CHAPTER 1. INTRODUCTION

Complexes of transition metal ions with multidentate organic ligands have been the subject of intensive research because they not only have interesting spectral and magnetic properties, but they also possess a diverse spectrum of biological activities [1-6]. These complexes often possess remarkable and unique spectroscopic, photophysical and electrochemical properties which may be exploited in sensory and diagnostic applications and there have been a number of reviews [7-12] on the utilisation of transition metal complexes as ion and molecular sensors. Based on the widely diverse coordination environment of the transition metal complexes, and variation in the identities of the coordinating ligands, synthesis of such complexes with desired molecular geometry can be realized. It is well known that several metal chelates have been shown to inhibit tumor growth [13] and some drugs even exhibit increased activity when administered as metal complexes [14-16]. Thus, the study of the coordination of transition metal ions with different types of ligands has been amplified by the recent developments in the field of bioinorganic chemistry and medicines [17]. The rich diversity of transition metal coordination chemistry, therefore, provides exciting prospects for the design of novel coordination ligands having unique structures and valuable functional characteristics [18-24] and significant efforts directed toward the design of specific architectures formed by the self-assembly processes have been carried out in a number of fields of synthetic chemistry [25-27]. In many cases, transition metal ions and their complexes play a central role in controlling the reactivity and mechanism of the chemical reactions of
interest. The unique ability of transition metal ions and their complexes to control the chemistry of environmental, industrial, and biological processes has increased the importance of clarifying their mechanistic behavior in simple and complex chemical processes.

While the knowledge of coordination chemistry is essential to the understanding of the structural and functional features of various biomolecules like metalloproteins, its medical application ranges from the development of MRI contrasting agents, radiopharmaceutical chemotherapeutics to the treatment of metal toxicity [17]. Studies on the complex formation of metal ions with a number of biomolecules or biologically active ligands have, in fact, attracted a lot of interest during the last few years because they act as models for the interactions of metalloenzymes [28] and other complicated proteins [29] in the biological systems. Thus, the bioinorganic chemistry of nickel is a topic of increasing interest [30, 31] because the study of the interactions of Ni(II) with nucleotides offers an unique opportunity for understanding various properties of Ni(II) complexes such as the carcinogenicity of some nickel compounds [32] and the antineoplastic activity recently detected in some nickel complexes [33].

Furthermore, development in the field of bioinorganic chemistry has also led to an increased interest in complexes of N, O-donor ligands since it has been recognized that many of these complexes may serve as models for biologically important species having N and O as bonding sites [28]. Amino acids and their derivatives are extensively studied as typical N, O-donor ligands. In the N-protected amino acids, the introduction of a substituent such as acetyl, benzoyl
or benzylo carbonyl group directly on the amino group could reduce the ligand field of the in-plane donor thus diminishing the affinity of the amino group for the metal ion and permitting a variety of coordinating type. Aroyl hydrazones derived from amino acids and N-protected amino acids are of special interest in that they not only possess many potential donor sites but there is also possibility of keto-enol tautomerism which may lead to varied bonding and stereochemical behavior in the complexes in which they act as neutral or mononegative or even as dianionic ligands depending on the aroyl substituents and the reaction conditions [34, 35]. Their chemistry has also been intensely investigated owing to their cooperative capability [36, 37], their pharmacological activity [38-40] and their use in analytical chemistry as metal extracting agents [41]. The interest in the study of these compounds arose from their tendency to form chelates with transition metals, lanthanides, and main group metals, and their interactions have served as model systems for the study of many biomolecules and metalloproteins.

To understand the complexation reactions of metals, complex formation ability of the ligands and the activities of the complexes formed, it is necessary to have a detailed knowledge about the thermodynamic and solution equilibria involved in these reactions. The extent to which a ligand binds to a metal ion is normally expressed in terms of the stability constants and the information about the concentration of a metal complex in equilibrium mixture can be predicted on the basis of their formation constants in solution. Most of the reported studies on the formation and stability constants of the metal complexes are carried out in aqueous or mixed aqueous organic solvent media. Although there are reports [42, 43]
on the effect of micelles in the reacting systems of many chemical reactions, not
enough attention has been given to understand the role of micelles in the metal
complexation reactions. Since micelles represent a multiphase system where a
species may be distributed in both the bulk aqueous phase and on the micelle’s
surface, study of the metal-ligand complexation reactions in micellar media would
assume a critical significance in view of the fact that reaction behavior observed at
surfactant interfaces are expected to be more representative of many biological
reactions than are reactions studied in dilute aqueous solutions [44].

An extensive literature survey reveals that there are a number of reports on the
synthesis, characterization and physicochemical properties of a number of metal
complexes of various N, O-donor ligands, and mention may be made here of only
the transition metal complexes of N, O-donor Schiff bases and determination of
stability constants of the transition metal complexes. Although an effort has been
made to make an exhaustive survey of the existing literature on the reports on the
study of the various physicochemical constants like stability constant and
thermodynamic parameters, only the abstracts that appeared in the last ten years in
the above fields and relevance to the present work are given below.

Binary and ternary Co(II), Ni(II), Cu(II) and Zn(II) complexes of the type MY
and MXY [X = N-(2-hydroxy-1-naphthylidene)-2,6-diisopropylaniline and Y = N-
(2-hydroxybenzylidene)-2,3-dimethylaniline] had been examined pH-metrically
[45] at 27±0.5°C and 0.1 M ionic strength in 75:25 % (v/v) 1,4-dioxane-water
medium. The values of stability constants for binary and ternary systems were
calculated.
Tayade et al. [46] synthesized 2-amino-4-hydroxy-6-methylpyrimidine and 1-(4-hydroxy-6-methyl pyrimidino)-3-phenylthiocarbamide and the interactions of Cu$^{2+}$, Cd$^{2+}$, Cr$^{3+}$ ions with both the ligands were studied at 0.1 M ionic strength in 70% dioxane-water mixture by Bjerrum method [47] as adopted by Calvin and Wilson [48]. It is observed that these metal ions would form 1:1 and 1:2 complexes. The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k) and the effect of substituents were studied from estimated data.

Thermodynamic protonation constants of 5-aldehydosalicylic acid-aniline Schiff base, and o-, m-, p-Toluidine Schiff bases with 5-aldehydosalicylic acid were determined [49] by Calvin-Bjerrum pH titration technique [47, 48] as used by Irving and Rossotti [50]. The thermodynamic formation constants of the chelates of Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Mg(II) with these four ligands were determined at four different temperatures in 50% (v/v) water-ethanol mixture; the stabilities of complexes follow the Irving-Williams order [51].

Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes were prepared [52] by template reaction of 5-acetyl 2,4-dihydroxyacetophenone (H2-ADA) and ethylenediamine in the presence of metal ions and characterized on the basis of elemental analyses, conductivity, magnetic moments, infrared and electronic spectral data. The Schiff base was reported to bind to metal ions in bis-multidentate ONNO mode leading to two dimensional Schiff base polymers. All the complexes have been assigned octahedral stereochemistry.
Complexation of Cu(II) ion with dapsone in solution was studied spectrophotometrically [53] at absorption maximum of 680 nm at temperatures 25°C, 45°C and 60°C. The stoichiometry of the complex was determined using mole ratio and Job’s continuous variation methods. The data showed that Cu(II) and dapsone combined in 1:1 molar ratio at pH 7.4 with ionic strength maintained at 0.1 M using KNO₃. The stability constants were 0.086 x 10³, 0.090 x 10³ and 0.137 x 10³, 0.142 x 10³ at 25°C and 45°C, respectively.

The complexation equilibria of L-norvaline (Nva) and ferulic acid (FA) were studied [54] in aqueous solutions at 298 K and in fixed ionic strength (0.15 mol·dm⁻³ NaNO₃) by means of potentiometry and spectrophotometry techniques. The complexing capacities of Nva and FA with Fe³⁺, Cr³⁺ and Cu²⁺ ions and their overall stability constants in aqueous solutions were obtained by the HYPERQUAD 2008 program [55] from the potentiometric data. The concentration distributions of the various complex specia in solution were evaluated and discussed. The spectroscopic UV–visible measurements were carried out to give qualitative information about the confirmation of the complexes formed in these solutions.

The complex formation between a new Schiff base and Ni²⁺, Co²⁺, Cu²⁺, and Zn²⁺ ions in ethanol, dimethylformamide (DMF), and acetonitrile (AN) was studied [56] spectrophotometrically using rank annihilation factor analysis (RAFA). According to molar ratio data and Job’s plots, the stoichiometry of complexation between the Schiff base and the cations was 1:2, and that between the Schiff base and Cu²⁺ in all solvents and Zn²⁺ in AN was 1:1. Formation
constants of these complexes were derived using RAFA on spectrophotometric data. The effect of surfactants such as sodium dodecyl sulfate, cetyltrimethylammonium bromide and Triton X-100 on the complex formation constant of Cu$^{2+}$ with the Schiff base in DMF was investigated.

A series of complexes of divalent transition metal ions with malonyl bis(salicyloylhydrazone) (H4MSH) were prepared and characterized [57] with the help of conductometric and potentiometric methods. The proton-ligand and metal-ligand stability constants were obtained pH-metrically. The low molar conductance values measured at 289 K for these complexes indicated their non-electrolytic behavior. The elemental analyses of the complexes showed that the complexes were 1:1 and 2:1 (M:L) stoichiometry with the existence of water, chloride, acetone molecules inside the coordination sphere as evidence from the IR spectral studies and UV–visible spectra of the complexes had been discussed.

Patil et al [58] synthesized a series of Co(II), Ni(II) and Cu(II) complexes of the type ML$_2$ with Schiff bases derived from methylthiosemicarbazone and 5-formyl-6-hydroxy coumarin/8-formyl-7-Hydroxy-4-methylcoumarin. The complexes were non-electrolytes in nature. Based on the analytical, spectral (IR, UV–Vis, ESR, FAB-mass and fluorescence), magnetic and thermal studies, octahedral geometry for all the metal complexes was proposed in which ligand was coordinated to metal ion through azomethine nitrogen, thione sulphur and phenolic oxygen atom via deprotonation.

The condensation reaction of succinyldihydrazide with glyoxal in the presence of divalent metal ions resulted [59] in the formation of the complexes of type
\[ \text{[M(C}_6\text{H}_8\text{N}_4\text{O}_2)\text{X}_2], \quad [M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{Cd(II)} \text{and X = Cl}^{-}, \text{NO}_3^{-}, \text{CH}_3\text{COO}^{-}] \].

The complexes were characterized based on elemental analyses, conductivity measurements and electronic, NMR, infrared spectral studies. A six-coordinated distorted octahedral geometry in which two nitrogen and two carbonyl oxygen atoms were suitably placed for coordination toward metal ion, had been proposed for all the complexes.

Cu(II), Ni(II), Co(II), Mn(II) and Fe(II) complexes with an asymmetric tetradentate Schiff base derived from dehydroacetic acid, 4-methyl-o-phenylenediamine and salicylic aldehyde were synthesized and characterized [60] by elemental analysis, conductometry, magnetic susceptibility, UV–Vis, IR, \(^1\)H-NMR spectroscopy, powder X-ray diffraction analysis of samples and thermal analysis, and screened for antimicrobial activity. The ligand behaved as a dibasic tetradentate ligand towards the central metal ion with an ONNO donor atoms sequence and formed 1:1 (metal:ligand) complexes. The physico-chemical data suggested square planar geometry for the Cu(II) and Ni(II) complexes and octahedral geometry for the Co(II), Mn(II) and Fe(II) complexes. The powder X-ray diffraction data suggested a monoclinic crystal system for the Co(II), Mn(II) and Fe(II) complexes.

A new series of homo- and heteropolynuclear Cu(II) complexes of \(\text{N, N}^{-}\)-bis[1-biphenyl-2-hydroxyimino-2-(4-acetylanilino)-1-ethylidene]diamines were prepared and characterized [61] by different physichemical techniques. Homodi-, homotrinuclear and heterodinuclear Cu(II) perchlorate complexes of tetradentate Schiff bases which possess \(\text{N}_4\) donor sets derived from the condensation of
4-(arylaminoisonitrosoacetyl)biphenyl and diamine derivatives were synthesized and characterized. Elemental analyses, stoichiometric and spectroscopic data of the metal complexes indicated that the metal:ligand ratio of dinuclear Cu(II) complexes were found to be 2:1 while this ratio was 3:2 in trinuclear Cu(II) complexes and the metal complexes indicated that the metal ions are coordinated to the oxime and imine nitrogen atoms. The extraction abilities of the novel ligands were also evaluated in chloroform by using several transition metal picrates such as Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Hg$^{2+}$. Both ligands showed a high affinity to Cu$^{2+}$ ions.

Potentiometric and spectrophotometric methods were employed to investigate [62] the complexation reactions of the two novel tripodal ligands, cis,cis-1,3,5-tris{(2-hydroxybenzilidene)aminomethyl}cyclohexane and cis,cis-1,3,5-tris{[(2-hydroxyphenyl)ethylidene]aminomethyl}cyclohexane with H$^+$ and Fe(III) at an ionic strength of 0.1 M KCl and at 25 ± 1°C in aqueous medium. Three protonation constants each for the ligands were determined and were used as input data to evaluate the formation constants of the metal complexes. Formation of metal complexes of the types FeLH$_3$, FeLH$_2$, FeLH, FeL and FeLH$_{-1}$ were depicted in solution.

A novel Schiff base was prepared [63] via condensation of 4-aminoantipyrine and 2-aminobenzoic acid and characterized based on elemental analysis, mass, IR and $^1$H NMR spectra. The molar conductance data revealed that all the metal chelates prepared were non-electrolytes. IR spectra showed that the ligand was coordinated to the metal ions in a uninegatively tridentate manner with NNO
donor sites of the azomethine-N, amino-N and deprotonated carboxylic-O. Magnetic and solid reflectance spectra suggested that these complexes were octahedral. The thermal behavior of these chelates showed that the hydrated complexes lose water molecules of hydration in the first step followed immediately by decomposition of the anions and ligand molecules in the subsequent steps.

The formation constants of Cu(II), Ni(II), Co(II) and Mn(II) complexes of 3-[(3’-chloro phenyl)-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one were studied [64] by using Irving-Rossoti method [50] at 30 ±1°C and 0.1 M dm$^{-3}$ ionic strength using sodium nitrate as an electrolyte. The factors influencing formation and stabilities of binary complexes were discussed.

The acid-base equilibria of Schiff bases containing cyclobutane and thiazole functional groups and their CuII), Ni(II) and Zn(II) complexes were investigated [65] potentiometrically in 60 % dioxane-water media at 25.0 ± 1°C and ionic strength 0.10 mol L$^{-1}$ NaClO$_4$. The values of the protonation constants determined in this study, log $K_{\text{OH}}$, log $K_{\text{NH(1)}}$ and log $K_{\text{NH(2)}}$, were related to the protonation of the phenolate oxygen atom, the nitrogen atom on the thiazole ring and the imine nitrogen atom, respectively. The variation of the protonation constants of the Schiff bases was interpreted on the basis of structural factors. The Schiff bases form stable complexes with Cu(II), Ni(II) and Zn(II) metal ions. Complex stabilities follow the trend: Cu(II) > Ni(II) > Zn(II), which is in agreement with the Irving-Williams series [51].
Shaker et al. [66] prepared a bidentate Schiff base (L) by condensation of the \( p\)-amino-2,3-dimethyl-1-phenyl-3-pyrozoline-5-on with salicylaldehyde in methanol. Ethanolic solutions of the Schiff base and 8-hydroxyquinoline (Q) reacted with aqueous solution of bivalent metal salts to give complexes of the general formula \([M(L)(Q)]\) where \(M=\text{Fe, Co, Ni and Cu}\). The solid products had been characterized using elemental analyses, magnetic susceptibility, conductivity, FTIR and UV-Vis spectral data.

Protonation constants of Schiff bases derived from 2-hydroxy-3-methoxy benzaldehyde and 2-aminopyridine, 2,3-diaminopyridine, 2,6-diaminopyridine, or 3-aminomethylpyridine were determined spectrophotometrically [67] in the 1:4 methanol/water. The effect of Cu(II) ions on absorption and emission spectra of these ligands was examined in the buffered dioxane/water 1/1 system (pH 5.8). Strong complexation of Cu(II) and formation of a 1:1 complex were observed for the bis-Schiff base derived from 2,3-diaminopyridine. Cu(II) complex with the base with 2-aminopyridine was isolated and characterized by elemental analysis, magnetic susceptibility measurement, UV–Vis and IR spectrometry.

Synthesis of novel Ni(II) complexes with a new hydrazone derived from isoniazid had been reported [68]. In the complexes \([\text{Ni}(L)_2X_2]\) or \([\text{Ni}(L)_3](\text{ClO}_4)_2\), where \(L = \text{N-isonicotamidofurfuraldimine}\) and \(X = \text{Cl}^-\) or \(\text{NCS}^-\), the hydrazone behaves as neutral bidentate coordinating through the carbonyl oxygen and azomethine nitrogen. On the basis of elemental analysis, molecular weight determinations, magnetic susceptibility/moment, thermogravimetric,
electrochemical, and spectroscopic studies, the new complexes were characterized with octahedral geometry.

Cu(II), Co(II), Ni(II), Cr(III), and Fe(III) complexes of a Schiff base derived from the condensation reaction between leucine and 2-acetylpyridine were prepared and characterized [69] by elemental analyses, spectral analyses (IR, UV), thermal analyses (TGA), magnetic measurements, and molar conductivities. IR spectra showed that the ligand acts as a neutral tridentate species coordinating to Cu(II), Co(II), or Ni(II) through the pyridyl nitrogen, azomethine nitrogen, and carbonyl oxygen. It had been suggested that the Schiff base can also act as a mononegative tridentate ligand coordinating to Fe(III) or Cr(III) through the pyridyl nitrogen, azomethine nitrogen, and carboxyl oxygen after displacement of hydrogen from the hydroxyl group. The results suggest tetrahedral geometry around Co(II) and Ni(II), octahedral geometry around Fe(III) and Cr(III), and square-planar geometry around Cu(II).

Complexes of the type \([M(\text{apabh})\text{Cl}]\) and \([M(\text{Hapabh})(\text{H}_2\text{O})\text{SO}_4]\), where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); Hapabh = acetone p-aminoacetophenone benzoylhydrazone were synthesized and characterized [70]. Electronic spectra and \(\mu_{\text{eff}}\) values suggested a square planar geometry for Co(II), Ni(II) and Cu(II) chloro complexes and octahedral geometry for the sulfato complexes. ESR data showed isotropic spectra for \([\text{Cu(}\text{apabh})\text{Cl}]\) and axial spectra for \([\text{Cu(}\text{Hapabh})(\text{H}_2\text{O})\text{SO}_4]\) and \(d_{x^2-y^2}^2\) as the ground state for both Cu(II) complexes. The ligand acts as tridentate monobasic in all chloro complexes bonding through two \(\geq\text{C=N-}\) and a deprotonated enolate groups, whereas
tridentate neutral in all sulfato complexes coordinating through two >C=N- and a >C=O groups. Thermal analysis (TGA & DTA) of [Ni(apabhlCl] complex indicated a multi-step exothermic decomposition pattern.

Coordination complexes of Co(II) and Cu(II) with Pyrrolyl-2-carboxaldehyde isonicotinylhydrazone were synthesized and characterized [71] by elemental analysis, conductance measurements, magnetic susceptibility measurements, $^1$H NMR spectroscopy, IR spectroscopy, UV-Vis absorption spectroscopy, ESR spectroscopy and thermal analysis. IR spectra suggested that the ligand would act as a dibasic donor coordinating through the azomethine nitrogen atom and enolic oxygen atom. ESR and ligand field spectra suggested a tetrahedral geometry for Co(II) complex and a square planar geometry for Cu(II) complexes.

Complexes of the type [M(apash)Cl] and [M(Hapash)(H$_2$O)SO$_4$], where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); Hapash = acetone p-amino acetophenone salicyloyl hydrazone were synthesized and characterized [72] by elemental analyses, molar conductance, magnetic moments, electronic, ESR and IR spectra, thermal studies (TGA & DTA) and X-ray diffraction studies. The ligand coordinates through two >C=N and a deprotonated enolate group in all the chloro complexes, whereas through two >C=N– and a >C=O group in all the sulfato complexes. The electronic spectra suggested a square planar geometry for Co(II), Ni(II) and Cu(II) chloride complexes and an octahedral geometry for the sulfate complexes. ESR data showed an isotropic symmetry for [Cu(apash)Cl] and [Cu(Hapash)(H$_2$O)SO$_4$] in solid state. The X-ray diffraction parameters for [Co(apash)Cl] and [Cu(Hapash)(H$_2$O)SO$_4$] complexes were indexed for a
tetragonal and an orthorhombic crystal lattices, respectively. Thermal studies of [Co(apash)Cl] complex showed a multi-step decomposition pattern. Most of the complexes showed better antifungal activity than the standard miconazole against a number of pathogenic fungi.

Saghatforoush et al [73] described the synthesis and characterization of two new Zn(II) and Cd(II) complexes of the tetradeinate dissymmetric Schiff base, 2-((E)-(2-(2-(pyridine-2-yl)ethylthio)ethylimino)methyl)-4-bromophenol, prepared from 1-(2-pyridyl)-3-thia-5-aminopentane and 5-bromosalicylaldehyde. The complexes were synthesized by treating an ethanolic solution of the ligand with equimolar amounts of appropriate metal salts in 1 M methanolic solution of NaOH or alternatively, by a more direct route in which the two reactants are added to a solution of the ligand immediately after formation of the latter and prior to any isolation. The complexes were characterized by elemental analysis, FTIR, $^1$H-NMR, electronic spectra and molar conductivity. The probable coordination geometries of Zn and Cd in these complexes with mixed N, S and O donor atoms are tetrahedral - and octahedral-like, respectively. Both complexes were found to be 1:1 electrolyte systems in acetonitrile.

Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with a potentially tridentate Schiff base, formed by condensation of 2-amino-3-carboxyethyl-4,5-dimethylthiophene with salicylaldehyde were synthesized by Daniel and co-workers [74] and characterized on the basis of elemental analyses, molar conductance values, magnetic susceptibility measurements, UV–Vis and IR spectral data.
Mn(II) and Co(II) complexes with 1-benzotriazol-2-yl-1-[(p-methoxyphenyl)-hydrazono]propan-2-one (BMHP) were synthesized and characterized [75] by the elemental analysis, magnetic and different spectral techniques. Proton dissociation constant of the free ligand and the stepwise stability constants of its metal complexes were determined potentiometrically in 0.1 M KC1 and 40% (v/v) ethanol-water. The dissociation process was found to be non-spontaneous, endothermic and entropically unfavorable. The values of (-\(\Delta G^0\)) and (-\(\Delta H^0\)) were in the order: Mn(II) < Co(II) < Ni(II) < Cu(II), in accord with the Irving-Williams order [51]. The complexes were found to be stabilized by both enthalpy and entropy changes and the results suggested that complexation is an enthalpy-driven process. The distribution diagrams of the complexes in solution were evaluated.

El-Wahab [76] synthesized Co(II), Ni(II), Cu(II) and Zn(II) complexes of two Schiff base ligands bearing organic acid moiety, N-(2-thienylmethylidene)-2-amino-4-chlorobenzoic acid and N-(2-hydroxybenzylidene)-2-amino-4-chlorobenzoic acid and characterized on the basis of analytical data, molar conductance, IR, \(^1\)H NMR, UV–Vis, mass spectra, magnetic measurements, thermal analysis and X-ray powder diffraction technique. The molar conductance data revealed that these complexes were non-electrolytes. The ligands were coordinated to the metal ions in a terdentate manner with ONO/ONS donor sites of the carbonyl oxygen, azomethine nitrogen and phenolic oxygen or thiophenic sulphur. An octahedral structure was proposed for the prepared metal complexes and some ligand field parameters (\(D_q\), B and \(\beta\)) in addition to CFSE were calculated. The thermal stability of the metal complexes was also evaluated.
Jeragh and co-workers [77] synthesized and characterized the Schiff base, 3-(3-hydroxypyridin-2-ylimino)-1-phenylbutan-2-one (HPIB). The proton-ligand dissociation constant of HPIB and the stepwise stability constants of Cu(II), Ni(II), Co(II), and Mn(II) complexes were also determined potentiometrically in a 40 % (v/v) ethanol-water mixture in the presence of 0.100 M KCl under nitrogen at different temperatures. The stabilities of the complexes follow the order: Cu > Ni > Co > Mn. The dissociation constants of HPIB and the stability constants, log K, of its metal complexes and the corresponding thermodynamic parameters were derived and discussed. The proton-ligand dissociation was found to be nonspontaneous, endothermic, and entropically unfavorable. The different thermodynamic parameters suggested that the complex formation was an enthalpy-driven process. The speciation of the complexes was determined.

The solid complexes of Mn(II), Fe(III), Co(II) and Cu(II) with Schiff bases derived from 3-acetyl-6-methyl-(2H)-pyran2,4(3H)dione (dehydroacetic acid) and 3-chloroaniline and 3-aminophenol, were synthesized and characterized [78] by elemental analysis, conductometry, thermal analysis, magnetic, IR, NMR, UV-Vis spectral studies and X-ray powder diffraction. From the analytical data, the stoichiometry of the complexes was found to be 1:2 (metal:ligand). The low conductance values suggested that the complexes were non-electrolytes. IR spectral data showed that the ligand behaved as a dibasic bidentate ligand with N, O-donor ligand towards metal ions. The powder X-ray diffraction study suggested that the complex had monoclinic crystal system with P2/m space group. The
physico-chemical data indicated that all the complexes possess octahedral geometry. They were also screened for antifungal activity.

A chiral Schiff base N-(S)-2-(6-methoxynaphthyl)-propanoyl-N’-(2-hydroxylbenzylidene) hydrazine (H$_2$L) had been synthesized [79]. Reaction of H$_2$L with Cu(OAc)$_2$·H$_2$O led to the formation of a metal complex {[CuL]·H$_2$O·2DMF}$_x$. In the complex, the potential dinegative tridentate L$^{2-}$ ligand acting as tetradentate bridging ligand coordinate to two metal ions so as to form a novel infinite metal–organic coordination chain structure. The enantiomerically pure ligand H$_2$L presents two different sets of signals in the $^1$H NMR spectrum either in chloroform solution or in dimethylsulfoxide solution, showing the presence of both (E) and (Z) isomers. The X-ray structural investigations of H$_2$L revealed that it is the fully extended E-configuration in the solid state.

Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 4-[2’-hydroxy salicylidene 5’ (2”-thiozylazo] chlorobenzene were synthesized and characterized [80] by elemental analysis, molar conductance, magnetic susceptibility, spectral studies, IR, electronic, ESR and X-ray diffraction studies. The metals coordinate with Schiff base nitrogen atom, azo nitrogen atom and phenolic hydroxyl oxygen atom of the ligand. The ONN donor ligand acts as a tridentate ligand in all complexes. The spectral analysis indicated tetrahedral geometry for Co(II), Ni(II), Zn(II) and Cd(II) complexes while distorted tetrahedral geometry for Cu(II) complex. The X-ray powder diffraction of some complexes suggested tetragonal
crystal system. The ligand and complexes had been screened for their antimicrobial activity against some bacterial and fungal activity.

Stability constants of some metal complexes of 1-Phenyl-2-[2-hydroxy-3-sulfo-5-nitrophenylazo] butadione-1,3 synthesized from benzoylacetone were determined \cite{81} by potentiometric and conductometric titrations. The stability of these complexes decreased in the following order: Fe > Cu > UO$_2$ > Ni > Co > Zn > Cd > Mn > Mg > Ca.

Equilibrium studies \cite{82} of the Schiff base complex systems viz. Co(II), Ni(II), Cu(II) and Zn(II)-vanillin (van) (A) and -L-valine (val)/L-glutamine (gln)/L-glutamic acid (glu)/L-histidine (his) (B) demonstrated the presence of MAB, MA$_2$B or MA$_2$B$_2$ complexes. The stability constant values in the M(II)-van-val/gln/glu systems indicated that the Schiff base ligand (AB) was tridentate in its M(AB) complexes, while it was tetradentate in the M(II)-van-his systems. The results showed that the MA$_2$B and MA$_2$B$_2$ complexes can best be represented, respectively, as M(AB)A and M(AB)$_2$.

Al-Kandary and co-workers \cite{83} reported synthesis and characterization of Zn(II), Cd(II), Pb(II), Hg(II) and phenylmercury(II) complexes of 4-amino-6-hydroxy-2-mercapto pyrimidine (AHMP) on the basis of elemental analyses, IR and $^1$H NMR measurements. The stoichiometry of the complexes was found to be 1:2 except for the phenylmercury(II) complex where the ratio was 1:1. In these complexes, the ligand was bonded to the metal through its sulfur atom. The potentiometric results showed the formation of both 1:1 and 1:2 complexes and the corresponding stability constants were determined for both Zn$^{2+}$ and Cd$^{2+}$ ions.
The high insolubility of Hg(II), phenylmercury(II) and Pb(II) complexes prevented the determination of their stability constants. The concentration distribution of the complexes in solution was evaluated. The effect of temperature on the dissociation constant of AHMP and the formation constants of both the Zn-AHMP and Cd-AHMP complexes were studied and the thermodynamic parameters were calculated.

A new dipodal ligand, N,N′-bis{2-[(2-hydroxybenzylidine)amino]ethyl}malonamide (BHAEM) was synthesized [84] by Schiff base condensation of N,N′-bis(2-aminoethyl)malonamide with two equivalent of salicylaldehyde and characterized on the basis of elemental analyses and various spectral data. The complexation reaction of the ligand with H⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ in solution was investigated by spectrophotometric and potentiometric method. Two protonation constants of BHAEM assigned for two hydroxyl groups of aromatic ring were determined and its hydrolysis mechanism was proposed through potentiometric result. In presence of metal ions, BHAEM shows different coordination properties. All metal ions form ML type complex where the ligand coordinates to the metal ion through two N-amine and two O-phenolate groups. In addition, Ni²⁺ and Cu²⁺ form additional complex species of the type MLH⁻¹ and MLH⁻², respectively due to ionization of amide protons.

Schiff bases derived from the condensation of 3-hydrazino-6-methyl[1,2,4]triazin-5(4H)one and aromatic aldehyde derivatives formed [85] Co(II) and Ni(II) complexes. The structural formulae, the mode of bonding, and geometry of the complexes were characterized by elemental and thermal
analyses as well as IR, electronic spectra, molar conductance and magnetic moment measurements.

Esin et al [86] determined the stoichiometric protonation constants of L-tyrosine, L-cysteine, L-tryptophane, L-lysine, and L-histidine, and their methyl and ethyl esters in water and ethanol–water mixtures of 30, 50, and 70%(v/v) ethanol, potentiometrically using a combined pH electrode system calibrated as the concentration of hydrogen ion. Titrations were performed at 25°C and the ionic strength of the medium was maintained at 0.10 mol·L⁻¹ using sodium chloride. Protonation constants were calculated by using the BEST computer program [87]. The effect of solvent composition on the protonation constants is discussed. The log₁₀ K₂ values of esters generally decreased with increasing ethanol content. However, the log₁₀ K₁ values of the esters of L-tyrosine, L-cysteine, and L-tryptophane were found to increase with increasing ethanol content in contrast those of L-lysine and L-histidine esters.

Protonation constant of an unsymmetrical Schiff base, salicylidene(N-benzoyl)glycyl hydrazone (SalBzGH), and formation constants of its complexes were determined [88] potentiometrically at different temperatures in aqueous dioxane medium. Complexes of SalBzGH with VO(IV), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) had been prepared. Elemental analyses, pH-metric, molar conductance, magnetic susceptibility, electronic, IR, ESR, XRD (powder) and NMR studies was carried out to study the coordination behaviour of SalBzGH toward these metal ions. pH-metric and ¹H NMR studies showed the presence of two dissociable protons in the ligand. IR and NMR spectra suggested
the tridentate nature of the ligand, coordinating as a uninegative species in the Mn(II) complex and as a dinegative species in all the other complexes. Presence of two different conformers of the ligand at room temperature and stabilization of a single conformer upon complex formation was established from 1H NMR spectra of the metal-free ligand, Zn(II) and Hg(II) complexes recorded at 296 K. Electronic and ESR spectra indicated highly distorted tetragonal geometry for VO(IV) and Cu(II) complexes. XRD powder patterns of the Zn(II) complexes were indexed for an orthorhombic crystal system.

Reddy et al. [89] synthesized Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of a dibasic bis-chelating ligand, 5-acetyl 2,4-dihydroxy acetophenone semicarbazone (H$_2$-ADAS) and characterized on the basis of their elemental analyses, conductivity, magnetic moments, IR and electronic spectral data. Metal to ligand ratio in all the chelates had been found to be 1:1. The Schiff base behaves in a dibasic pentadentate manner with OO and ONN donor atoms. All the complexes had been assigned octahedral stereochemistry. The ligand H$_2$-ADAS forms polymeric metal complexes with first row divalent transition metal ions.

Complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and UO$_2$(VI) with N-(2-pyrdylidene)-benzothiazole-2-ylacetoxydrazone were prepared [90] in ethanolic solution and characterized by physical and spectral methods. IR, electronic, TGA, and ESR spectra of the complexes, as well as IR, $^1$H NMR and mass spectra of the ligand had been obtained. IR spectra showed that the ligand coordinates as an anionic tridentate ligand via the azomethine nitrogen, pyridyl nitrogen and enolic oxygen. A tetrahedral structure was proposed for Co(II) and Ni(II) complexes
while an octahedral structure was suggested for the Fe(III) complexes. All Cu(II) complexes had square-planar geometry.

Golcu et al. [91] reported the synthesis and potentiometric studies of Cd(II) and Cu(II) complexes of 4-[(4-bromo-phenylimino)-methyl]-benzene-1,2,3-triol, 4-[(3,5-di-tert-butyl-4-hydroxy-phenylimino)-methyl]-benzene-1,2,3-triol, 3-(p-tolyl imino-methyl)-benzene-1,2-diol, 3-[(4-bromo-phenylimino)-methyl]-benzene-1,2-diol, and 4-[(3,5-di-tert-butyl-4-hydroxy-phenylimino)-methyl]-benzene-1,3-diol. The structure of the ligands and their complexes was investigated using elemental analysis, FT-IR, UV–Vis, $^1$H and $^{13}$C NMR, mass spectra, magnetic susceptibility and conductance measurements. In the complexes, all the ligands behaved as bidentate ligands, oxygen in the ortho position and azomethine nitrogen atoms of the ligands coordinate to the metal ions. The keto-enol tautomeric forms of these Schiff bases had been investigated in polar and non-polar organic solvents. Protonation constants of these Schiff bases and stability constants of their Cu(II) and Cd(II) complexes were determined in 50% DMSO–water media at 25.00 ± 0.02°C under nitrogen atmosphere and ionic strength of 0.1 M sodium perchlorate. All the Schiff bases had been observed to possess two protonation constants. The variation of protonation constant of these compounds was interpreted on the basis of structural effects associated with the substituents. Cu$^{2+}$ and Cd$^{2+}$ ions formed stable 1:2 complexes with these bases.

Co(L)$_2$, Ni(L)$_2$, Cu(L)$_2$ and Zn(L)$_2$ complexes were synthesized [92] from p-aminoacetophenoneoxime and 5-Chlorosalicylddehyde and Co(AcO)$_2$.4H$_2$O or Ni(AcO)$_2$ or Cu(AcO)$_2$.H$_2$O or Zn(AcO)$_2$.2H$_2$O in 1:2 molar ratio, employing a
template approach. Based on elemental analyses, molar conductivity and magnetic susceptibility data, IR, $^1$H and $^{13}$C NMR and UV-Vis spectra, as well as thermal analyses (TG), a tetrahedral geometry for the complexes was determined. The data showed that the ligand coordinates to the metal ion via –C=N- and –C-O- groups.

Omar and Mohamed [93] reported the synthesis and characterization of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II) and UO$_2$ (II) chelates of 1-(2-thiazolylazo)-2-naphthalenol (TAN). The dissociation constants of the ligand and the stability constants of the metal complexes were calculated pH-metrically at 25°C and 0.1 M ionic strength. The solid complexes were characterized by elemental and thermal analyses, molar conductance, IR, magnetic and diffuse reflectance spectra. The molar conductance data revealed that the chelates are non-electrolytes. IR spectra showed that the ligand was coordinated to the metal ions in a terdentate manner with ONN donor sites of the naphthyl OH, azo N and thiazole N. An octahedral structure was proposed for Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II) and UO$_2$ (II) complexes and a square planar structure for Cu(II) and Pd(II) complexes. The thermal behaviour of these chelates showed that water molecules (coordinated and hydrated) and anions were removed in two successive steps followed immediately by decomposition of the ligand molecule in the subsequent steps.

Garg and co-workers [94] prepared and characterized the complexes of Cu(II), Ni(II), Co(II), and Zn(II) with 2-[2-(6-methylbenzothiazolyl)azo]-5-dimethylamino benzoic acid by elemental analysis, vibrational spectra, magnetic susceptibility measurements, conductance measurements and EPR spectra.
Stability constants had been evaluated potentiometrically. Electronic spectra, magnetic susceptibility measurements and molecular modeling studies support a distorted square planar geometry around the metal ions. Vibrational spectra indicated the coordination of the azo group, nitrogen of benzothiazole, the carboxylate anion and the acetate ion on complexation with the metal ion. All complexes were found to be monomers.

The stability of the complexes followed the order: Cu(II) > Ni(II) > Co(II) > Zn(II). The binary and mixed-ligand complexes formed between ligands (histidine (His), histamine (Him) and glycine (Gly)) and some transition metals (Cu(II), Ni(II) and Zn(II)) were studied potentiometrically [95] in aqueous solution at (25.0 ± 0.1)°C and ionic strength 0.10 M KCl in order to determine the protonation constants of the free ligands and stability constants of binary and ternary complexes. The complexation model for each system has been established by the software program BEST [87] from the potentiometric data. The most probable binding mode for each binary species of histidine and for all mixed species was also discussed based upon derived equilibrium constants and stability constants related to the binary species. The ambidentate nature of the histidine ligand, i.e. the ability to coordinate histamine-like, imidazolepropionic acid-like and glycine-like modes was indicated from the results obtained. The concentration distributions of various species formed in solution were also evaluated. In terms of the nature of metal ion, the complex stability followed the trend: Cu(II) > Ni(II) > Zn(II), which was in agreement with the Irving-Williams order [51].
4-Acrylamidobenzenesulfonylazide (ABS) was synthesized [96] and characterized by elemental analyses and IR spectroscopy. Proton-monomeric ligand dissociation and metal-monomeric ligand stability constants of ABS with some metal ions were also determined potentiometrically in 0.1 M KCl and a 50% (v/v) ethanol–water mixture. In the presence of 2, 2'-azobisisobutyronitrile as an initiator, the dissociation and stability constants of ABS were determined in its polymeric form (PABS). The influence of temperature on the dissociation of ABS and the stability constants of its complexes in monomeric and polymeric forms were precisely studied. The pK$_{\text{H}}$ value of PABS was found to be higher than that for ABS, indicating that the vinyl group in the monomeric form decreases the electron density and hence reduces the N bond H bond strength. The stability constants of the metal complexes with the polymeric form were higher than those of the monomeric form. This revealed that the ligand in a polymeric form could be considered as a better complexing agent.

Hankare et al [97] synthesized and characterized Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of a Schiff base obtained by condensation of 5-(2'-thiazolylazo) salicylaldehyde and p-methoxy aniline by elemental analysis, magnetic susceptibility, molar conductance, IR, electronic spectra, ESR and thermal analysis (TGA). The ONN environment of the metal ion was realized in the complexes by involvement of the -N=N- group in coordination. The analysis of magnetic moment and electronic spectral data indicated tetrahedral geometry for the complexes except Cu(II) complex which had a distorted tetrahedral geometry.
Kabir et al [98] determined the stability constants ($\Delta \log K$) of the ternary Cu(II) and Ni(II) complexes of folic acid and some amino acids such as tryptophane, tyrosine, dipicolinic acid and adenosine triphosphate by potentiometric method and their redox behavior had been examined by cyclic voltammetric method. A statistical increased in the value of mixed ligand formation constants was observed by small negative or positive value of $\Delta \log K$. The potentiometric and cyclic voltammetric study showed that Ni(II) complexes were more stable than Cu(II) complexes.

Dogan and co-workers [99] determined the stoichiometric protonation constants for some $\alpha$-amino acids (glycine, L-alanine, L-methionine, L-phenylalanine, and L-threonine), the Schiff bases derived from them and 2-hydroxy-1-naphthaldehyde, along with the stoichiometric stability constants of Schiff base–Mn(III) complexes. These equilibrium constants were determined potentiometrically using a combined pH electrode system calibrated in concentration units of the hydrogen ion at 25°C, and at an ionic strength of 0.10 mol-dm$^{-3}$ NaCl in 30 and 50 % dimethyl sulfoxide–water mixtures. The calculations of these constants were carried out using the PKAS and the BEST [87] computer programs. In addition, the effects of solvent composition and structures on the protonation and the complex formation constants were investigated. The mole ratio of Mn(III) to amino acid-Schiff bases was also determined and it was found that the complexes were of the MnL$_2$ type.

The protonation constants of a number of mono-substituted anilines were determined [100] potentiometrically in 0, 20, 30, 40, 50, and 60 % (v/v) dioxane –
water mixtures at \((25.00 \pm 0.02)\, ^0\text{C}\) at an ionic strength of \(0.1\, \text{mol}\cdot\text{dm}^{-3}\) in sodium perchlorate. The data from the potentiometric titrations were evaluated using the BEST [87] computer program. The trends in the values of the protonation constants of anilines were explained in terms of the nature of substituent and the solute–solvent and solvent–solvent interactions. Furthermore, the effects of the substituents on the basicity of aniline, the additivities of these effects, and the applicability of the Hammett equation to the behavior of these substituents are discussed.

Formation and protonation constants of seventeen Schiff bases-derived from 2-hydroxyaniline with some substituted benzaldehydes, and the stability constants of Cu(II) complexes of these Schiff bases were determined [101] potentiometrically in 20, 40, and 60\%(v/v) dioxane–water media. The data from the potentiometric titrations were evaluated with the BEST [87] computer program. For all Schiff bases studied, it was observed that the \(\log K_{\text{OH}}\) values related to the protonation equilibria of the phenolic oxygen increase while the \(\log K_{\text{NH}}\) values related to the protonation equilibria of the azomethine nitrogen decrease with increase in the dioxane content. The variation of these constants was discussed on the basis of specific solute–solvent interactions and structural changes of Schiff bases from water to the dioxane–water media. The titrimetric-pH investigation of substituted benzilidene-2-hydroxyaniline systems had also revealed the formation of stable mono-Schiff base complexes with \(\text{Cu}^{+2}\) ion.

The proton dissociation constant of 5-(40-sulfonylazidophenylazo)-3-phenyl-2-thioxothiazolidin-4-one (SPT) and the stability constants of its complexes with
some metal ions were calculated \cite{102} potentiometrically in 0.1 M KCl and 40 % (v/v) ethanol–water mixture. The order of stability was found to be Mn < Co < Ni < Cu < Zn. The effect of temperature on the dissociation of SPT and the stability of its complexes were studied. The corresponding thermodynamic functions were derived and discussed. The dissociation process is unspontaneous, endothermic, and entropically unfavorable. The formation of the metal complexes was found to be spontaneous, endothermic and entropically favorable.

Raman \textit{et al} \cite{103} carried out the synthesis of Cu(II), Co(II), Ni(II) and Zn(II) chelates with a new Schiff base derived from benzil-2,4-dinitro-phenylhydrazone with aniline. Microanalytical data, molar conductance, and magnetic susceptibility values have been obtained, and IR, $^1$H NMR, $^{13}$C NMR, UV-Vis, CV and EPR spectral studies have been carried out to suggest tentative structures for the complexes.

Ni(II) and Cu(II) complexes with Schiff bases 4-dimethylaminobenzylidene-4-chloroaniline (DABCA)/4-dimethylaminobenzylidene-4-bromoaniline(DABBA) /4-dimethylamino benzylidene-3-nitroaniline (DABNA) of general formula $\text{ML(H}_2\text{O)}_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$ and $\text{MLCl}_2\text{(H}_2\text{O)}_2\cdot 2\text{H}_2\text{O}$ have been synthesized \cite{104}. Coordination of azomethine nitrogen in the Schiff base to the metal has been proposed. Ligand field parameters of some of the complexes have been calculated.

The dissociation constant of 4-sulfamethoxazoleazo-3-methyl-2-pyrazolin-5-one and metal-ligand stability constants of its complexes with Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$ ions have been determined \cite{105} potentiometrically in 0.1 M KCl and 40 % ethanol-water mixture. The order of the stability constants of the complexes
decreases in the sequence Cu > Ni > Co > Mn. The effect of temperature was studied and the corresponding thermodynamic parameters (ΔG, ΔH, and ΔS) were derived and discussed. The dissociation of the ligand and the formation of the metal complexes were spontaneous, endothermic, and entropically favourable.

Mukherjee et al [106] investigated the complex formation equilibria of Co(II), Ni(II), Cu(II) and Zn(II) with anthranilic acid N, N-diacetic acid (H₃ada) in the absence and presence of 1,10-phenanthroline (phen), bipyridine (bipy), ethylenediamine (en), glycinate (gly') and oxalate (ox²⁻) (B) in aqueous solution at 25 °C at a fixed ionic strength 0.1 M (NaNO₃) pH-metrically and indicates the formation of simple binary complexes M(ada) and M(B) and ternary complexes M(ada)(B). M(ada)(B) complexes are formed according to equilibria M(B) + adaH M(ada)(B) + H, with B = phen and bipy, and M(ada) + BH M(ada)(B) + H, with B = en, gly' and ox²⁻ ligands.

A tripodal tetraamine ligand N{(CH₂)₃NH₂}{(CH₂)₂NH₂}²⁺ (pee), has been investigated [107] as an asymmetrical tetraamine chelating agent for bivalent Co, Ni, Cu, Zn and Cd metal ions. The protonation constants for this ligand and the formation constants for its complexes have been determined potentiometrically in 0.1 M KCl at 25 °C. The successive protonation constants (log Kⁿ) are: 10.22, 9.51, 8.78 and 1.60 (n = 1-4). One complex with formula M(pee)₂ (M = Co, Ni, Cu, Zn and Cd) is common to all five metal ions and the formation constant (log β_ML) is: 12.15, 14.17, 16.55, 13.35 or 9.74, respectively. In addition to the simple complexes, Co, Cu and Zn also give hydroxo complexes, and Cu and Ni give complexes with monoprotonated pee. [Zn(pee)](ClO₄)₂ and [Cd(pee)Cl](ClO₄)
complexes were isolated and are believed to have tetrahedral and trigonal-bipyramidal structures, respectively.

Merce et al. [108] reported the stability constants of the complexes Al(III), Cd(II), Gd(II) and Pb(II) with vitamin D₃ in a 30/70 % v/v water-ethanol medium at 25.0°C. The logarithms of the overall stability constants are: $\log K_1 = 12.4 \pm 0.5$, $7.6 \pm 0.3$, $9.33 \pm 0.07$, and $9.1 \pm 0.5$, respectively, whereas the logarithms of $\log K_2$ are $24.4 \pm 0.5$ (Al$^{3+}$), $14.3 \pm 0.3$ (Cd$^{2+}$), and $15.4 \pm 0.5$ (Pb$^{2+}$). Gd$^{3+}$ ion forms only the 1:1 complex. These values are compared to those reported previously and correlations are established between the stability constants and physical properties, such as the ionization energy.

Acid-base equilibria and metal ion chelating tendency of 3-(acetophenone hydrazone)-6-phenylpyridazine (AHP) and its para-substituted derivatives (XAHP), $X = \text{NH}_2$, Cl, O\text{H} and OMe were potentiometrically investigated [109] in 75 % (v/v) dioxane-water at 298 K and 0.1 M KNO₃. For the same metal ion, the order of stability decreases in the sequence: $\text{NH}_2\text{AHP} > \text{OHAHP} > \text{OMeAHP} > \text{AHP} > \text{CIAHP}$, which is the same order of decreasing the electron-repelling property of the substituent ($X$) and consequently the basicity of the ligands. The thermodynamic parameters have been evaluated.

Kubicek et al. [110] synthesized bis(aminomethyl)phosphinic acid, ($\text{NH}_2\text{CH}_2$)$_2\text{PO}_2\text{H}$ (HL), using a new procedure and studied its coordination ability towards Co(II)/(III), Ni(II), Cu(II) and Zn(II) both in solution and in the solid state. Because of the presence of two nitrogen atoms, the ligand exhibits a higher overall basicity than common (aminoalkyl)phosphinic acids. Consequently, the
values of the determined stability constants are comparable with those found for (aminoalkyl)phosphonic acids. NMR titrations of Zn(II) point to the interaction of phosphinate with the metal ion in a strong acid solution. The X-ray structures show several coordination modes in the solid state. In Co(II)/(III), Ni(II), Cu(II) complexes, the central ion is octahedrally coordinated with two phosphinate oxygen atoms, two molecules of water and two chlorides in all-trans arrangement. Participation of the donor groups in crystals isolated from neutral solutions depends on the metal ion. In the zinc(II) complex, two phosphinate oxygen atoms and two amine nitrogen atoms (trans to each other) of two different ligand molecules are coordinated in an equatorial plane and two amino groups of the two other ligand molecules are bound in axial positions. Thus, each molecule of the amino acid forms a five-membered N, O-chelate to one Zn$^{2+}$ ion and the other amino group is bound to the neighbouring ion creating an infinite chain. Ni forms a trans-O,O$^\prime$-[Ni(H$_2$O)$_2$(L-N,N)$_2$] complex in which the metal ion is chelated by four amine nitrogen atoms forming two six-membered chelates in an equatorial plane and the octahedron is completed with two water molecules at the apical positions. The phosphinate group is not coordinated. The above results point to a relatively low coordination ability of the phosphinate group; however, due to its low pK$_A$, it is able to bind metal ions at lower pH than other coordinating groups do.

Garg et al [111] carried out the chemical-speciation and molecular modelling studies for accessing the interactions of metal ions with some amide containing ligands by using the BEST program [87] and method of Bjerrum and
Calvin [48,49] as modified by Irving and Rossoti [51] has been used to find out the values of stability constants. The order of stability constants is found to be fairly in agreement to Irving-Williams order [52]. Molecular modelling studies have been carried out to determine the ideal site for metal binding to the ligands PCPAH and PCBAH.

Weyhermüller and co-workers [112] described the ligating properties of a tridentate ligand, methylamino-N,N-bis(2-methylene-4,6-dimethylphenol), H$_2$L, with [O,N,O]-donor atoms and characterized its complexes [Fe(III)$_2$L$_3$] (1), [Fe(III)L$_2$]$^-$ (1a), [Mn(IV)L$_2$] (2), [Mn(III)L$_2$]$^-$ (2a), and [Cr(III)L$_2$]$^-$ (3) by various physical techniques, including IR, MS, UV–Vis, electrochemical, EPR, Mössbauer and magnetic susceptibility measurements. Complex 1 contains a dinuclear Fe$_2$L$_3$ unit with two different 5- and 6-coordinated Fe(III) centers. The overall geometry around the Mn(IV) ion in 2 and the Cr(III) ion in 3 is best described as a distorted meridional octahedron with two trans-positioned nitrogens of the aminebis(phenolate) ligand. The isoelectronic [Cr(III)L$_2$]$^-$ (3) and [Mn(IV)L$_2$] (2) with distinctive metal–ligand covalent binding characteristics have been used as probes for comparison of EPR spectra. Complex 2 containing Mn(IV) with its higher ionic charge and covalency has a significantly larger zero-field splitting parameter D than that of Cr(III) in 3. That the electrochemical oxidations are ligand-centered, i.e. formation of phenoxy radicals from the coordinated phenolates, except for the Mn(III) compound 2a, where the first oxidation occurs at metal center generating Mn(IV) species 2, have been shown by voltammetric methods.
PS-LCuDMF, PS-LNi3DMF, PS-LCo3DMF, PS-LFeCl2DMF, PS-LZnDMF, PS-LCdDMF, PS-LMn3DMF, PS-LMoO\textsubscript{2}DMF, PS-LZr(OH)\textsubscript{2}2DMF and PS-LUO\textsubscript{2}DMF (DMF = dimethylformamide compounds were synthesized [113] by the reaction of metal salt/metal coordination compounds with the polystyrene supported Schiff base (PS-LH\textsuperscript{2}) obtained by the reaction of chloromethylated polystyrene, 3-formylsalicylic acid and ethanolamine compounds and characterized by elemental analyses, IR, electronic, ESR spectral and magnetic susceptibility measurements. The Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) compounds are paramagnetic while the Zn(II), Cd(II), Zr(IV), Mo(VI) and U(VI) compounds are diamagnetic. The magnetic and ESR data indicate the magnetically dilute nature of the metal centres. The shifts of the \(\nu(C=\text{N})(\text{azomethine})\), \(\nu(C-O)(\text{phenolic})\) and \(\nu(C-O)(\text{alcoholic})\) stretches have been monitored to find out the donor sites of PS-LH\textsuperscript{2}. A square planar structure for PS-LCuDMF; a tetrahedral structure for PS-LZnDMF and PS-LCdDMF; an octahedral structure for PS-LNi3DMF, PS-LCo3DMF, PS-LFeCl2DMF, PS-LMn3DMF, PS-LMoO\textsubscript{2}DMF and PS-LUO\textsubscript{2}DMF have been suggested for the compounds. PS-LZr(OH)\textsubscript{2}2DMF is pentagonal bipyramidal.

A new ligand, N-isonicotinoyl-N'-thiobenzoylhydrazone (HINTB), has been prepared [114] by the reaction of isonicotinic acid hydrazide and carboxym ethyl dithiobenzoate. The addition complexes [M(HINTB)\textsubscript{2}Cl\textsubscript{2}] [M=Co(II), Ni(II), Zn(II)], [Cu(HINTB)Cl\textsubscript{2}], M(HINTB)\textsubscript{2}(CH\textsubscript{3}COO)\textsubscript{2} [M=Co(II), Ni(II)] and deprotonated complexes [Cu(INTB)(CH\textsubscript{3}COO)] and [Zn(INTB)\textsubscript{2}] also have been prepared and characterized by elemental analyses, magnetic susceptibility,
electronic, NMR and IR spectral data. The room temperature ESR spectra of [Cu(HINTB)Cl₂] and [Cu(INTB)(CH₃COO)] are characteristic of monomeric and dimeric species, respectively.

Hacht et al [115] performed a quantitative study of Zn(II) and Cu(II) complex formation with orotic acid under physiological conditions (37°C; 0.15 mol-dm⁻³ NaCl) using the glass electrode potentiometric technique. Several species have been identified within the pH range 2–10 for the metal-to-ligand concentration ratios investigated. Three mononuclear complexes, ML, ML₂, and ML₂H⁻, have been characterized with both metals. In addition, the polynuclear species M₃L₂H⁻₂ has been found with Cu(II). Formation constants for all these species have been calculated with the help of the SUPERQUAD computer program [116]. UV absorption and IR spectroscopic measurements combined with speciation calculations have been used to confirm corresponding structures.

2-Acrylamidosulphadiazine (ASD) was synthesized [117] and characterized by elemental analyses, IR and ¹H NMR spectra. Proton-monomeric ligand dissociation and metal-monomeric ligand stability constants of ASD with some metal ions were determined potentiometrically in 0.1 M KCl and 40 % (v/v) ethanol-water mixture. In the presence of 2,2’-azobisisobutyronitrile as initiator, the dissociation and stability constants of ASD were determined in polymeric form (PASD). The influence of temperature on the dissociation of ASD and the stability constants of their complexes in monomeric and polymeric forms were critically studied. The pK₂⁺ value of PASD was found to be higher than ASD, this means that the vinyl group in the monomeric form decreases the electron density
and hence reduces the N–H bond strength. The stability constants of the metal complexes in polymeric form are higher than those of the monomeric form. This is quite reasonable because the ligand in a polymeric form is considered as a better complexing agent.

Proton-ligand dissociation and metal-ligand stability constants of cinnamaldehyde anthranilic acid (CAA) with some transition metal ions were determined potentiometrically [118] in 0.1 M KCl and 50 % (v/v) ethanol–water mixture. The effect of temperature on the dissociation of CAA and the stability of its complexes were studied in monomeric and polymeric forms. The corresponding thermodynamic functions were derived and discussed. The dissociation process is non-spontaneous, endothermic and entropically unfavourable. Formation of the metal complexes was spontaneous, endothermic and entropically favourable.

The equilibria involved in the formation of Mn(II), Fe(II), Co(II), Ni(II), Zn(II) complexes with different ligands like (1) di-N-phenyl pyromellitic di-imide, (2) di-N-pyridyl pyromellitic di-imide, (3) N-2,thiazolin O-amino benzamide, (4) 4-oxo-4(2-thiazolin) amino butanoic acid (5) 4-oxo-4(2-thiazolin amino butenoic acid), (6) 3-hydroxy pyridine 2-carboxamide were studied by pH titration technique [119] at different ionic strength, different percentages of solvent and different temperatures. The stability constants of the binary complexes have been evaluated by Irving and Rossotti’s method [50]. The variation of the stability of binary metal complexes is discussed in terms of the effect of (1) ionic
strength (2) dielectric constant (3) temperature and (4) correlation of stabilities of metal complexes.

Matho and Chandra [120] isolated the complex compounds of pyridine-3-carboxylic acid hydroxy methyl amide, LH with Ni(II), Cu(II), Fe(II) and Cr(III) and characterized on the basis of their elemental analysis, IR, magnetic and electronic studies. The tridentate character of the ligand and the presence of intrahydrogen bonding in it are evidenced from the IR spectral study. It forms complex with Cu(II) and Cr(III) after losing one proton (H+) from its imidolic form at pH 8 but no proton is lost in the formation of Ni(II) and Fe(II) complexes at pH = 6. The complexes are tetrahedral except Cu(II) complex, which is square planar. All complexes are paramagnetic.

Deepa et al [121] carried out synthesis and characterization of a series of transition metal complexes of N-methyl and N-ethyl acetoacetanilide isonicotinyl hydrazones (L1H2 and L2H2 respectively) by using elemental analysis, magnetic susceptibility measurements and UV-VIS, IR, 1H NMR spectral studies. IR spectral studies revealed that the ligand behaves as tridentate di- or mono-anions co-ordinating through the anilide oxygen and isonicotinyl carbonyl oxygen and azomethine nitrogen atoms. Thermogravimetric studies of Mn(II), Co(II), Ni(II) and Cu(II) complexes of N-methyl acetoacetanilide (L1H2) were also carried out. Antifungal studies of L2H2 and Mn(II), Co(II), Ni(II) and Cu(II)andZn(II) complexes of both the ligands were also carried out.

Equilibrium-based computer models on eight Schiff base complex systems, viz. Co(II)/Ni(II)/Cu(II)/Zn(II)-2-pyridinecarboxaldehyde(A)-L-threonine (thr)
and L-glutamin (gln) (B) systems demonstrated [122] the formation of Schiff base complexes having the stoichiometry MAB, MA₂B and Ma₂B₂. The Schiff base (AB) binds the metal ion in a tridentate manner. Tetrahedral geometry for CoAB and NiAB, square-planar geometry for CuAB and octahedral geometry for M(AB)₂ complexes are indicated.

Transition metal complexes of furfurylidene(N-benzoyl)glycyl hydrazone, FBzGH, of the formulae [M(FBzGH)₂Cl(H₂O)]Cl (M = Mn, Cu, Zn, Cd, Hg), [Co(FBzGH)₂]Cl₂·H₂O and [Ni(FBzGH)₂Cl₂]·H₂O were isolated [123] from acidic solutions and the complexes [M(FBzG)₂ (H₂O)₂] (M = Co, Ni, Cu), from neutral solutions. Elemental analyses, molar conductances, magnetic susceptibilities, electronic, pH-metric, ESR, IR, and NMR studies had been carried out on these complexes to illuminate the ligational behavior of FBzGH toward the divalent metal ions. Formation constants of the metal chelates were determined pH-metrically in aqueous-dioxane. Bidentate nature of the hydrazone coordinating as a neutral species in the adducts and as a uninegative one in the neutral complexes was suggested. ¹H NMR spectra indicated the presence of two different conformers of the ligand at room temperature even after complexation which would coalesce at a temperature higher than 340 K indicating that one of the conformers was stabilized. A highly shielded chemical shift value of ¹¹³Cd NMR showed a strongly bound but weakly coordinated Cd²⁺ ion.
The literature survey reveals the following noteworthy points:

1. There are reports on the synthetic, magnetic and spectral studies of transition metal complexes of a number of hydrazones in aqueous and organic media.

2. Amidst the abundant literature on the transition metal complexes of various N, O-donor ligands, a considerable number of reports appear on the determination of the stability constants and thermodynamic parameters of the transition metal complexes. However, most of the studies reported were carried out in aqueous and/or mixed solvent media.

3. There are a few reports on the complexes of N-benzoylglycine hydrazide and its hydrazones with transition metal ions [88, 123, 124-129] and lanthanide ions [130-138].

4. There is no report in the literature till date on the complexation reactions, stability constants and thermodynamic data of the transition metal complexes of Schiff bases derived from N-benzoylglycine hydrazide in aqueous, organic and/or aqueous-micellar media.

We have, thereof, synthesized two novel Schiff bases from the condensation of N-benzoylglycine hydrazide with two carbonyl containing compounds, 4-dimethylaminobenzaldehyde and 3-aminoacetophenone, and carried out a detailed study on the interactions of the transition metal ions with the two bases employing potentiometric titration and various physico-chemical techniques. Proton - ligand and metal - ligand formation constants of the bases and their
Ni(II), Cu(II) and Cd(II) complexes along with the thermodynamic parameters associated with the protonation and complexation reactions have been evaluated. The studies have been carried out in both aqueous and micellar media containing nonionic and ionic surfactants and the effect of the micelles on the reactions are being studied. The Cu(II), Ni(II) and Cd(II) complexes are also isolated and characterized. Studies have also been made on the spectral properties of the complexes. Results of the investigations are described in the following chapters.
References


structures of \([\{\text{Cu}(\text{Hsb})(\text{CCl}_3\text{CO}_2)\}_2]\) and \([\{\text{Cu}(\text{Hsb})\ (\text{ClO}_4)\ (\text{C}_2\text{H}_5\text{OH})\}_2]\) and the related salicylaldehyde acetylhydrazone (H_2sa) complex, \([\text{Cu}(\text{Hsa})\text{Cl}((\text{H}_2\text{O}))\cdot\text{H}_2\text{O}]. \text{Inorg. Chim. Acta.}, 267, 27-38 (1998).


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nickel(II), cobalt(II), iron(III), zinc(II), cadmium(II), manganese(II), molybdenum(VI), zirconium(IV) and uranium(VI). *Indian J. Chem.*, 41A:7, 1385-1390 (2002).


