The continued interest and quest in designing new macrocyclic ligands and complexes in view of their variety of applications was the main goal behind the compilation of this thesis. The whole thesis is written in four different chapters.

First chapter gives a general introduction to macrocyclic complexes and the pioneering work done by eminent scientists. This also describes the general characteristic features of macrocyclic complexes. The synthesis and application of the macrocyclic moieties involving N, P, O and S atoms were a subject of considerable interest in the recent years. It is only during the past two decades that a large number of synthetic macrocyclic compounds capable of binding cations or anions have been prepared and investigated. The application of these macrocycles in various fields have received much attention in the recent past. These macrocycles can be synthesized by different methods in which template condensation is one of the most effective method.

Second chapter deals with the various instruments used in the characterization of the newly synthesized macrocyclic complexes viz. infrared spectroscopy, nuclear magnetic resonance spectroscopy, electron paramagnetic resonance spectroscopy, ultraviolet and visible spectroscopy
magnetic susceptibility measurements, molar conductance measurements and elemental analysis. A brief description involved in the theory of these instrumental methods is also given. The model of instruments and the place from where the spectra were recorded are also mentioned.

Third chapter describes the synthesis and characterization of different novel polyazaamacrocyclic complexes.

The first part of this chapter deals with the preparation and characterization of 13-membered oxotetraazaamacrocyclic complexes. Synthesis of dichloro/nitrato (2-oxo-4-methyl-1,5,8,11-tetraazaacyclotrideca-4-ene) metal(II), [MLX_2] (M=Mn^{II}, Co^{II}, or Zn^{II}; X=Cl or NO_3), and 2-oxo-4-methyl-1,5,8,11-tetraazaacyclotrideca-4-ene) metal (II) dichloride/nitrate, [ML]X_2 (M=Ni^{II} or Cu^{II}; X=Cl or NO_3), was carried out by reacting triethylene tetraamine with ethylacetoacetate or methyl acetoacetate with metal ion in a 1:1:1 molar ratio. The complexes are in general insoluble in water and other common solvents except dimethylsulfoxide (DMSO) and dimethylformamide (DMF). The main features of the IR spectra were the appearance of four characteristic amide bands in the region 1680-1710, 1530-1570, 1250-1270 and 650-680 cm^{-1} and the imine v(C=N) band at 1620 cm^{-1}. The ^1H NMR spectrum of Zn^{II} complexes in DMSO-d_6 exhibits resonance peaks at around 8.56, 6.30,3.50, and 2.52 ppm which may be assigned to (NH-C=0),
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(C-NH-C), (CH$_2$-N=C) and (CH$_3$-C=N) protons, respectively. The EPR spectra of Cu$^{ll}$ complexes with $g_{||}$ and $g_{\perp}$ values at 2.23 and 2.09 confirm the square planar geometry. However, the magnetic susceptibility data and the band positions in the electronic spectra confirm the octahedral geometry for the rest of the complexes except the Ni$^{ll}$ complexes which have square planar geometry.

The second part of this chapter consists of the synthesis of dioxotetraazamacrocyclic complexes by incorporating peptide bonds. The dichloro/nitrato (6,7:14,15-dibenzo-8,13-dioxo-2,4-dimethyl-1,5,9,12-tetraazacyclopentadecane-1,4-diene) metal (II), [MLX$_2$] (M=Mn$^{ll}$, Co$^{ll}$, Ni$^{ll}$, Cu$^{ll}$ or Zn$^{ll}$; X=Cl or NO$_3$) and dichloro/nitrato [6,7:15,16-dibenzo-8,14-dioxo-2,4-dimethyl-1,5,9,13-tetraazacyclohexadecane-1,4-diene] metal(II), [MLX$_2$] (M=Mn$^{ll}$, Co$^{ll}$, Ni$^{ll}$, Cu$^{ll}$ or Zn$^{ll}$; X=Cl or NO$_3$), complexes resulted from the template condensation reaction of o-aminobenzoic acid, diaminoethane/1,3-diaminopropane and 2, 4-pentanedione with metal ion in a 2:1:1:1 molar ratio. The elemental analysis suggests 1:1 metal to ligand stoichiometry and the molar conductance values indicate that the compounds are non-electrolytic in nature. The IR spectra of all the macrocyclic complexes show bands in the region expected for the amide group vibrations. The involvement of nitrogen-metal bonding can be indicated by the appearance of sharp band at
ca. 3240 cm\(^{-1}\) expected for a co-ordinated amino group and also a strong medium intensity band at ca. 1610 cm\(^{-1}\), assignable to the coordinated imine; as well as the M-N stretching vibration at around 400 cm\(^{-1}\). The spectra of nitrato complexes gave bands at ca. 1230, 1020 and 890 cm\(^{-1}\) indicating the nitrate group vibrations. The \(^1\)H NMR and EPR spectra results further supports the formation of the said macrocyclic framework. The magnetic susceptibility and the electronic spectral studies confirm the octahedral geometry for these complexes.

The third part of this chapter describes the synthesis and characterization of octaazatetraone macrocyclic complexes. The dichloro (5,10,15,20-tetramethyl -2,7,12,17-tetraone-3,4,8,9,13,14,18,19-octaazacycloeicosane-4,9,14,19-tetraene)metal(II), [MLCl\(_2\)] (M=Mn\(^{II}\), Fe\(^{II}\), Co\(^{II}\), Ni\(^{II}\), Cu\(^{II}\) or Zn\(^{II}\)) complexes were prepared by the reaction of hydrazine hydrate, methyl acetoacetate or ethyl acetoacetate with metal ion in a 4:4:1 molar ratio. All the complexes are crystalline in nature and stable at room temperature. The low molar conductance values in DMSO suggest their non-ionic nature.

The characteristic features of the IR spectra is the appearance of amide bands at around 1700, 1570, 1280 cm\(^{-1}\) and imine nitrogen band around 1610 cm\(^{-1}\) region, and the absence of NH\(_2\) and alkoxy
The $^1$H NMR spectra also show absence of peaks corresponding to NH$_2$ protons of hydrazine as well as the absence of alkoxy protons of the acetato groups of methyl acetoacetate and ethyl acetoacetate which is in further support of the said macrocyclic framework. The EPR spectra of polycrystalline copper(II) macrocyclic complexes show a single signal for $g_{||}$ and $g_{\perp}$ in the 2.25 and 2.09 regions in which $g_{||} > g_{\perp}$ suggesting that $d_{x^2-y^2}$ is the ground state and the G values which appeared in the range of 2.77 suggests that exchange interaction is present in these complexes. The magnetic susceptibility measurements and the electronic spectral results are consistent with the proposed octahedral geometry for all the macrocyclic complexes.

The fourth part of this chapter describes the synthesis of tetraiminetetraamide macrocyclic complexes. The present study is concerned with the characterization of the newly synthesized complexes: Dichloro/nitrato (8,11,19,22-tetraoxo-3,5,14,16-tetramethyl-1,2,6,7,12,13,17,18-octaazacyclobicosane-2,5,13,16-tetraene) metal(II), [MLX$_2$] (M=Mn$^{II}$, Co$^{II}$, Ni$^{II}$ or Zn$^{II}$; X=Cl or NO$_3$); (8,11,19,22-Tetraoxo-3,5,14,16-tetramethyl-1,2,6,7,12,13,17,18-octaaza-cyclobicosane-2,5,13,16-tetraene) copper(II) dichloride/nitrate, [CuL]X$_2$, (X=Cl or NO$_3$); Dichloro/nitrato(9,10,20,21-dibenzo-8,11,19,22-tetraoxo-3,5,14,16-tetramethyl-
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1,2,6,7,12,13,17,18-octaazacyclobicosane-2,5,13,16-tetraene) metal(II), [MLX₂] (M=Mn^{II}, Co^{II}, Ni^{II} or Zn^{II}; X=Cl or NO₃) and (9,10,20,21-Dibenzo-8,11,19,22-tetraoxo-3,5,14,16-tetramethyl-1,2,6,7,12,13,17,18-octaazacyclobicosane-2,5,13,16-tetraene) copper(II) dichloride/nitrate [CuL]X₂, (X=Cl or NO₃). These were obtained by the template condensation reaction of hydrazine hydrate, dicarboxylic acids and acetyl acetone with metal ion in a 2:2:4:1 molar ratio. The molar conductivity studies indicate that copper (II) complexes are electrolytic in nature while other complexes are non-electrolytic.

The IR spectral data gave bands characteristic of amide group in all complexes. The position of the ν(C=N) stretching vibration in the 1580-1610 cm⁻¹ region and that of amide I band ν(C=O) in the 1670-1720 cm⁻¹ region is in support of coordination through amide nitrogen ruling out the possibility of coordination through amide oxygen. The absence of characteristic NH₂ or OH bands give further evidence for the formation of the proposed macrocyclic framework. The ¹H NMR spectra of all the zinc(II) complexes showed peak around 8.38 ppm which may be assigned to CO-NH protons of the amide group. It showed the phenyl ring peaks at 7.15 ppm and the methylene proton peaks at 3.30 ppm. The absence of carboxylic protons (COOH) of carboxylic acid and NH₂ protons of hydrazine moiety supports the proposed macrocyclic framework.
The EPR spectra of none of the copper (II) complexes showed hyperfine splitting indicating that the paramagnetic centers were not diluted. The existence of \( g_{\|} > g_{\perp} \) suggests that for the \( d^9 \) \( \text{Cu}^{2+} \) complex ion the ground state is \( d_{x^2-y^2} \) i.e. \( (eg)^4 (a_{1g})^2 (b_{2g})^2 (b_{1g})^2 \). The electronic spectra of the copper(II) complexes showed three bands attributed to the \( 2B_{1g} \rightarrow 2B_{2g} \), \( 2B_{1g} \rightarrow 2A_{1g} \) and \( 2B_{1g} \rightarrow 2E_g \) transitions which is in support of a square planar geometry around the \( \text{Cu}^{II} \) ion. The electronic spectra of all other complexes indicate their octahedral geometry around the metal ion. The observed magnetic moment values for all metal complexes are in close agreement with their electronic spectral data.

The fifth part of this chapter describes the synthesis and characterization of tetraoxotetraimine macrocyclic complexes. Synthesis of dichloro/nitrato(1,2-diphenylethane-1,2-dione dihydrazone) metal(II) complexes, \([\text{M(DPEDDH)}_2X_2] \) \( (\text{M}=\text{Mn}^{II}, \text{Co}^{II}, \text{Ni}^{II}, \text{Cu}^{II} \) or \( \text{Zn}^{II} ; X=\text{Cl} \) or \( \text{NO}_3 ; \) DPDDEDH=1,2-diphenylethane-1,2-dione dihydrazone) was carried out by the reaction of 1,2-diphenylethane-1,2-dione dihydrazone with metal ions in a 2:1 molar ratio. Synthesis of dichloro/nitrato(6,9,16,19-tetraone-2,3,12,13-tetraphenyl-1,4,5,10,11,14,15,20-octaazacycloicosane-1,3,11,13-tetraene) metal(II) \([\text{ML}_1X_2] \) \( (\text{M}=\text{Mn}^{II}, \text{Co}^{II}, \text{Ni}^{II}, \text{Cu}^{II} \) or \( \text{Zn}^{II} ; X=\text{Cl} \) or \( \text{NO}_3 \) and those of dichloro/nitrato \( (7,8:17,18\text{-dibenzo}-2,3,12,13\text{-tetraphenyl}-6,9,16,19\text{-tetraone}-1,4,5,10,11,15,20\text{-octaazacycloicosane}-\)
1,3,11,13-tetraene) metal(II) [ML²X₂] (M=Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺ or Zn²⁺; X=Cl or NO₃) complexes was carried out by the reaction of [M(DPEDDH)₂X₂] with succinic or phthalic acid in a 1:2 molar ratio. The low molar conductance values for all the complexes indicate their non-electrolytic nature.

The IR spectra of 1,2-diphenylethane-1,2-dione dihydrazone (DPEDDH) and its complexes are somewhat complex. The IR spectra of all the [M(DPEDDH)₂X₂] complexes are similar but are different from the spectra of free ligand. The behaviour of characteristic NH₂ and C-N stretching vibrations in the free ligand and in the metal complexes have been explained on the basis of a possible trans structure for DPEDDH which transforms into a cis configuration upon chelation in [M(DPEDDH)₂X₂] complexes. These complexes exhibit a strong intensity v(C=N) band at ca. 1600 cm⁻¹. In the complexes the symmetry is lowered, which consequently enhances the v(C=N) band intensity.

The significant feature of the IR spectra of the macrocyclic [ML¹X₂] and [ML²X₂] complexes is the existence of four new bands at ca. 1690, 1540, 1250 and 650 cm⁻¹ attributable to the non-coordinated amide I, II, III and IV bands, respectively. The proposed macrocyclic skeleton is further supported by the absence of uncondensed functional groups (-OH and -NH₂). The ¹H NMR spectra of the [ZnL¹X₂] and [ZnL²X₂] complexes showed a band at ca. 8.43 ppm which is characteristic of amide protons.
Further, the disappearance of bands corresponding to either the -NH$_2$ protons of [Zn(DPEDDH)$_2$X$_2$] or the carboxylic acid protons support cyclization with the formation of amide bonds. The copper complexes show a broad band maximum at ca. 19000 cm$^{-1}$ with a shoulder on the low energy side at ca. 16000 cm$^{-1}$ assignable to $^2$B$_{1g}$ $\rightarrow$ $^2$E$^g$ and $^2$B$_{1g}$ $\rightarrow$ $^2$B$_{2g}$ transitions, respectively, which are attributable to a distorted octahedral geometry around the metal ion. The electronic spectral results for all other complexes suggest an octahedral geometry around the metal ion. The magnetic susceptibility measurements for all complexes are consistent with their respective electronic spectra.

The fourth chapter gives the conclusion of the work done.