and $[CuL_1]$ X_2 (where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); X=Cl, NO_3) have been prepared by the template condensation reaction of 2-6dibenzoylpyridine dihydrazone, 'L' and formaldehyde in methanol medium in a 2:2 ratio (Scheme 1). An attempt was made to synthesize metal free macro cyclic ligand which resulted in an oily product. These complexes are found to be stable to atmosphere at room temperature. These complexes are soluble in distilled water, DMSO and DMF. The results of elemental analyses (Table 1) correspond to the proposed macro cyclic framework. The low conductivity data ascertain the non-electrolytic nature of these complexes, except that of copper complexes, which were found to be 1:2 electrolyte[10]. The preliminary information regarding the formation of 'L' ($C_{19}H_{17}N_5$) has been inferred from bands observed in its IR spectrum. The disappearance of band corresponding to ν(C=O) and appearance of a new strong intensity band at 1625cm-1 assigned to ν(C=N) of imine group strongly suggest the formation of 'L' ($C_{19}H_{17}N_5$). A strong doublet around 3360 cm-1 may be assigned to ν(N-H) stretching mode of uncondensed primary amine group of hydrazine moiety. The appearance of bands at 2925 and 985 cm^{-1} may be assigned to ν(C-H), ν(N-N) stretching vibration respectively in 'L' ($C_{19}H_{17}N_5$). The IR spectra of all the complexes exhibit no band corresponding to ν(C=O) of formaldehyde group rather a new strong intensity band appears in the region 3210-3260 cm^{-1} attributable[11] to the ν(N-H) stretching mode of secondary amines. This suggests that condensation between CO of formaldehyde moiety and NH_2 of hydrazine moiety has occurred in presence of metal ion. The IR spectra of all the macrocyclic complexes exhibit a medium intensity band in the region 1590- 1620 cm^{-1} which may be assigned[12-15] to a coordinated imine reasonably, be assigned to ν(C=N) stretching vibration. The band in the region 1140-1220 cm^{-1} may reasonably, be assigned to ν(C- N) stretching vibration. An absorption band appears in the region 2850-2920 cm^{-1} in all the complexes, may reasonably be ascribed to the ν(C-H) stretching vibrational modes. A medium intensity band around 940-975 cm^{-1} may be ascribed to the ν(N-N) stretching mode[16]. All the complexes show bands around 403, 601 and 1578 cm^{-1} consistent[17,18] with the ring deformation, respectively. These vibrations do not suffer significant shift towards higher frequencies suggesting that pyridine nitrogen in the macrocyclic complexes is not coordinated to the metal atom[19]. The presence of band in the region 330-490 cm^{-1} may be due to the ν(M-N)[20,21]. Bands observed in the regions 207-220 cm^{-1} and 228-240 cm^{-1} may be assigned[22] to ν(M-Cl) and ν(M- O) stretching vibrations respectively. However, in the copper complex additional bands observed at 1630, 1280, 870 and 705 cm^{-1} may be reasonably assigned to the free nitrate group. The 1H NMR spectrum of 'L' ($C_{19}H_{17}N_5$) shows peaks at 12.63 ppm which may be assigned to the phenyl protons (C_6H_5; 12H) of the 2,6-dibenzoylpyridine moiety. Multiplets in the region 7.75 and 7.38 ppm may be assigned[23] to aryl proton (H_α) and to ($2H_\beta$) of 'L'. Multiplets in the region 4.99 ppm may be attributed[24] to ($N\text{-}NH_2$; 4H) protons of 'L'. The 1H NMR spectra of the **Zn(II) complexes** show a major peak at 7.74-7.77 ppm and 7.35-7.39 ppm which may be assigned to the aryl[25] protons ($2H_\alpha$) and ($4H_\beta$) respectively. A singlet at 2.68-2.70 ppm may be reasonably assigned to the methyl (CH_3; 12H) protons of the 2,6-dibenzoylpyridine moiety. The multiplets observed at 3.11-3.13 ppm may be assigned to the methylene protons ($N\text{-}CH_2\text{-}N$; 4H) of the aldehyde moiety. The multiplets observed at 6.83-6.84 ppm may be assigned to the secondary amino group of the hydrazine moiety. But, no NMR signal has been observed in the complexes $[ZnL_1Cl_2]$ and $[ZnL_1(NO_3)_2]$ which correspond to the NH_2 protons of 'L' ($C_{19}H_{17}N_5$) suggesting that condensation has taken place (Scheme 1). The EPR spectra of both the polycrystalline Cu(II) macrocyclic complexes were recorded at room temperature, and their $g_\parallel$ and $g_\perp$ were calculated. Neither of the decaazamacrocyclic Cu(II) complexes studied shown any hyperfin splitting, but gave only a derivative curve giving $g_\parallel$ and $g_\perp$ values Table (2), a characteristic[26] of square planar copper(II) complexes. This suggests that the unpaired electron is present in the $dx^2\text{-}y^2$ orbital as g$g_\parallel > g_\perp > 2.02$[27]. In an axis symmetry, the g values are related by the expression $G=(g_\parallel-2)/(g_\perp-2)$, which measures the interaction between copper centres in the unit cell. The calculated 'G' values for the present complexes appeared in the range 3.42 and 3.66 suggest[28] the existence of a considerable exchange interaction between copper, G<4. All the complexes show $g_\parallel<2.3$ indicating that the present complexes exhibit considerable covalent character. The appearance of two bands in the electronic spectra **(Table 2)** of the manganese complex in the regions 18750- 18800 cm^{-1} and 22300-22350 cm^{-1} may reasonably correspond[29] to the $^6A_{1g} \rightarrow {}^4T_{1g}$ and $^6A_{1g} \rightarrow {}^4T_{2g}$ transitions, respectively consistent with an octahedral geometry around the manganese (II) ion. The electronic spectra of the iron complexes exhibit a weak intensity (d-d) transition in the region 11450-11850 cm^{-1}, which may be reasonably assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition, consistent with a high-spin octahedral environment around iron (II) ion. However, the electronic spectra of the cobalt complexes exhibit two bands in the region 16500-16800 cm^{-1} and 22200- 22400 cm^{-1} which may reasonably correspond to the $^4T_{1g}$ (F) → $^4A_{2g}$ (F) and $^4T_{1g}$ (F) →$^4T_{1g}$ (P) transitions, respectively, suggesting[30] an octahedral geometry for the complexes. The ligand field spectra for nickel(II) macrocyclic complexes show two bands in the regions 11500-12000 cm^{-1} and 17400-17850 cm^{-1} which may be ascribed[31] to the $^3A_{2g}$ (F) → $^3T_{1g}$ (F) and $^3A_{2g}$ (F) → $^3T_{1g}$ (P) transitions, respectively, indicating an octahedral environment around the nickel(II) ion. The copper complexes gave three bands in their electronic spectra in the regions 12100-13000 cm^{-1}, 16100-16200 cm^{-1} and 21600-21950 cm^{-1} and these bands may reasonably assigned to the $^2B_g \rightarrow {}^2B_{2g}$; $^3B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively. The above results are consistent with the square planar geometry of copper (II) complexes[32-36]

Table (1): Analytical data and molar conductance values for the compounds

Compound	**Yield**	**M.pt (0°C)**	**Colour**	**Caled.(Found) %**					**Λ_m (cm^3 Ohm/ mol^{-1})**
				M	**Cl**	**C**	**H**	**N**	
$(C_{19}H_{17}N_5)$	45	155	White	-	-	72.23 (72.38)	5.15 (5.39)	22.05 (22.22)	-
$[Mn(C_{14}H_{34}N_{10})Cl_2]$	50	292	Dull Green	6.81 (7.04)	9.0 (9.10)	61.41 (61.51)	4.20 (4.35)	7.80 (7.95)	20
$[Mn(C_{14}H_{34}N_{10})(NO_3)_2]$	52	292	Dull Green	6.42 (6.59)	-	57.50 (57.62)	3.90 (4.08)	20.02 (20.16)	20
$[Fe(C_{14}H_{34}N_{10})Cl_2]$	60	>310	Wine Red	7.0 (7.15)	8.92 (9.09)	61.30 (61.47)	4.25 (4.35)	17.80 (17.92)	25
$[Fe(C_{14}H_{34}N_{10})(NO_3)_2]$	55	>305	WineRed	6.60 (6.69)	-	57.43 (57.56)	3.93 (4.07)	20.0 (20.14)	25
$[Co(C_{14}H_{34}N_{10})Cl_2]$	40	>305	Dark Brown	7.40 (7.51)	8.98 (9.05)	61.12 (61.22)	4.20 (4.33)	17.70 (17.85)	22
$[Co(C_{14}H_{34}N_{10})(NO_3)_2]$	45	>310	Dark Brown	6.91 (7.04)	-	57.25 (57.35)	3.93 (4.06)	20.0 (20.07)	22
$[Ni(C_{14}H_{34}N_{10})Cl_2]$	38	190	Rust	7.40 (7.49)	8.94 (9.05)	61.12 (61.24)	4.22 (4.33)	17.76 (17.86)	18
$[Ni(C_{14}H_{34}N_{10})(NO_3)_2]$	45	205	Rust	6.94 (7.01)	-	57.25 (57.36)	4.0 (4.06)	20.0 (20.07)	18
$[Cu(C_{40}H_{34}N_{10})Cl_2]$	55	225	Yellow	7.94 (8.05)	8.0 (9.0)	60.77 (60.87)	4.22 (4.31)	17.65 (17.75)	110
$[Cu(C_{40}H_{34}N_{10})(NO_3)_2]$	60	205	Yellow	7.45 (7.55)	-	56.95 (57.03)	3.96 (4.04)	19.86 (19.96)	120

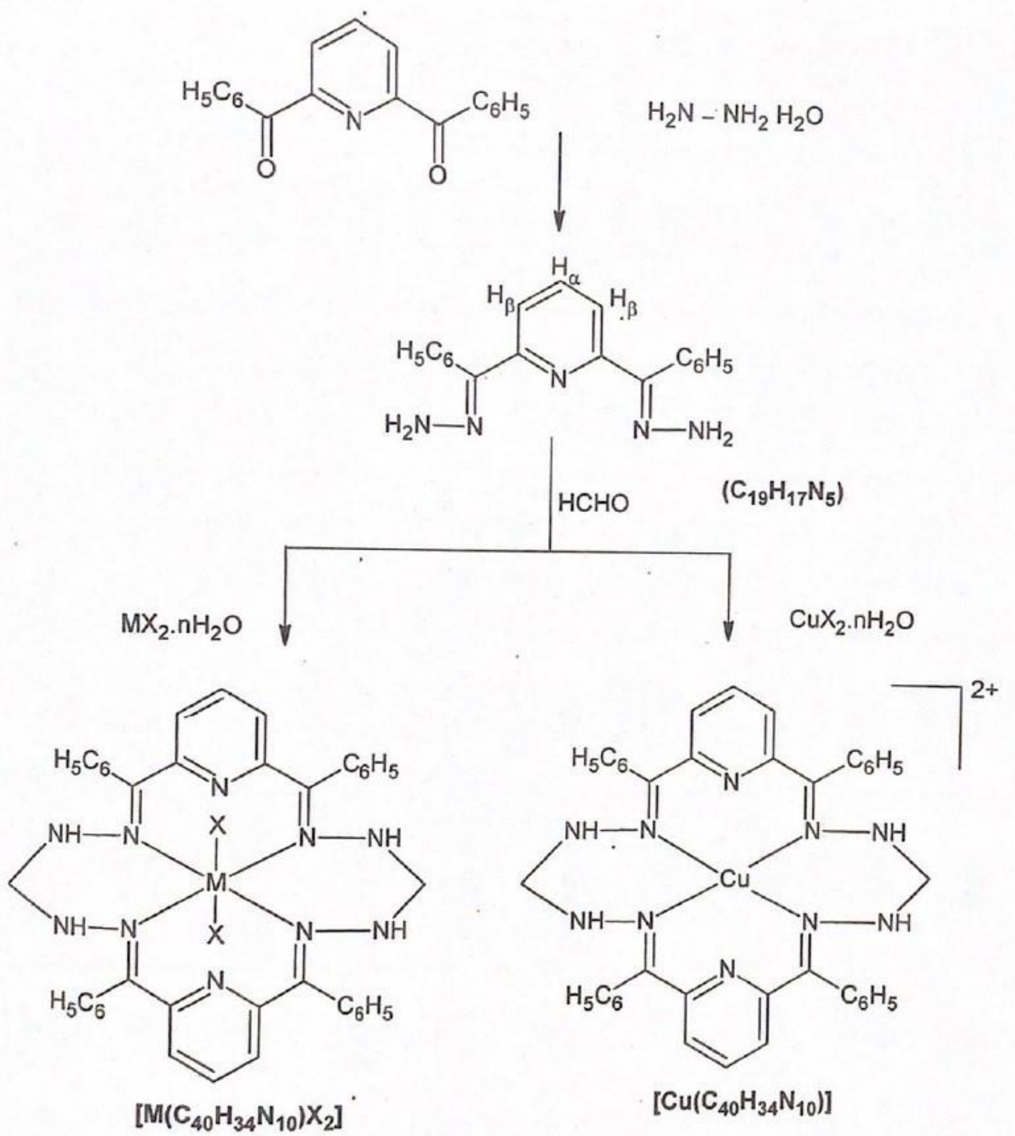
[Zn($C_{40}H_{34}N_{10}$)Cl_2]	55	>310	Colourless	8.20 (8.27)	8.85 (8.99)	60.61 (60.73)	4.20 (4.30)	17.62 (17.71)	20
[Zn($C_{40}H_{34}N_{10}$)(NO_3)$_2$]	65	>310	Colourless	7.62 (7.71)	-	56.82 (56.91)	3.95 (4.03)	19.83 (19.92)	20

Table (2.1): Magnetic moment values, electronic spectral data assignments and EPR dataof the compound

Compound	**μeff (B.M.)**	**Bond Position (cm^{-1})**	**Assignments**	**EPR**		
				g‖	**g⊥**	**G**
[Mn($C_{40}H_{34}N_{10}$)Cl_2]	5.78	22300 18750	$^{6}A1g \rightarrow {}^{4}T2g$ $^{6}A1g \rightarrow {}^{4}T1g$	-	-	-
[Mn($C_{40}H_{34}N_{10}$)(NO_3)$_2$]	5.80	22350 18800	$^{6}A1g \rightarrow {}^{4}T2g$ $^{6}A1g \rightarrow {}^{4}T1g$	-	-	-
[Fe($C_{40}H_{34}N_{10}$)Cl_2]	5.40	11450	$^{5}T_{2g} \rightarrow {}^{5}E_{g}$	-	-	-
[Fe($C_{40}H_{34}N_{10}$)(NO_3)$_2$]	5.79	11850	$^{5}T_{2g} \rightarrow {}^{5}E_{g}$	-	-	-
[Co($C_{40}H_{34}N_{10}$)Cl_2]	4.56	16800 22200	$^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ $^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$	-	-	-
[Co($C_{40}H_{34}N_{10}$)(NO_3)$_2$]	4.54	16500 22400	$^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ $^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$	-	-	-
[Ni($C_{40}H_{34}N_{10}$)Cl_2]	3.06	11500 17850	$^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ $^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$	-	-	-
[Ni($C_{40}H_{34}N_{10}$)(NO_3)$_2$]	3.08	12000 17400	$^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ $^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$	-	-	-
[Cu($C_{40}H_{34}N_{10}$)Cl_2]	1.78	13000 16100 21950	$^{2}B1g \rightarrow {}^{2}B2g$ $^{2}B1g \rightarrow {}^{2}A1g$ $^{2}B_{1g} \rightarrow {}^{2}E_{g}$	2.22	2.06	3.66
[Cu($C_{40}H_{34}N_{10}$)(NO_3)$_2$]	1.76	12100 16200 21600	$^{2}B1g \rightarrow {}^{2}B2g$ $^{2}B1g \rightarrow {}^{2}A1g$ $^{2}B_{1g} \rightarrow {}^{2}E_{g}$	2.24	2.07	3.42

Table (2.2): Electronic Spectral and Magnetic Data Complexes*

Compound	**$\square_{max}$ cm^{-1}**	**DQ^{xy}**	**DQ^{x}**	**DT/DQ**	**Dq^{xy}**	**Dq^{z}**	**D_1**	**DT**	**DS**	**DQ**
$[Ni(C_{40}H_{34}N_{10})Cl_2]$	34900, 27850, 18200, 11730, 10750	32200	26670	0.052	1170	970	115	1570	11700	30350
$[Ni(C_{40}H_{34}N_{10})Br_2]$	34100, 26200, 18240, 17730, 11740	32350	26600	0.054	1180	969	120	1620	11290	30430
$[Ni(C_{40}H_{34}N_{10})(NO_3)_2]$	35200, 38300, 18300, 11800, 10670	32400	26560	0.058	1182	950	125	1650	11560	30460
$[Ni(C_{40}H_{34}N_{10})(NCS)_2]$	34800, 2830, 18290, 11700, 10600	32150	25930	0.059	1170	952	130	1760	11495	30070
		Dq	**B**	**v_1/v_2**	**$\square$**					
$[Co(C_{40}H_{34}N_{10})Cl_2]$	21600, 16620, 15940, 8620	1080	830	1.80	0.85					
$[Co(C_{40}H_{34}N_{10})Br_2]$	21620, 18500, 16260, 8240	1035	810	1.98	0.88					
$[Co(C_{40}H_{34}N_{10})(NO_3)_2]$	21500, 18550, 15760, 8600	1070	820	1.85	0.80					
$[Co(C_{40}H_{34}N_{10})(NCS)_2]$	21510, 18450, 16100, 8790	1098	798	1.88	0.89					



Where M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}; X = Cl or NO_3; n = 1, 3, 6

Scheme 1

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