ABSTRACT

This work deals with the synthesis and physico chemical studies of macrocyclic complexes bearing N, O or 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 chapter [1] deals with a brief introduction to macrocyclic chemistry with its synthetic methods and pioneering work done by eminent scientists. It also describes the various applications of these macrocyclic complexes. The Chapter [2] gives the details of physico-chemical methods, the instruments and the experimental conditions involved in the characterization of various macrocyclic complexes synthesized.

The Chapters [3] to [7] are related with the actual research work describing the synthesis and characterization of the various macrocyclic complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The templation was the main method adopted for synthesizing these complexes because the metal ion restricts the possible number of coordination modes and is an efficient route to synthesize macrocyclic complexes in good yield. However, it could be possible to isolate free macrocyclic ligands 1:2, 8:9 - diphenyl - 7,10 – diaza – 3, 14-dioxocyclotetradecane (L') and 1:2, 7:8 – diphenyl- 6,9 – diaza – 3,12 – dioxocyclodidecane (L^) by the condensation reaction of o-phenylenediamine, 1,2-dibromoethane or 1,3-dibromopropane and catechol.

The chapter [3] describes the synthesis and characterization of tetraazamacrocyclic complexes: dichloro/nitrato [3,6,10,13-tetraaza-4, 5:11,12-dibenzophenone cyclo tetradecane] metal(II), [MLX₂] [M=Co(II), Ni(II), Cu(II) and Zn(II); X = Cl or NO₃]. The reactions were carried out by treating 3,4-diaminobenzophenone with 1,3-dibromopropane in the presence of respective metal salts in 2:2:1 molar ratio in methanol. The complexes are stable to atmosphere at room temperature. The complexes are colored and obtained in good yield. The low molar conductance values suggest their non-
electrolytic nature. The most significant feature of IR spectra of all these complexes is the appearance of sharp single band in the 3215-3270 cm\(^{-1}\) region assigned to coordinated \(\nu(N-H)\) vibrations of secondary amine. The involvement of nitrogen of the secondary amine in coordination has been further confirmed by the appearance of a medium-intensity band in the 385-410 cm\(^{-1}\) region corresponding to \(\nu(M-N)\). The other prominent bands like \(\nu(C-N)\), \(\delta(N-H)\), \(\nu(M-O)\), \(\nu(M-Cl)\) and phenyl ring vibrations appeared at their expected positions. The \(^1\)H NMR spectra of the zinc(II) complexes show a multiplet in the region 6·71-6·81 ppm assigned to secondary amino protons which confirm the condensation between primary diamine and dibromopropane moieties. A triplet in 6·85-6·89 ppm and a doublet in 6·95-7·01 ppm region assigned to the \(H_a\) and \(H_b\) phenyl protons of the diaminobenzophenone. The spectral and magnetic moment data support the formation of high spin octahedral complexes which show that the ligand field effect is weak. Further, the EPR spectra of copper complexes suggest that the unpaired electron occupy the \(d_{\gamma\gamma}\) orbital, so the pairing of electrons should be in \(d_z^2\) orbital. This unsymmetrical filling of electrons in \(e_g\) orbitals may lead to the tetragonal distortion with two long bonds along the \(z\)-axis.

The chapter [4] explains the synthesis and physico-chemical studies of tetraazamacrocyclic complexes: dichloro [1,4,7,10-tetraaza-5, 6,11,12-tetramethyl-4, 6,10,12-tetraene-2,3:8,9-dibenzylcyclodidecane] metal(II), [ML\(^1\)Cl\(_2\)], [M=Co(II), Ni(II) and Zn(II)]; [1,4,7,10-tetraaza-5,6,11,12-tetramethyl-4,6,10,12-tetraene-2,3:8,9-dibenzyl cyclodidecane] copper(II) chloride, [CuL\(^1\)]Cl\(_2\); dichloro [1,4,8,11-tetraaza-5,7,12,14-tetramethyl-4,7,11,14-tetraene-2,3:9,10-dibenzyl cyclotetradecane metal(II), [ML\(^2\)Cl\(_2\)] [M=Co(II), Ni(II) and Zn(II)] and [1,4,8,11-tetraaza-5,7,12,14-tetramethyl-4,7,11,14-tetraene-2,3:9,10-dibenzyl cyclotetradecane] copper(II) chloride, [CuL\(^2\)]Cl\(_2\). The synthesis of these macrocyclic complexes have been accomplished by the template condensation reaction of o-phenylenediamine and 2, 3-butanedione or 2, 4-pentanedione with metal salts in 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, $^1$H NMR, EPR, UV/Vis spectroscopy, magnetic susceptibility and conductivity measurements. The copper (II) complexes exhibit square planar geometry, whereas an octahedral geometry is suggested for all the other complexes. The low molar conductance values of all the compounds except the copper complexes indicate their non-electrolytic nature while the copper complexes were 1:2 electrolytes.

The IR spectra of these complexes exhibit a single sharp absorption band in the 1590-1630 cm$^{-1}$ region, attributed to the coordinated imine $v(C = N)$ stretching vibration. The bands characteristic of free primary amine or carbonyl groups of ketone moieties were not observed. The other prominent bands like $v(C-N)$, $v(M-N)$ and phenyl ring vibrations appeared at their estimated positions. The appearance of bands corresponding to $v(M-Cl)$ further confirm the involvement of chloro groups in the complexes. The $^1$H NMR spectrum of Zn(II) complexes in DMSO-d$_6$ show a sharp signal in the 2.46-2.51 ppm region assigned to imine methyl (CH$_3$C=N; 12H) protons. The singlet at around 2.18 ppm is assigned to central methylene (C–CH$_2$–C; 4H) protons of the 2,4-pentanedione moiety. The observed values of magnetic moments and the position of absorption bands in the electronic spectra confirm an octahedral geometry for Co(II), Ni(II) and Zn(II) ions whereas square planar geometry for Cu(II) ions.

The chapter [5] reports the synthesis and spectral studies of transition metal-tin pentaazamacrocyclic complexes: dichloro/nitrato (1-phenyl amino 4:5, 9:10 diphenyl – 1, 3, 6, 8, 11 – pentaaza cyclododecane) metal (II) – dimethyl tin (IV), [MLX$_2$ Sn (CH$_3$)$_2$] [M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); X = Cl or NO$_3$]. The complexes have been prepared by the condensation reaction of o-phenylenediamine, formaldehyde, p-phenylenediamine, dimethyl tin (IV) dichloride and the respective transition
metal salt in a 2:2:1:1:1 molar ratio in methanolic solution. They are slightly soluble in methanol and benzene but freely soluble in DMF, DMSO and THF. The elemental analyses results are acceptable with the proposed stoichiometry of the complexes. All the complexes gave molar conductance values consistent with their non-electrolytic nature.

The explicit feature of the IR spectra is the presence of Sn-N bands in the 445-480 cm⁻¹ region. The formation of macrocyclic framework has been further confirmed by the appearance of a band at 3230-3280 cm⁻¹ region ascribed to the coordinated secondary amino group. The other vibrations appeared at their expected positions. The ¹H NMR spectra of Zn(II) complexes appear to be more complex. All the complexes gave multiplets between 6.72-6.97 ppm and between 2.72-2.94 ppm which can be assigned to the N-H and the methylene protons of the secondary amine and formaldehyde respectively. The ¹¹⁹Sn NMR spectra of all the complexes gave signal between 78-118 ppm, which is associated with a tetra-coordinated Sn atom. The observed EPR data $g_\parallel > g_\perp$ for Cu(II) complexes show that there is distortion from $Oh$ symmetry in Cu(II) complexes and the unpaired electron occupy the $d_{x^2-y^2}$ orbital. The calculated $G$ values (2.166 - 1.721) for these complexes further indicate that there is existence of considerable exchange interactions between Cu(II) centers. 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 [6] describes the synthesis and spectrochemical studies of octaazamacrocyclic complexes: dichloro/nitrato [2,5,8,10,13,16-hexamethyl-3,4,6,7,11,12,14,15-octaazacyclohexadecane-2,7,10,15-tetraene] metal(II), [MLX₂] (M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); X = Cl or NO₃). The reaction of hydrazine, acetaldehyde and 2,4-pentanedione with respective metal salts in 4:2:2:1 molar ratio resulted in the isolation of this new class of Schiff base octaazamacrocyclic complexes.
The appearance of a new weak absorption band in the IR spectra of all the complexes in the 1580-1620 cm\(^{-1}\) region may be assigned to the imine v(C=N) stretching vibration whose position is consistent with that of a coordinated C=N group which indicates the formation of azomethine group during condensation. This result was further confirmed by the appearance of v(C–N) band at 1160-1200 cm\(^{-1}\) region. The characteristic v(C–H), v(M–N), v(N–H) v(M–O) and v(M–Cl) bands appeared at their expected positions. The \(^1\)H NMR spectra of the Zn(II) complexes show a sharp signal observed at 2.45-2.50 ppm corresponding to imine methyl (CH\(_3\)C=N; 12H) protons. The room temperature EPR spectra of copper(II) complexes showed g\(_{||}\) and g\(_{\perp}\) values at 2.21-2.24 and 2.10-2.11 regions, respectively, characteristic of octahedral geometry having the unpaired electron in the \(d_{x^2-y^2}\) orbital. The spectral and magnetic moment data are entirely consistent with six coordination at the metal centers.

The chapter [7], which is the last chapter, describes the synthesis and characterization of the free nitrogen-oxygen donor macrocyclic ligands L\(^1\) and L\(^2\) (L\(^1\) = 1:2, 8:9 – diphenyl - 7,10 – diaza – 3, 14- dioxocycloptetradecane, L\(^2\) = 1:2, 7:8 – diphenyl- 6,9 –diaza – 3,12 – dioxocyclodidecane) and their metal complexes: ML\(^1\)Cl\(_2\) and ML\(^2\)Cl\(_2\) [M=Co(II), Ni(II),Cu(II) and Zn(II)]. The free ligands were derived from the reaction of o-phenylenediamine with 1,2-dibromoethane or 1,3-dibromopropane and catechol in 1:2:1 molar ratio in ethanolic medium and their complexes were obtained by subsequent addition of the respective metal ions. The nature of bonding was established on the basis of the results of the elemental analyses, FT-IR, \(^1\)H NMR and \(^13\)C NMR studies. The metal to ligand complexation ratio have been deduced from Job’s Plot was found to be 1:1. All the complexes were freely soluble in DMSO, DMF and THF and were stable at room temperature. The observed low molar conductance values for all the complexes indicate their non–ionic nature. The IR spectra of all the macrocyclic complexes exhibit a strong intensity band in the 3200 – 3290 cm\(^{-1}\) region ascribed to the N-H stretching vibration. The
bands observed at around 1175 cm\(^{-1}\) and 1340 cm\(^{-1}\), assigned to \(\nu\) (C-N) and \(\nu\) (C-O) respectively, support that cyclization has taken place. Other significant bands show \(\nu\) (M-N), \(\nu\) (M-O) and \(\nu\) (M-Cl) at their estimated positions. The EPR spectra of all the powder samples of the copper(II) complexes showed that \(g_\perp\) values are lower than \(g_\parallel\) values indicating that the unpaired electron is present in the \(d_{x^2-y^2}\) orbital having \(^2B_1\)g as a ground state term. The results of electronic spectra and the magnetic moment values suggest an octahedral geometry for Co(II), Ni(II) and Zn(II) whereas distorted octahedral geometry for Cu(II) complexes.

Thus, the preceding arguments conclude the formation and characterization of a variety of novel macrocyclic complexes.