

## ABSTRACT

This work deals with the synthesis and physico-chemical studies on macrocyclic moieties containing N, O and S as donor atoms and their complexes with first row transition metal ions Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The whole work is divided into eight chapters. The chapter [1] deals with a general introduction of macrocyclic complexes. This also describes the general characteristics of macrocyclic molecules and different types of synthesis of macrocyclic moieties containing N, O and S atoms and the application of these macrocycles in various fields. The chapter [2] gives the details of physico-chemical methods, the instruments and the experimental conditions involved in the characterization of various macrocyclic moieties synthesized.

The chapter [3] explains the synthesis and physico-chemical studies of octaazamacrocyclic complexes: 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<sub>3</sub>) and dichloro/nitrato (1:2.10:11-Diphenyl-6.15-dimethyl-4.5.7.8.13.14.16.17-octaazacyclooctadecane-3, 8, 12, 17 -tetraene) metal(II),  $[ML^2X_2]$  (M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); X= Cl or NO<sub>3</sub>). The synthesis of these macrocyclic moieties have been accomplished by the template condensation reaction of hydrazine hydrate, o-phthalaldehyde and formaldehyde or acetaldehyde with metal salts in 4:2:2:1 molar ratio in methanolic medium. The nature of bonding and stereochemistry of the complexes have been deduced from the elemental analyses, FT-IR, <sup>1</sup>H NMR, EPR, UV/Vis Spectroscopy, magnetic susceptibility and conductivity measurements. An octahedral geometry has been suggested for all the complexes and the observed low molar conductance values indicate their non-ionic nature.

The IR spectra of these complexes exhibit a single, sharp absorption band in 1570-1660 cm<sup>-1</sup> region, attributed to the coordinated imine  $\nu(C=N)$  stretching vibration. The bands characteristic of free primary amine or carbonyl

groups of aldehyde moieties were not observed. The single sharp absorption band appearing in  $3200\text{-}3290\text{ cm}^{-1}$  region may be assigned to the coordinated  $\nu(\text{N-H})$  stretching vibrations of a secondary amine moiety. The other prominent bands like  $\nu(\text{C-H})$ ,  $\nu(\text{N-N})$  and  $\nu(\text{M-N})$  appeared at their estimated positions. The appearance of bands corresponding to  $\nu(\text{M-O})$  and  $\nu(\text{M-Cl})$  further confirm the involvement of nitrate and chloro groups in the complexes. The  $^1\text{H}$  NMR spectra of all the Zn(II) complexes show the multiplet in 2.96-3.10 ppm region assigned to methylene protons ( $\text{N-CH}_2\text{-N}$ ; 4H). The singlet in 8.32-8.38 ppm region is assigned to the four equivalent carboximine protons ( $\text{CH=N}$ ; 4H). The observed magnitudes for magnetic moments and molar conductivity as well as the bands observed in the electronic spectra of the complexes indicate an octahedral geometry for the complexes. However, the geometry is distorted in copper(II) complexes. The EPR spectra of copper(II) complexes gave  $g_{\parallel}$  and  $g_{\perp}$  values in the 2.190-2.252 and 2.040-2.059 regions respectively, indicating that the unpaired electron is in the  $d_{x^2-y^2}$  orbital.

The chapter [4] describes the synthesis and characterization of decaazamacrocyclic complexes: 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).  $[\text{ML}]\text{X}_2$  ( $\text{M} = \text{Mn(II)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$ ;  $\text{X} = \text{Cl}$  or  $\text{NO}_3$ ). These complexes have been synthesized by the reaction of pyridine-2,6-dicarboxylic acid, hydrazine hydrate and formaldehyde in presence of transition metal ions in 2:4:2:1 molar ratio in methanol, resulted in the formation of a new series of tetraamide decaazamacrocyclic complexes  $[\text{ML}]\text{X}_2$  ( $\text{M} = \text{Mn(II)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$ ;  $\text{X} = \text{Cl}$  or  $\text{NO}_3$ ). The analytical results suggest that the proposed macrocyclic complexes have 1:1 metal to ligand stoichiometry. The observed molar conductance values are indicative of the 1:2 electrolytic nature for all of these complexes.

The most significant feature of IR spectra of all these complexes is the appearance of four amide bands in the 1670-1720, 1450-1520, 1240-1285 and

640-675  $\text{cm}^{-1}$  region assigned to amide I [ $\nu(\text{C}=\text{O})$ ], amide II [ $\nu(\text{C}-\text{N})+\delta(\text{N}-\text{H})$ ], amide III [ $\delta(\text{N}-\text{H})$ ] and amide IV, wagging [ $\rho(\text{C}=\text{O})$ ] vibrations, respectively. All complexes exhibit a single sharp band in the 3220-3260  $\text{cm}^{-1}$  region ascribed to the coordinated secondary amino group whose position was found to be shifted to lower energy suggesting that the nitrogen of the amide group is involved in coordination to the metal ions. The involvement of the pyridine nitrogen in coordination has been further confirmed by the appearance of a medium intensity band in the region 230-260  $\text{cm}^{-1}$  corresponding to  $\nu(\text{M}-\text{N})_{\text{py}}$ . The other prominent bands like  $\nu(\text{C}-\text{H})$ ,  $\nu(\text{C}-\text{N})$ ,  $\nu(\text{N}-\text{N})$  and  $\nu(\text{M}-\text{N})$  appeared at their expected positions. The  $^1\text{H}$  NMR spectra of the Zn(II) complexes show a broad singlet in 8.38-8.40 ppm region assigned to the amide protons ( $\text{CO}-\text{NH}$ ; 4H). A triplet in 8.42-8.44 ppm and a doublet in 7.83-7.86 ppm region assigned 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. The calculated  $g_{\parallel}$  and  $g_{\perp}$  values of the copper(II) complexes appeared in the 2.35-2.37 and 2.09-2.10, respectively and calculated G values are in the 3.7-3.8 region. In these complexes  $G < 4$  is indicative of the considerable exchange interaction. The results of electronic spectra, molar conductivity and magnetic moment values suggest an octahedral geometry.

The chapter [5] deals with the synthesis and characterization of dioxotetraamine macrocyclic complexes: 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),  $[\text{MLX}_2]$  (M = Mn(II), Co(II), Ni(II) and Zn(II); (X = Cl or  $\text{NO}_3$ ) 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  $[\text{CuL}]\text{X}_2$ ; X = Cl or  $\text{NO}_3$ . The complexes have been prepared via the template condensation reaction of o-aminobenzoic acid, with o-phenylenediamine and 2,4-pentanedione in 1:2:1:1 molar ratio in methanolic solution. The elemental analyses results are consistent with the proposed 1:1 metal to ligand stoichiometry. All the complexes show non electrolytic nature in DMSO except copper complexes which show 1:2 electrolytic nature.

The IR spectra of all the complexes show bands mainly in the regions 1680-1735, 1480-1530, 1240-1270 and 640-670  $\text{cm}^{-1}$  assignable to amide I, II, III and IV vibrations, respectively. This result has been further confirmed by the appearance of a strong medium intensity band in the 1590-1620  $\text{cm}^{-1}$  region, assigned to the coordinated imine  $\nu(\text{C}=\text{N})$ . A single sharp band at ca 3240  $\text{cm}^{-1}$  region is assigned to coordinated secondary amino groups. However, the characteristic bands of the  $\nu(\text{M}-\text{N})$ ,  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{Cl})$  appeared at their estimated positions. The  $^1\text{H}$  NMR spectra of the Zn(II) complexes show singlet in 8.32-8.35 ppm region which may be ascribed to the amide protons ( $\text{CO}-\text{NH}$ ; 2H). A sharp singlet observed for all the complexes in 2.48-2.55 ppm region may be assigned to the imine methyl protons ( $\text{CH}_3-\text{C}=\text{N}$ ; 6H) of the 2,4-pentanedione moiety. The EPR spectra of copper complexes showed  $g_{\parallel}$  and  $g_{\perp}$  values at 2.13-2.23 and 2.05-2.08 regions respectively. In these complexes  $g_{\parallel} < 2.3$  and  $G < 4$  is indicative of the exchange interaction in the solid complexes. The observed values of magnetic moments and the position of absorption bands in the electronic spectra confirm an octahedral geometry for Mn(II), Co(II), Ni(II) and Zn(II) and square planar geometry for Cu(II) complexes.

The chapter [6] describes synthesis and characterization of mixed nitrogen-sulfur donor set macrocyclic complexes: dichloro/nitrato (2,3:8,9-dibenzo-4,7-dithia-1,10-diazacyclotridecane)metal(II),  $[\text{MLX}_2]$  ( $\text{M} = \text{Mn(II)}$  and  $\text{Co(II)}$ ;  $\text{X} = \text{Cl}$  or  $\text{NO}_3$ ) and (2,3:8,9-dibenzo-4,7-dithia-1,10-diazacyclotridecane)metal(II) dichloride/nitrate  $[\text{ML}]\text{X}_2$ , ( $\text{M} = \text{Ni(II)}$  and  $\text{Cu(II)}$ ;  $\text{X} = \text{Cl}$  or  $\text{NO}_3$ ). The template condensation of metal salt with o-bromoaniline, 1,2-ethanedithiol and 1,3-dibromopropane in 1:2:1:1 molar ratio resulted in the formation of this new series of dithiadiazamacrocyclic complexes.

The IR spectra of all the macrocyclic complexes exhibit a strong intensity band in the 3250-3310  $\text{cm}^{-1}$  region ascribed to the N-H stretching vibration. The bands observed in 1160-1200  $\text{cm}^{-1}$  region are reasonably assigned to  $\nu(\text{C}-\text{N})$  which strongly support that the cyclization has been taken place. In addition to this strong intensity band in the 330-380  $\text{cm}^{-1}$  region are assignable

to M–S stretching vibration. Other important bands show  $\nu(\text{M–N})$ ,  $\nu(\text{M–O})$  and  $\nu(\text{M–Cl})$  at their estimated positions. The EPR spectra of all copper(II) complexes show  $g_{\parallel}$  and  $g_{\perp}$  values in the 2.09-2.12 and 2.03-2.04 range respectively, which represent ( $g_{\parallel} > 2.3$ ) that  $d_{x^2-y^2}$  may be the ground state. The spectra and magnetic moment values suggest that Mn(II) and Co(II) complexes exhibit octahedral geometry while the square planar geometry is proposed for Ni(II) and Cu(II) complexes.

The chapter [7] describes the synthesis and spectrochemical studies of hexaaza macrocyclic complexes: dichloro/nitrato(2:14,7:9-dipyridyl-4,5,11,12-tetramethyl-1,3,6,8,10,13-hexaazacyclotetradecane-3,5,10,12-tetraene)metal(II),  $[\text{ML}^1\text{X}_2]$  (M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); X = Cl or  $\text{NO}_3$ ) and dichloro/nitrato(2:16,8:10-dipyridyl-4,6,12,14-tetramethyl-1,3,7,9,11,15-hexaazacyclohexadecane-3,6,11,14-tetraene)metal(II),  $[\text{ML}^2\text{X}_2]$  (M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); X = Cl or  $\text{NO}_3$ ). The reaction of 2,6-diaminopyridine and 2,3-butanedione or 2,4-pentanedione with respective metal salt in 2:2:1 molar ratio resulted in the isolation of this new class of schiff base hexaazamacrocyclic complexes.

The appearance of a new weak absorption band in the IR spectra of all the complexes in the  $1570\text{--}1620\text{ cm}^{-1}$  region may be assigned to the imine  $\nu(\text{C=N})$  stretching vibration whose position is consistent with that of a coordinated C=N group which indicates the formation of the azomethine group during the condensation. This result provides evidence for the formation of the macrocyclic frame work. However, characteristic bands of the  $\nu(\text{C–H})$ ,  $\nu(\text{M–N})$ ,  $\nu(\text{M–O})$  and  $\nu(\text{M–Cl})$  appeared at their expected positions. The  $^1\text{H}$  NMR spectra of the Zn(II) complexes show a sharp signal observed at 2.42-2.53 ppm corresponding to imine methyl ( $\text{CH}_3\text{–C=N}$ ; 12H) protons. A triplet at 8.34-8.42 ppm and a doublet at 7.55-7.72 ppm may reasonably be assigned to pyridine moiety of 2,6-diaminopyridine molecule corresponding to  $\text{H}_\alpha$  and  $\text{H}_\beta$  of pyridine ring. At room temperature EPR spectra of copper(II) complexes showed  $g_{\parallel}$  and  $g_{\perp}$  values at 2.21-2.28 and 2.10-2.15  $\text{cm}^{-1}$ , respectively. In these complexes  $G < 4$  is indicative of the considerable exchange interaction. The

electronic spectra and the magnetic moment data are consistent with the hexacoordination at the metal centers maintaining the octahedral geometry around the metal ions.

The chapter [8] discusses the synthesis of pentaazamacrocyclic complexes of few first row transition metal series derived from 2,6-diaminopyridine: 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  $NO_3$ ). This class of pentaazamacrocyclic complexes have been synthesized by the template condensation reaction of 2,6-diaminopyridine with 1,2-diaminoethane and 1,3-dibromopropane in 1:1:1:2 molar ratio. All the complexes are non electrolytes in DMSO, except the copper complexes which were of 1:2 electrolyte type.

The IR spectra of all the complexes did not show bands corresponding to primary amine. The bands at ca.  $3200\text{ cm}^{-1}$  assignable to the coordinated secondary amino stretching mode indicated that the proposed condensation has occurred. The other prominent bands like  $\nu(C-N)$ ,  $\nu(C-H)$ ,  $\delta(C-H)$  and  $\nu(M-N)$  appeared at their estimated positions. The appearance of bands corresponding to  $\nu(M-O)$  and  $\nu(M-Cl)$  further confirm the involvement of nitrato and chloro groups in the complexes. The  $^1H$  NMR data for all mononuclear Zn(II) complexes show a multiplet in the 6.94-6.98 ppm region which can be assigned to the secondary amino (C-NH-C; 4H) protons of the 1,2-diaminoethane and 1,3-dibromopropane moiety. The EPR spectra of the Cu(II) complexes showed  $g_{\parallel}$  and  $g_{\perp}$  values in 2.15-2.23 and 2.05-2.08 regions respectively. In these complexes  $G < 4$  is indicative of the considerable exchange interaction. The observed values of magnetic moments and the position of absorption bands in the electronic spectra confirm an octahedral geometry for Mn(II), Co(II), Ni(II) and Zn(II) ions whereas square planar geometry for Cu(II) ions.

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