This thesis is a small addition to the coordination chemistry of metal chelates with multidentate ligands. The syntheses and characterization of number of macrocyclic ligands and their transition metal complexes is described, and the mode of coordination behaviour of central metal ion(s) is proposed on the basis of available consistent spectroscopic and physico-chemical data. Attempts have been made to study the novel transition-transition and transition-nontransition bimetallic salts. Rare-earth trivalent ions have been interacted in aqueous solution with a biologically important molecule (phytic acid) and a hexaaaza-macrocyclic ligand. Latter's complexes of trivalent lanthanide nitrates have also been synthesized and studied. In continuation of dithiocarbamate chemistry, syntheses and characterization of stable eight-membered ring complexes of methylenebis(piperidinedithiocarbamate) with Group IV metals is described. Herein the introductory Chapter I embodies a succinct account of the past works described in literature and present objectives of undertaking the studies of the above subject(s).

Chapter II includes a direct reaction of triethylenetetramine and diethyl oxalate in DMF in a 1:1 ratio resulting in the formation of a 12-membered tetraaza-macrocycle triethylenetetramine oxamide (L₁). A condensation reaction of triethylenetetramine
and diethyl oxalate in the presence of divalent hydrated metal chlorides (of Cu(II), Ni(II), Co(II), Mn(II) and Cd(II)) and ZnCl₂ in absolute methanol in an equimolar ratio (1:1:1) yields ionic 12-membered macrocyclic complexes. The results show that two water molecules are bound to the central metal ion (Cu(II), Ni(II), Co(II), Mn(II) and Cd(II)) resulting in an octahedral environment while zinc maintains a tetrahedral geometry for being free from water. The i.r. spectral bands show that the two C=O groups of the oxalato species do not participate in coordination. The slight decrease in \( \nu(C=O) \) suggest bonding of the nitrogen of the amide group to the metal ion. The complexes decompose on dissolution in DMSO. Also a 16-membered tetraazamacrocycle, tetrabeno-[1,6,9,14]tetraazacyclohexadecan[2,5,10,13]-tetraone (L²) has been synthesized by the reaction of 1,2-diaminobenzene and phthalic acid in dioxane, and characterized by various spectroscopic and physico-chemical methods. The complexes of the type [CoL²Cl]Cl, [CuL²Cl₂] and [NiL²Cl₂] were obtained by the interaction of the ligand with the corresponding divalent metal chlorides. Studies reveal the [CoL²Cl]Cl complex being a low-spin square pyramidal, while [CuL²Cl₂] and [NiL²Cl₂] exist in an octahedral geometry. The electrochemical studies confirm the formation of a reversible copper(II) \( \rightleftharpoons \) copper(I) redox couple for [CuL²Cl₂], whereas irreversible reduction cobalt(II) \( \rightleftharpoons \) cobalt(I) is exhibited by the
[CoL₂Cl]Cl complex in DMSO. These results are the contribution of the large cavity size of the macrocyclic ligand L².

Chapter III presents the phenomena of stabilization of an MCl₄⁻ moiety (M = copper, nickel, cobalt, manganese, zinc, cadmium, and mercury) by bis(ethylenediamine)copper(II) cation and halide abstraction ability of Sn(IV) from bis(diethylenetriamine)copper(II) dichloride. New ionic bimetallic complexes of the type [Cu(en)₂][MCl₄], (M = Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II) and Hg(II)) have been prepared by reacting bis(ethylenediamine)copper(II) dichloride (1 mol) with the respective dichlorides (1 mol) in absolute alcohol. Elemental analyses, conductivity and magnetic susceptibility measurements, and spectroscopic data (such as i.r., UV-Vis and e.p.r.) confirm that the compounds are 2:2 electrolytes in MeOH and that the copper(II) ion is paramagnetic, maintaining its square planar geometry while metal ions in the anionic moiety of the complexes achieve their omnipresent tetrahedral environment. An increase in magnetic moment values has been observed in the complexes [Cu(en)₂][CuCl₄], [Cu(en)₂][NiCl₄] and [Cu(en)₂][CoCl₄] which is significantly attributed to the ferromagnetic effect and TIP. Novel salts of the type [Cu(dien)₂][Bu₃SnCl₃], [Cu(dien)₂][Ph₂SnCl₄], [Cu(dien)₂][SnCl₆], [Cu(dien)₂][SnBr₄Cl₂] and [Cu(dien)₂][SnI₄Cl₂] prepared by reacting [Cu(dien)₂]Cl₂ with Bu₃SnCl, Ph₂SnCl₂, SnCl₄, SnBr₄ and SnI₄ in MeOH in a 1:1 ratio,
respectively, were characterized by elemental analyses, electronic, i.r. and e.p.r. spectroscopy, magnetic susceptibility and conductivity measurements. The results of these studies reveal that the compounds are 2:2 electrolytes, and copper(II) ion is paramagnetic in an octahedral field. The magnetic moment value suggests that tin(IV) does not interact with the unpaired electron of copper(II) and therefore ferromagnetic or antiferromagnetic effects are ruled out.

Chapter IV describes the investigation of interaction between phytic acid and trivalent rare earth metal ions, viz., Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III) potentiometrically at 25°C in aqueous NaClO₄ and KClO₄ media (μ = 0.1 M NaClO₄ and 0.1 M KClO₄, respectively). The proton-ligand stability constants (pKₗ) of phytic acid and the stability constants (logK) of metal complexes have been evaluated. The results indicate that eight protons of phytic acid are highly acidic, two are weakly acidic and two very weakly acid, titratable in the pH ranges 1.2-4.9, 5.0-8.15 and 8.3-11.0, respectively, in NaClO₄ medium. The stability of each phytic acid-lanthanide ion complex decreases with an increase in the pH and follows the usual trend through the series. This chapter also deals with the coordination behaviour of trivalent lanthanide nitrates of cerium, praseodymium, neodymium, gadolinium, terbium and dysprosium towards a Schiff-base.
hexaaza-macrocyclic ligand \( L^3 \) derived from benzil and diethylenetriamine. The template syntheses of the complexes of the type 
\[ [\text{Ln}L^3(\text{NO}_3)][\text{NO}_3]_2 \] (Ln = lanthanide ion) in methanol was achieved and their characterization by elemental analyses, conductivity and magnetic moment measurements, electronic and i.r. spectroscopic methods reveal that the complexes are 1:2 electrolytes. Results also indicate that one nitrate group is coordinated to the lanthanide metal ion while the other two form the anionic part of the complexes, and the 4f electrons do not participate in bond formation in these complexes. The solution studies of this ligand \( (L^3) \) were also performed in NaClO\(_4\) and KClO\(_4\) media \((\mu = 0.1 \text{ M})\). Results reveal the dibasic behaviour \((H_2L^3)\) of the ligand and forms 1:1 complexes with trivalent lanthanide chlorides in both the media.

Finally the miscellaneous Chapter V embodies (the preparation of three macrocyclic ligands \( L^3, L^4 \) and \( L^5 \) and their transition metal complexes. New 18- and 12-membered macrocycles \( L^3 \) and \( L^4 \) have been prepared from the reaction of diethylenetriamine or 1,2-diaminobenzene, respectively, with benzil in 1:1 ratio in MeOH. They were characterized by elemental analyses, spectroscopy and molecular weight data. The macrocycles \( L^3 \) and \( L^4 \) react with CuCl\(_2\) in MeOH to give octahedral complexes \([\text{Cu}L^3\text{Cl}_2]\) and \([\text{Cu}L^4\text{Cl}_2]\) respectively. C.V. studies indicate a reversible redox couple \((\text{Cu(II)} \rightleftharpoons \text{Cu(I)}) E^0 = \)
-0.48 V) for the complex $[\text{CuL}^3\text{Cl}_2]$ in DMSO, while $[\text{CuL}^4\text{Cl}_2]$ shows no electrochemical activity. Another novel double-ring macrocyclic ligand $L^5$ has been synthesized by a condensation reaction of oxamide-$N,N'$-diacetic acid ($H_4L$) with diethylenetriamine in absolute alcohol in a 1:2 ratio. Its copper(II), nickel(II) and cobalt(II) complexes have been prepared and characterized. The results indicate that the complexes are non-electrolytes and each metal ion with a spin-free state is surrounded by an octahedral configuration. The high magnetic moment values observed have been attributed to a ferromagnetic effect. This chapter also describes the syntheses of new compounds of the type $\text{MCl}_4L^6$, $R_2\text{SnL}_2\text{Cl}_2$, $R_3\text{SnL}_2\text{Cl}$ and $R_4\text{SnL}_2$ $M = \text{Si, Ge, Sn, Ti and Zr}; L^6 = \text{methylenebis(piperidinedithiocarbamate and } R = \text{phenyl).}$ The results indicate the coordination of the two terminal sulphur atoms (C=S) to the metal resulting in the formation of eight-membered ring complexes. (An octahedral geometry has been proposed for the Group IV metal in which the chlorines are adopting cis-configuration.)