1-INTRODUCTION

1.1. General Introduction

In recent years several studies have linked the concentrations of specific transition metal ions to various diseases. Low serum copper level is used as a marker for wilson´s disease. Serum copper levels are elevated in a large number of chronic and acute illnesses such as Hodgkin´s disease, leukemia, and many other malignancies**(1)**. Zinc is an important nutritive factor as well as a cofactor for many metalloenzymes. Zinc is necessary for the growth and division of cells, especially during the stages of life when growth rates are high. Zinc deficiency is associated with syndromes that cause short stature and dwarfism**(2)**. Also, iron and cobalt are all trace essential elements for human bodies. Lack of these essential elements can induce some diseases while it is harmful and deleterious for overtaken**(3)**. Iron is the fourth most abundant element in the earth´s crust occurring in nearly all types of rock and soil minerals as both Fe^{2+} and Fe^{3+} ions. Iron plays a central role in the biosphere, serving as the active center of proteins responsible for O_2 and electron transfer and of metalloenzymes such as oxidases, reductases and dehydrases**(4)**. A new modeling study of the role of transition metal ions on cloud chemistry has been performed. Developments of the model of multiphase cloud chemistry are described, including the transition metal ions reactivity emission, deposition processes and variable photolysis in the aqueous phase**(5)**. In the present work, Compounds containing an azomethine group (CH=N-), Schiff bases, are used for determination of the studied transition metal ions. Schiff bases are generally bi or tri dentate ligands capable of forming very stable complexes with transition metal ions. The wide use of antibiotics in man and animals and their extensive use in areas other than the treatment and prophylaxis of disease have resulted in a serious problem of drug resistance. Many of the well-known antibiotics, penicillin, streptomycine, tetracycline ect; are chelating agents, their action is improved by the presence of small amounts of metal ions. The antimicrobial activity of the ligands and their transition metal complexes against different bacteria are also reported. Copper complexes have more antibacterial activity against the bacteria staphyloccus aureus, klebsiella pneumoniae **(6)**.

Schiff base can be used in dyestuff production , liquid crystal industries and also in pharmacology.They are synthetic oxygen carriers and they have been produced from intermediate products in enzymatic reactions and used as antitumors.therefore , it is very important to prepare its transition metal complexes**(7)**.

1.2. Literature survey of ligands

1.2.1. Literature survey of Schiff bases

The synthesis and characterization of Schiff bases derived from 2-amino-5mercapto-1,3,4-thiadiazole has been studied.The structures of the titled Schiff bases were elucidated by elemental analysis, electronic absorption, infrared, ^{1}H-and ^{13}C-NMR spectral measurements.The dpendance of λ_{max} upon the type of the substituntes and their positions was investigated using UV-Vis spectra **(8)**.

Several Schiff bases were synthesised from sulphonamide and resacetophenone. The characterisation was done by CHN analysis, IR and NMR spectral data. These Schiff bases were evaluated for their antimicrobial activity against both Gram-positive and Gram-negative bacteria as well as fungi. The comparison of antimicrobial activities of the ligands and complexes shows that the presence of metal causes more inhibition i.e., more activity. Out of the four metals studied, cobalt and iron were found to have more antimicrobial activity **(9)**

The following Schiff bases have been synthesized: (1) 4-[(2-chlorobenzylidene) amino] benzoic acid [JP1], (2)4-[(furan-2-ylmethylene) amino] benzoicacid [JP2],(3)4[phenylallylidene)amino] benzoic acid [JP3], (4) 4-[(2- hydroxybenzylidene) amino] benzoic acid [JP4], (5) 4-[(4-hydroxy-3- methoxybenzylidene)amino] benzoic acid [JP5] and (6) 4-[(3-nitrobenzylidene)amino]benzoic acid[JP6]. They were screened as potential antibacterial agents against a number of medically important bacterial strains **(10)**.

A series of Schiff base and 2-azetidinones of 4,4’-diaminodiphenylsulphone have been synthesized. 4,4’-diaminodiphenylsulphone was condensed with various aromatic or heterocyclic aldehyde in ethanol in the presence of concentrated sulphuric acid as a catalyst to yield the Schiff base **(**Ia-e**)**. These Schiff bases on treatment with chloroacetylchloride in the presence of triethylamine gave substituted 2- azetidinone **(**IIae**)**. The structure of synthesized compounds has been established on the basis of their spectral (IR, ^{1}H NMR and Mass) data. The purity of the compounds was confirmed by TLC. All these compounds were evaluated for their in vitro activity against several microbes **(11)**.

Schiff bases of *N*-methyl and *N*-acetyl isatin derivatives with different aryl amines have been synthesized and screened for anticonvulsant activities against maximal electroshock (MES) and subcutaneous metrazole (ScMet). *N*-methyl-5-bromo-3-(*p*-chlorophenylimino) isatin (**2**) exhibited anticonvulsant activity in MES and ScMet with LD50 > 600 mg kg^{-1}, showing better activity than the standard drugs phenytoin, carbamazepine and valproic acid. Thus, compound **2** may be chosen as a prototype for development of new anticonvulsants **(12)**.

Schiff bases, products of the reaction of primary amines and carbonyl compounds, are involved in many metabolic processes. Hence, physicochemical studies of Schiff bases as model substances can contribute to a better understanding of biological systems. In this work, the one and two-dimensional homo- and heteronuclear ^{1}H and ^{13}C NMR spectra of 2-hydroxy-1-naphthylidene Schiff bases with differently chloro- and hydroxyl- substituted aniline moiety were studied. The spectra were analyzed on the basis of chemical shifts, substituent effects, spinspin couplings as well as connectivities**(13)**.

Two small sets of aromatic Schiff bases and 2,3-diaryl-1,3-thiazolidin-4-one derivatives have been prepared and tested for antiinflammatory and antinociceptive activities. The thiazolidinone derivatives have been obtained from the azomethines through the addition of α-mercaptoacetic acid. Both types of compounds displayed good level of activity against carrageenan induced edema in rat hind paw, while only moderate activity was observed in the writhing test in mice **(14)**.

Twenty new Schiff bases derived from ortho-hydroxyaryl aldehydes and aromatic or heteroaromatic amines have been synthesized in high yields via condensation in ethanol in the presence of catalytic amounts of sulfuric acid. These azomethines, useful as ligands, intermediates in organic synthesis or potential biologically active substances, have been characterized by elemental analysis, IR, ^{1}H- and ^{13}C-NMR spectra **(15)**.

2-Amino-4-(2-naphthalenyl) thiazole (1) was prepared from 2-acetylnapthalene. This amine on facile condensation with aromatic aldehydes afford Schiff Base/anils/azomethines. These anils on cyclocondensation reaction with chloro acetyl chloride and thio glycolic acid (i.e. mercapto acetic acid) yields 2-azetidinones and 4-thiazolidinones respectively. The prepared compounds have been screened on some stains of bacteria**(16)**.

New Schiff bases derived from 2-aminopyridene and 2-aminopyrazine have been synthesized. The UV-Visible spectra of the compounds have been investigated in acetonitrile and toluene. The compounds were in tautomeric equilibrium (enol-imine O– H···N, keto-amine O···H–N forms) in polar and non polar solvents. For some derivatives the keto-amine form was observed in both toluene and acetonitrile. ^{1}H-NMR and IR results showed that all Schiff bases studied favor the enol-imine form over the keto form in a weakly polar solvent such as deuterochloroform**(17)**.

Two new Schiff bases, $[NiL]ClO_4$ and$[CuL]ClO_4.O.5H_2O$ **(18)** were synthesized and characterized where L is the 1:1 condensation product of salicylaldehyde and diethylenetriamine. Their crystal structures and magnetic properties were detrmined and investigated.

1.3. Literature survey of transition metal ions determination

1.3.1. Conductometric determination of transition metal ions

The stoichiometries of Mn(II), Co(II), Ni(II), Cu(II) complexes with azosulfonamide derivatives were determined conductometrically and indicated the formation of 1:1 and 1:2 metal to ligand**(19)**. The main benefit of using conductometric titration in the present work is the gaining of stiochiometry of ligand –metal complexes.

A conductometric study**(20)** was evaluated for Cu(II), Ni(II) and Zn(II) complexes with the Schiff base derived from 1,2-Bis-(o-Aminophenoxy)ethane and salicylaldehyde. Stability constants were measured by a conductometric method. Furthermore, the stability constants for complexation between $ZnCl_2$ and $Cu(NO_3)_2$ salts and N ,N´-bis(salicyidene)-1,2 bis- (o-aminophenoxy)-ethane(H_2L) in 80 % dioxane / water and pure methanol, were determined from conductance measurement.

A conductometric method**(21)** was developed for determination of stability constant of Cu(II) complex with 4- amino-3ethyl-1,2,4-triazol-5-

thione(AETT) in 0, 20, 40, 60, and 80 % (v/v) ethanol–water mixtures. Stability constants of resulting 1:1 complexes were larger by increasing of temperature and ethanol percent.

Electrical behaviour of phthalimide derivatives and their complexes with transition metals**(22)** was studied.the electrical conductivity of these compounds and their complexes with Co(II), Ni(II), Cu(II) or Zn(II) has been measured in the temperature range 290-435 k.Conductometric titration and IR spectra were used to characterize the structure of studied samples.

The complexation reactions between Cu(II), Zn(II), Cd(II) and Pb(II) metal cations with 18-crown-6 (18C6) **(23)** were proposed in methanol (MeOH)–dimethylformamide (DMF) and ethyl acetate (EtOAc)-dimethylformamide (DMF) binary mixtures at different temperatures using the conductometric method. The conductance data show that the stoichiometry of the complexes in all cases is 1:1 (ML).

1.3.2. Potentiometric determination of transition metal ions

The equilibrium constants and species distribution of Schiff base involving salicylaldehyde and tridentate α-aminoacids with Cu(II),Ni(II), and Zn(II)**(24)** was determined potentiometrically. The binary stability constants follow the order Cu(II)>Ni(II)>Zn(II). The influence of additional coordination sites such as OH, -$CONH_2$ and –COOH in the formation of ternary complexes is also discussed.

Proton–ligand formation constants of isatin-3-thiosemicarbazone (HIT); n-acetylisatin-3-thiosemicarbazone(HAIT) and 5(p-nitrobenzyl)-1,2,4-triazino[5,6-b indole-3-thione (HBITR) ligands and their corresponding metal-ligand formation constants with Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, UO_2^{2+} and Th^{4+} ions were determinated pHmetrically at 10, 20, 30, and 40 °C in 75 % (v/v) ethanol water(25). The thermodynamic parameters (ΔG, ΔH and ΔS) were also evaluated.

Equilibrium and solution structural study of mixed–metal-mixed ligand complexes of Cu(II), Ni(II) and Zn(II) with L-cysteine, L-threonine and imidazole(26) was proposed which are conducted in aqueous solution by potentiometry and spectrophotometry. Stability constants of the binary, ternary and quaternary complexes are determined at 25 ± 1°C and in I = 0.1 M $NaClO_4$.

Proton-ligand dissociation constant of 4-(4-nitrophenylazo)-3-methyl-1-(2-hydroxy-3-morpholinopropan -1-)-2-pyrazoline-5-one (NAMP) and metal-ligand stability constants of its complexes with some transition metal ions were measured potentiometrically(27). The order of stability constants was found to be $K(UO_2^{+2}) > K(Ce^{3+}) > K(La^{3+}) > K(Mn^{2+}) < K(Co^{2+}) < K(Ni^{2+}) < K(Cu^{2+}) > K(Zn^{2+})$. The stoichiometries of the complexes were determined specrophotometrically and conductometrically and indicate the formation of n (metal) : n (ligand) 1:1 and 1:2 complexes.

The interactions of Co(II), Ni(II) and Cu(II) with 1-(4-hydroxy)-1,3,5-triazino-3-methyl thiocarbamide and 1-(4-hydroxy-6-methyl)-1,3,5-triazino-3-methyl thiocarbamide have been investigated potentiometrically(28), in 70% dioxane-water mixture at constant ionic strength. Bjerrum's potentiometric titration method as adopted by Calvin and Wilson is applied in this research. Proton ligand and metal-ligand stability constants have been determined by Irving-Rossotti's expression at 27 ± 0.1 °C. The pK values are determined by half-integral method and by point wise calculations.

Proton dissociation constant of the ligand and the stability constants of the complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 2-hydroxy-benzilidine-o-aminobenzothiazole have been determined potentiometrically(29) at 30 ± 0.1 °C and at ionic strength 0.1 M in 75 : 25 (V/V) dioxane-water medium. log K_1 and log K_2 values have been determined. The stabilities of the chelates follow the order Cu > Cd > Co > Ni > Zn.

The formation constant of mixed ligand complexes of copper(II) with Schiff bases 1- (2' -hydroxyl benzamido) -2 -phenyl azomethine (L1) and 1-(2' -hydroxyl benzamido) -2-(2-methyl phenyl) azomethine (L2) as primary ligands and glycine (R1), DL-naline (R2) as secondary ligands(30) was determined potentiometrically in 40% (v/v) THF-water mixture at 30 ºC and ionic strength of 0.1 M $NaClO_4$. The protonation constants of free ligands and stability constant for ternary systems involving Schiff bases and amino acids were also determined under identical conditions.

Hydroxamic acids, RCONHOH, form highly stable complexes with vanadium(IV) in 1:1, 1:2 and 1:3 molar ratios(31). The stability constants of the complexes were determined through spectrophotometric and potentiometric methods at various pH and found to be comparable. Acetohydroxamate, benzohydroxamate and salicylhydroxamate were selected for the study. Using the spectrophotometric method, graphical calculations were applied to confirm the results. Potentiometric method associated with computer calculation program was also applied to check the reproducibility of the results.

Formation and stability of binary and ternary complexes of copper (II) with 2,3-pyrazinedicarboxylic acid as a primary ligand and some biological important aliphatic , aromatic and heteroaromatic carboxylic acids as secondary ligands were determined by potentiometric technique(32).

The precise nature of the reaction between zinc and thiomalic acid(33) was investigated in aqueous 0.1 M KNO_3 potentiometrically and conductometrically. The formation of two complexes, one predominating at pH 5.5-7.0 and another at pH 8.0-9.5, was found.The stability constants of the complexes formed have been determined at three different temperatures. The log K values for 1:1 and 1:2 complexes computed by alternative methods at 25, 30, 35 ºC have been found to be 8.75, 8.85, 8.86, and 6.82, 6.75, 6.93, respectively.

1.3.3. Spectrophotometric determination of transition metal ions

The composition and stability of the complexes of isatin-thiosemicarbazone with Co(II), Ni(II), Cu(II), Zn(II), Pd(II), and Hg(II) have been investigated using spectrophotometric method(34). Schiff bases mentioned above are prepared under reflux and examined with the studied metal ions.The transition metal ions are determined in different samples with the aid of calibration curve which constructed by keeping the reagent concentration constant and increase the metal ion concentration.Different factors are studied such as the effect of pH, temperature, reagent concentration, organic solvents, time and selecting the suitable wavelength and best conditions for the desired estimation of studied transition metal ions.

A new method for the determination of Fe(II) with 5-nitro-6-amino-1,10 phenanthroline (NAF)(35) was studied. The reaction proceed quantitatively at 20 C°for 210 min in acidic medium. The absorption maximum was 520 nm. The molar ratio of Fe(II) to the reagent was determined as 1:3. The limiting concentration for interference by Co(II), Ni(II), Cu((II), Zn(II), Mn(II), Al(III), Ca(II) and Mg(II) cations are reported.

Copper(36) was determined in the soil of two allotment gardens in Lods and a forest area near lodz.Copper was determined by an adapted extraction–spectrophtometric method in the form of a complex with sodium(I) diethyldithiocarbamate. The influence of the extraction solvent, a masking agent and interfering elements Fe(III) and Cr(III) on determination of copper was examined.

A method(37) was developed for selective extraction of copper (II) using Schiff base ligands. The change in pendat arms and the distance between two imine–N donor atoms in ligands is carried out. Di-Schiff bas ligands,N,N–bis(2-quinolylmethylidene)- 1, 2 - diiminoethane(BQIE), N, N- bis (2-pyridylmethylidene) - 1, 3 - diimino- 2, 2 - dimethyl propane (BPMP) and N, N-bis(2-quinolylmethylidene)-1, 3 – diimino - 2, 2-dimethylpropane (BQMP), were used as complexation reagents for ion-pair extraction of divalent transition metal cations into nitrobenzene with picrate anion.

A spectrophotometric method was proposed for the extractive determination of copper(II) using benzildithiosemicarbazone (BDTSC) as a reagent(38). BDTSC reacts with copper (II) in the pH range 1.0–7.0 to form a yellowish complex. Beer´s law is obeyed in the concentration range 0.5 -0.4 μg cm^{-2}. The composition of Cu(II)–reagent complex is established 1:1 by molar ratio. The method is successfully applied in the determination of copper (II) in pharmaceutical samples.

The spectrophotometric determination of nickel in aquatict Tween 80 micellar solutions(39) was studied using 1-(2-Pyridylazo)-2-naphthol (PAN) as a sensitive reagent where a red coloured complex was formed .Molar absorptivity was found 4.62 x 10^4 Lcm^{-1} mol^{-1} at 569 nm. Spectrophotometric limit was 3 ng ml^{-1} and effects of diverse ions were studied .

Zinc and cadmium were determined spectrophotometrically(40) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol in the presence of cetylpyridinum chloride, a cationic surfactant. The molar absorption coefficient and analytical sensitivity of the 1:2 complex at 554 nm are 1.19 x 10^5 L mol^{-1} cm^{-1} and 0.56 ng Ml^{-1}, respectively. Zn(II) was determined in the range 0.06-.66 μg ml^{-1} while that of Cd^{2+} was 0.2-1.6 μg ml^{-1}.

Metal complexes of some divalent metal ions (Co(II), Ni(II) , Cu(II), and Zn(II)) with 3-[2-(1-acetylethylidene)-hydrazino]-5,6diphenyl – 1,2,4 –triazine (AHDT) as a Schiff base**(41)** were studied potentiometrically and spectrophotometrically. The stoichiometry of complexes was 1:1 and 1:2 (M):(L). Formation constants of the proton-ligand and metal-ligand complexes have been determined potentiometrically at different temperatures (10-50 C°).

Simple solid phase spectrophotometric method was developed **(42)** for both screening of eight transition metal ions plus lead and quantitative determination of copper, cadmium and zinc is described. The method is based on the preparation of a sensitive analytical zone by immobilization of the organic reagent 1-(2-pyridylazo)-2-naphthol (PAN) in a Dowex 50wx2-100 resin, in which Cd, Cu, Zn, Co, Fe, Ni, Ag, Pb, and Hg react at pH 10, to form coloured complexes on the surface of the resin.

The direct determination of copper with thiosemicarbazide**(43)** was evaluated by UV-VIS spectrophotometry at the presence of Pb^{2+}, Cd^{2+}, Sn^{4+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Fe^{2+}, Cr^{3+}, Cr^{6+}, Zn^{2+}, Mn^{2+}, As^{3+},As^{5+} ions . The peak of Cu^{2+} thiosemicarbazide complex at 356 nm in 0.1 M HNO_3 (aq) was taken to be reference.the amount of Cu^{2+} in tap water was determined to be 0.11 mg/L.

Bis(acetyl acetonato) ethylenediamine cobalt (II) complex**(44)** was studied potentiometrically and spectrophotometrically. The dissociation constant of the Schiff base conducted on a potentiometer established 12.2. Similarly, the stability constant for the formation of the complex was determined 1:1. Continuous variation analysis of the complex compound confirmed the 1:1 metal to ligand ratio .

The solvent extraction of metal dithiocarbamates**(45)** was investigated where the extraction of morpholine dithiocarbamic acid complexes of divalent metal ions Mn, Fe, Co, Ni, Cu, Zn, Pb, Cd, Hg,and Sn were carried out, and the extraction constants and the overall stability constants were determined.

Fluorescence characteristics of Schiff bases derived from aminopyridines and salicylaldehyde were studied**(46)**. These compounds were used for spectroflurometric determination of Cu^{2+} at pH 8.9, $\lambda ex = 340$ nm , $\lambda em = 385$ nm, C ligand = $1x10^{-5}$ M, the linearity range of the calibration curve was 30-350 µg L^{-1} Cu^{2+}.

Copper was determined after preconcentration with 1,5 diphenylcarbazone on microcrystalline naphthalene in the pH range 6.5-8.0 by spectrophotometric method at 542 nm**(47)**. The linear calibration range for copper was 0.04-5.0 µg ml^{-1} in DMF solution with a detection limit of 0.03 µg ml^{-1}.

Fe(II)**(48)** was detemined spectrophotometrically in pharmaceutical preparations using heterodiazophenols. 3-mercapto-5-(2´,4´-dihydroxyphenyloazo-1´)-1,2,4-triazol(METRIAP) and 5-(5´-mercapto-1,3,4-tiadiazolo-2´-azo)-2,4-dihydroxybenzoic acid (METIDAREZ) were used . The stability of the complexes with Fe(II) was expressed as log k at pH of 10.3 and with METRIAP it was 16.56, while with METIDAREZ – at the pH of 7.4 it was 14.25 .

Copper(II), nickel(II), and zinc(II) complexes**(49)** were studied with potentially tridentate and momodentate ligands where the complexes of these metals with L-cysteine,L-threonine and imidazole are conducted in aqueous solution by potentiometry and spectrophotometry . Stability constants of the binary, ternary and quaternary complexes are determined at ± 1C° and in I=0.1 M $NaClO_4$.

Trace amounts of vanadium**(50)** was determined using variamine blue (VB) as a chromogenic reagent. The method is based on the oxidation of variamine blue to form a violet colored species on reaction with vanadium (V), having an absorption maximum at 570 nm. Beer's law is obeyed in the range of 0.1-2.0 µg ml^{-1}. The molar absorptivity and Sandell's sensitivity were found tobe $1.65x10^4$ $lmol^{-1}$ and 0.003 µg cm^{-2}.

Spectrophotometric method**(51)** was developed for the determination of cobalt in industrial, environmental, biological, pharmaceutical and soil samples using bis (5bromosaicylaldehyde) orthophenylenediamine. (BBSOPD). The method is based on the reaction of nonsorbent BBSOPD in a slightly acidic(0.001-0.0025 M H_2SO_4 or pH 3.4-4.0) and 50 % N,N dimethylformamide media with cobalt to produce a highly absorbent orange colored chelate-product with an absorption maximum at 473 nm.

The extraction and spectrophotometric determinatrion of vanadium with 2-(2-Quinolylazo)-5-diethylaminophenol (QADEAP)**(52)** was studied. The solid phase extraction of the coloured chelate with C18 cartidge is carried out. The QADEAP reacts with V(V) in the presence of citric acid-sodium hydroxide buffer solution (pH=3.5) and cetyl trimethylammonium bromide (CTMAB) medium to form a violet chelate of a molar ratio 1:2 V(V) to QADEAP.

A simple sensitive spectrophotometric method**(53)** was developed for determination of vanadium in biological and environmental samples. The method is based on oxidation of 2,4-dinitro phenyl hydrazine(2,4-DNPH) by vanadium (V) followed by coupling reaction with N-(1-naphthalene-1-yl)ethane-1,2-diaminedihydrochloride(NEDA) in acidic medium to give red coloured derivative which having an λ_{max} 495 nm. Beer´s law is obeyed for vanadium (V) in the concentration range of 0.02-3.5µg ml^{-1}.

Cobalt (II), nickel (II) and copper (II)**(54)** were determined spectrophotmetrically with 1-(2 pyridylazo)-2-naphthol in aqueous phase using non-ionic surfactant Tween 80. Beer´s law is obeyed for Co(II), Ni(II), and Cu(II) over the range 0.5-4.0, 0.5-4.0 and 0.5-3.0 ng mL^{-1}.The max molar absorption, molar absorptivity, Sandell´s sensitivity of Co(II), Ni(II), and Cu(II) are 580 nm, 570 nm and 555 nm (104 mol^{-1} cm^{1}) is 0.87, 1.8 and 1.6 and 6.8, 3.3 and 3.9 ng cm^{-2} respectively.

The spectrophotometric determination of trace amounts of mercury with phenanthroline and eosin**(55)** was studied. The reaction occurs at pH 4.5.mercury limits are 0.2-1.2 ppm. Various metal ion interferences have been evaluated.

The stability constants of the Co(II), Ni(II), Cu(II) and Zn(II) complexes with 2-benzoylpyridine 4-phenyl-3-thiosemicarbazone**(56)** were determined using a spectrophotometric method at different temperatures (25, 30, 35 and 40 ± 0.1 C°). Plots of thermodynamic stability constants at zero ionic strength (ln k°) versus T^{-1} gave linear curves and ΔH° and ΔS°were also calculated from these plots.

2-Acetyl thiophene thiocyanate (ATT) was proposed**(57)** as extractant for development of extractive spectrophotometric method for determination of Co(II). The reagent coordinates with Co(II) to produce yellow coloured complex which was then extracted into ethyl acetate at pH 10.8-11.2 having absorption maxima at 450 nm. The thermal study showed that the extraction reactions are exothermic in nature with the reagent, and the stoichiometric ratio of Co(II) to 2-acetyl thiophenethiocyanate in organic phase was 1:2. The method permits separation and determination of cobalt from real and synthetic mixtures. The separation of Co(II) from bivalent metal ions has also been studied.

The spectrophotometric determination of cadmium (II) and mercury(II)**(58)** was studied with water soluble pyridinol azo dyes. 1-(2´,3´-dihydroxy pyridyl-4´-azo)benzene -4-sulphonic acid (DHP-4S) and 1-(5´-chloro-2´,3´-dihydroxy pyridyl-4´-azo) benzene-4-sulphonic acid (CPD-4S) have been used in this determination. The Sandell´s sensitivity of the colour reactions for Cd(II) are 0.0032 μg/cm^2, 0.0028 μg/cm^2 and for Hg(II) are 0.003 μg /cm^2, 0.0031 μg /cm^2 with DHP-4S and CPD-4S respectively.

Lead (II) and mercury (II) based on 2-(5-bromo-2piridylazo)-5-diethylaminophenol were determined spectrophotometrically**(59)**. A feed forward neutral network using back-propagation (BP) algorithm has been employed in this study. The input layer consisting of 13 neutrons, 10 neutrons in the hidden layer and 2 output neutrons were found appropriate for the simultaneous determination of Pb(II) and Hg(II).The limit of detection of the method was calculated to be 0.2 mg/L and 0.4 mg/L , respectively.

2,4-Dihydroxy-5-bromopropiophenone thiosemicarbazone (DHBPT) was synthesized**(60)**, and used as a spectrophotometric reagent for nickel. Ni(II) forms yellow coloured complex between pH range 7.0 to 10.0 and shows maximum absorption at 375 nm. Molar absorptivity for Ni(II)-DHBPT is 2.586 x 10^3 Lcm^{-1} mol^{-1}. Ni(II)-DHBPT has 1:2 (M:L) stoichiometry. Beer's law is obeyed up to 16.49 ppm for Ni(II). The reagent has been found to give satisfactory results for the analysis of nickel in German-silver alloy. Formation of the complex has been supported from the IR spectral data.

A new reagent**(61)** was proposed for vanadium determination. Vanadium (V) in trace amounts forms an intense green 1:3 (M:L) complex with 3-hydroxy-2- [1' - phenyl-3'- -(*p*-chlorophenyl)-4'-pyrazolyl]-4 -oxo-4*H*-l -benzopyran (HPCPB) in acetic acid medium (0.1 M) which is extractable into carbon tetrachloride and is stable for more than 3 h. Beer's law is obeyed in the vanadium concentration range of 0–1.4 mg mL^{-1}. Molar absorptivity, detection limit and Sandell's sensitivity when applying spectrophotometric determination at the wavelength of 410 nm, are 2.2×10^4 L mol^{-1} cm^{-1}, 5.48×10^{-5} g L^{-1} and 0.0023 mg V(V) cm^{-2}, respectively.

A novel method for the spectrophotometric determination of trace amount of iron (III) after separation of its BPA complex**(62)** was described by adsorption on microcrystalline naphthalene. The ε_{max} of the DMF solution of the adsorbate containing iron (III)-BPA complex at λ_{max} 437 nm has been found to be 4.47 x $l0^3$. The effect of variables and interfering ions on the efficacy of the method has been studied. Sensitivity (in Sandell's notation) is 1.25 **x** pg of iron (III)/cm and at a mean absorbance of 0.4000 is 1.25 %. The method is useful for the analysis of standard reference materials and environmental samples. The results are comparable with those obtained using orthophenanthroline.

Simple and convenient determination of trace Hg(II) with its 2-mercaptobenzothiazole (MBT) complex**(63)** was proposed in cetyltrimethylammonium bromide (CTAB).The Hg(II)-MBT complex in CTAB solution was very stable at pH 10.0.The optimum concentration of CTAB was 0.001 % .The calibration curve of Hg(II)-MBT complex with good linearity (R2=0.9985) was obtained at the concentration range between $1.0x10^{-7}$ and $1.0x10^{-5}$ M in 0.001 % CTAB media .

A highly selective and sensitive catalytic method**(64)** was developed for the determination of trace amount of vanadium (V) based on its catalytic effect on the oxidation of nuclear fast red with bromate. The reaction was followed spectrophotometrically by measuring the change in absorbance of nuclear fast red at 517 nm, 4 min after the initiation of the reaction. In this study experimental parameters were optimized and the effect of other cations and anions on the determination of vanadium (V) was examined. The calibration graph was linear in the range of 5.0 ng ml^{-1} of vanadium (V). The method was successfully applied to the determination of vanadium (V) in water and steel samples.

1.3.4. Determination of transition metal ions with different analytical methods

A new copper (II) ion-selective liquid polymeric membrane electrode**(65)** was developed based on 2,2´: 5´ ,2"-Terthiophene . When optimized, this electrode exhibits a linear Nernstian response over the range of 5.0 x 10^{-6} -1.0 x 10^{-1} M of copper (II) ion , with a slope of 29.88 mv per decade and detection limit was 2.34 x 10^{-6} M.

Fe(II) and Fe(III)**(66)** were determined in pharmaceutical samples by post-column derivatization HPLC. Detection limits were found to be 0.109 g/l for Fe(II) and 0.217 g/l for Fe(III), respectively. the determinations of Fe(II) and Fe(III) were also realized by the most common method of FAAS.

Copper and zinc**(67)** were determined in natural water samples by inductively coupled plasma atomic emission spectrometry (ICP-AES). The proposed method is based on the complexation of copper(II) and zinc(II) ions by 1-(2-thiazolylazo)-2-naphthol(TAN) and sorption on to Amberlite XAD-2 resin. Parameters such as: TAN amount, pH effect on the complexation and sorption of TAN complexes, agitation time for complete sorption, concentration of metal ion were studied .

A voltammetric method(68) was developed for the determination of Zn(II) in Zn-Fe alloy electroplating baths using square-wave voltammetry.The supporting electrolytes used in the analyses were 1.0 mol L^{-1} NH_3/0.2 mol L^{-1} NH_4Cl or 0.1 mol L^{-1} citric acid (pH=3), presenting peak potentials for zinc(II) respectively, at -1.30 V and -.99V vs.Ag/AgCl .The proposed voltammetric method showed a linear response range at 25 ºC between $1.0x10^{-5}$ and 2.2×10^{-4} mol L^{-1} for zinc(II), in both electrolytes studied.

Mercury(69) was determined at trace level in natural water samples by hydride generation atomic absorption spectrophotometry after cloud point extraction preconcentration . The effects of pH, concentration of surfactant, and equilibration time on cloud point extraction were discussed.The enhancement factor of 20 and the detection limit of 0.039 µg/L were obtained for mercury with relative standard deviation of (n= 11).

The preconcentration and determination of mercury (II) and methylmercury (70) was investigated in waters by immobilized 1,5-diphenylcarbazone and cold vapor atomic absorption spectrometry. The mercury (II) was directly measured by cold vapor atomic absorption spectrometry urilizing tin (II) chloride where as the total mercury was determined after the oxidation of methylmercury into the inorganic mercury.The procedure was applied to sprig water, well water and seawater.

Anodic stripping voltammetry(71) was used for determination of mercury(II) using Lectin-modified carbon paste electrode. The prepared electrode was found to have high affinity towards mercury (II) ions.

Analysis of mercury(II) was conducted by differential pulse adsorptive stripping voltammetry (DPAdSV) using 0.1 M NaOH as supporting electrolyte.The following conditions gave the best results ; pH 7,20% modifier composition, 240 sec accumulation time and 300 sec deposition time.

Mercury high selective electrode(72) was developed which is based on 4-(4-methoxybenzylidenimin) thiophenole. The electrode was prepared by coating the membrane ingredient on the surface of graphite electrode. The effect of various parameters including the membrane composition ,pH and possible interfering ions on the response properties of the electrode.The sensor exhibited Nernstion responses toward mercury over a wide concentration range from $2x10^{-6}$ to 0.1 M .

A PVC membrane(73) was developed incorporating p-tert-butyl calix[4] crown with imine units as an ionophore and used it in an ion-selective electrode for the determination of mercury (II) ions. An electrode based on this ionophore showed a good potentiometric response for mercury(II) ions over a wide concentration range of 5.0×10^{-5} – 1.0×10^{-1} M with a near-Nernstian slope of 27.3 mV per decade.

New PVC membrane potentiometric sensor(74) was prepared that is highly selective to Hg^{2+} ions, using bis(2-hydroxybenzophenone) butane-2,3-dihydrazone (HBBD) as an excellent hexadentates neutral carrier.The sensor works satisfactorily in the comcentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} (detection limit 4×10^{-7} mol L^{-1} with a Nernstian slope of 29.7 mV per decade. This electrode showed a fast response time (~8 s)and was used for at least 12 weeks without any divergence.

A new fluorescent sensor(75) consisted of fluorenyl and dioxotetraaza unit, namely, 2,10- dimethyl-6-(9-fluorenyl)-1,4,8,11-tetraazaundencane-

5,7-dione (L), was developed. It is a fluorescent sensor for transition metal ions in aqueous solution.

The interaction of nicotinamide (NA) with NH_4VO_3(76) was studied at the physiological pH (pH 7.4) was studied by voltammetry and UV-Vis spectroscopy. The reduction of V(V) ions complexed with NA in phosphate buffer (pH 7.4) was observed as a well-defined reversible reduction peak at – 0.35 V. The stoichiometric (metal : ligand) ratio of the complex of V(V) with NA was determined as 1:2 by the mole ratio method.

Rapid, simple and selective method(77) was proposed for the determination of mercury (II). Mercury (II) and other metal ions are first complexed with EDTA and the surplus EDTA is back titrated with lead nitrate at pH 5-6. A 0.2% solution of 2-thiazolinethiol in acetone is added to displace EDTA from the Hg(II)-EDTA. The released EDTA is titrated with a standard lead nitrate. Accurate results are obtained in the range of 0.8g l^{-1} – 1.5 g l^{-1} of mercury with a relative error less than ±0.25% and coefficient of variation (n = 6).

Copper was determined in ores(78), alloys and complexes by a complexometric method using DL-penicillamine as the masking agent. All of the ions present in the sample solution are initially complexed by EDTA and the excess of EDTA is titrated with zinc sulphate solution at ph 5.0-6.0(hexamine).the interference from various ions was studied.

Indirect complexometric method(79) was developed for determination of mercury (II) in synthetic alloys and complexes using ethanethiol as a selective masking agent. Mercury (II) present in a given sample solution is first complexed with an excess of EDTA and the unreacted EDTA is titrated against zinc sulphate solution at pH 5-6 (hexamine buffer).

An excess of a 0.3 % solution of ethanethiol is then added to displace EDTA from the Hg(II)0EDTA complex. Reproducible and accurate results are obtained for 4-85 mg of mercury (II) with a relative error of less than 0.46 %.

Simple, rapid and selective complexometric method**(80)** was proposed for the determination of mercury (II). Mercury (II) is first complexed with an excess of EDTA and the surplus EDTA is titrated against standard zinc sulphate solution at pH 5-6. Glutathione is then added to displace EDTA from the Hg-EDTA complex quantitatively and the EDTA released is back titrated against a standard zinc sulphate solution as before. The method works well in the range 4 to 80 mg of mercury.

The indirect complexometric determination of mercury**(81)** was studied using potassium iodide as selective masking agent. To the mixture of mercury (II) and other metal ion solution, EDTA solution was added in excess of the metal ions present. The pH of the solution was adjustede to 5.0-6.0 using solid hexamine (10±2 g) and surplus EDTA was titrated with zinc sulfate solution using xylenol orange indicator. An excess of solid potassium iodide was then added to decompose the Hg-EDTA complex and the released EDTA was titrated with standard zinc sulphate solution .

The formation equilibria of binary and ternary complexes of nickel (II) with ethylenediamine-N,N'-diacetic acid (EDDA)**(82)** was investigated as primary ligand and amino acid or peptide (HL) as secondary ligand. Stoichiometries and stability constants of the complexes were determined at 25 ºC and 0.1 M $NaNO_3$ ionic strength. The hydrolysis of the Ni (EDDA) complex and the deprotonation of the amide residue in the peptide complexes are discussed in relation to physiological conditions.

A new poly (vinyl chloride) -based membranes containing p-(4-n-butylphenylazo)calix[4]arene**(83)** was used as an electroactive material along with sodium tetraphenyl borate (NaTPB), and dibutyl (butyl) phosphonate in the ratio 10:100:1:200 (I:DBBP:NaTPB:PVC) (w/w) to fabricate a new cobalt (II)-selective sensor. It exhibited a working concentration range of 9.2×10^{-6} to 1.0×10^{-1} M, with a Nernstian slope of 29.0 ± 1.0 mV/decade of activity and the response time of 25 s. This sensor shows the detection limit of 4.0×10^{-6} M. Its potential response remains unaffected of pH in the range, 4.0–7.2, and the cell assembly can be used successfully in partially non-aqueous medium (up to 10%, v/v) without significant change in the slope of working concentration range metal ions.

Interactions between lead and ascorbic acid**(84)** was investigated by polarography and voltammetry. The following techniques were applied: sampled polarography, differential pulse anodic stripping voltammetry, and square-wave voltammetry. Electrochemical reaction of the lead (II) ascorbate complex was studied in various electrolyte compositions to find the optimal measurement conditions for determination of the corresponding stability constants ($[Pb^{2+}] = 4 \text{ x } 10^{-7}$ mol dm^{-3}, pH = 5.5; total concentration of ascorbic acid between 10^{-5} and 10^{-1} mol dm^{-3}). The computed stability constants were: log ß1 = 9.3 ± 0.2 and log ß 2 = 18.0 ± 0.1.

The identification of trace elements such as Cd, Cu, Fe, Mn, Pb and Zn**(85)** was studied in IAEA lichen-338 for a proficiency test (PT). The detection limits and characteristic masses of analytes obtained were 0.06 μg L^{-1} and 2.04 pg for Cd, 1.26 μg L^{-1} and 18.4 pg for Pb, 0.66 μg L^{-1} and 6.4 pg for Cu, 0.16 μg L^{-1} and 1.42 pg for Mn in ETAAS with (Ni + Pd + TA), and 72.1 μg L^{-1} for Fe and 20.1 μg L^{-1} for Zn in flame atomic absorption spectrometry (FAAS). Cd, Cu, Pb and Mn in tomato leaves

(1573a) from the National Institute of Standards and Technology (NIST) and hay powder (V-10) were detemined.

Aprocedure**(86)** was proposed for separation, preconcentration and determination of trace amounts of titanium in seawater samples by using inductively coupled plasma optical emission spectrometry (ICP-OES). The precision of the procedure, calculated and the relative standard deviations were 4.7 and 2.5 % for titanium concentration 1.0 and 2.5 μg L^{-1}, respectively. The limit of detection was 0.01 μg L^{-1}, for a sample volume of 400 ml .

Copper (II) ions were extracted from a synthetic sample**(87)**. The selective extraction of copper ions allows the use of N,N –Bis(1-hydroxy-2-acetophenone) propylenediamine as an ion-sensing material for fabricating a Cu(II) –ion-selective electrode . This sensor gave good Nernstion response of 29.7 ± 0.3 Mv /decade over a concentration range of 10^{-4} -10^{-1} M of copper ions , independent of pH in the range of 3.5-6.5 , with detection limit of $2x10^{-5}$ M and response limit of ‹ 20 s.

Vanadium (V) was determined in vanadium ores by using atomic absorotion spectroscopy**(88)**. The procedure is based on the oxidation of iodide by chlorate in acidic media in the presence of vanadium (V) which act as a catalyst. The limit detection for vanadium is 0.5 mg/dl a sampling throughput of 90 h^{-1}. the relative standard deviation over the range 0.5 -100 mg/dl is 0.4-1.0 % (n=5).

Zinc and lead were determined in water samples by solvent sublation using ion pairing of metal-naphthoate complexes and tetra-n-butylammonium ion**(89)**. After the metal–naphthoate complexes were formed by adding 1-naphthoic acid to the sample solution, tetra-nbutylammonium bromide was added in the solution to form the ion pair and sodium lauryl sulfate was added in the solution to make the ion –pair hydrophobic.

The extraction and separation of zinc (II) and Cu(II) from perchlorate media was studied using bis-2-ethulhexyl phosphoric acid (D2EHPA) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester(PC-88A) in toluene **(90)**. The extraction of Zn found to be quantitative in the pH range 2.5 to3.0 and 3.0 to 4.0 using $1.0x10^{-1}$ $moldm^{-3}$ D2EHPA and $1.0x10^{-2}$ $moldm^{-3}$ PC-88A in toluene, respectively, while Cu(II) was extracted quantitatively in the pH range 6.0 to 8.0 and 5.5 to 7.0 with $1.0x10^{-2}$ $moldm^{-3}$ and $1.0x10^{-3}$ mol dm^{-3} D2EHPA and PC-88A in toluene, respectively.

1.4. Literature survey of complexes

The synthesis and characterization of a Schiff base of p-tetra-butylcalix[4] arene (H_2L) and its complex with copper (II)**(91)** was described. The ligand and its complex with copper have been characterized on the basis of elemental analysis and spectral data. The prepared complex contains two p-tetra-butylcalix[4] arene moieties, which could be expect to have improved calixarene ability in the fields like molecular recognition, host-guest features and other calixrene related capabilities.

The synthesis and characterisation of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) Schiff bases complexes derived from o-phenylenediamine and acetoacetanilide**(92)** was studied. All the complexes were characterized on the basis of their microanalytical data, molar conductivity, magnetic susceptibility, IR, UV-Vis HNMR and ESR spectra .IR and UV-Vis spectra data suggest that all complexes are square-planner except the Mn(II) and VO(II) chelates, which are of octahedral and square pyramidal geometry respectively.

Some metal complexes**(93)** were prepared using the Schiff base formed by condensation of 2-thiophenecarboxaldehyde with 2-aminopyridine, N-(2-thienylmethylidene)-2-aminopyridine (TNAPY) .Elemental analysis of the chelates suggests the stoichiometry 1:2 (metal-ligand). The metal studied were Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The metal chelates were shown to possess more antibacterial activity than the uncomplexed Schiff base.

Ruthenium (II) complexes containing bidentate Schiff bases and triphenylphosphine**(94)** were studied. The reaction of ruthenium(II) complexes with bidentate Schiff base ligands derived by condensing o-hydroxyacetophenone with aniline, o- or p-methylaniline have been carried out. The products were characterized by analytical, IR, electronic and ^{1}H-NMR spectral studies .The new complexes were tested for their catakytic activities in the oxidation of benzyl alcohol to benzaldehyde.

A series of complexes of bivalent transition metal ions**(95)** were prepared and characterized with acetyl benzal dehydehydrazone and its derivatives of general formula ML with the help of conductometric, photometric and infrared studies. The stability constants and related thermodynamic functions of complexes were determined using the potentiometric technique at different temperatures. The formation of complexes is exothermic process with covalency nature. The electrical conductivity of some solid complexes was measured in the temperature range 289-353 K. The results revealed semiconducting properties for the studied complexes.

Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) complexes of 2-Benzoyl-3-hydroxy-1-naphthylamino-3-phenyl-2-propen-1-on**(96)** were prepared and characterized, which is a derivative of carboxamide, by elemental, spectral and magnetic methods. Based on the analytical results, electronic and infrared spectral data and magnetic susceptibility measurements, suitable structures have been proposed. The formation of the complexes in solution was investigated conductometrically.

Transition metal complexes of δ(3-carboxy, 4-hydroxy benzoyl) pentanoic acid**(97)** were studied.Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) form 1:2 complexes with the mentioned reagent. Their structures have been proposed on the basis of analytical, spectral, thermal and magnetic measurements.

Vaniline thiosemicarbazone complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II)**(98)** were prepared. Structures have been assigned to these complexes based on electrical conductivity, magnetic susceptibility and spectroscopic measurements.

Copper and manganese complexes containing Schiff bases as ligands**(99)** were characterized by mass spectrometry using ionspray ionization. Complete structural characterization of the complexes has been obtained by tandem mass spectrometry, by the analysis of the fragments formed after collisionally induced dissociation of selected precursor ions inside the collision cell of a triple quadrupole mass spectrometer.

Metal chelates of 5-aryl-1-phenyl -4-pentene-1,3-diones, Co^{2+}, Zn^{2+}, Pd^{2+}, Cu^{2+}, and Fe^{2+}**(100)** were synthesized. The electronic, IR, ^{1}H and ^{13}C NMR and mass spectral data of the compounds are discussed.

2,4-dinitrophenylhydrazone derivatives of Co^{2+}, Cu^{2+}, and Ni^{2+} complexes**(101)** were synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility and spectral data. The antimicrobial activities of the complexes have been studied.

Nickel (II) complexes**(102)** were synthesized by reacting nickel (II) chloride with hydrazones derived from terephthalic acid hydrazide and substituted salicylaldehyde in ethanolic medium. The complexes have been characterized on the basis of analytical and magnetic data. The synthesized Ni(II) complexes have been evaluated for their antibacterial and antifungal activities.

Cu(II), Ni(II), Zn(II) and oxovanadiuml (IV) complexes of [bis-(2-aminobenzaldehyde)] malonoyldihydrazone**(103)** was studied. The complexes have been characterized by elemental analysis, molar conductance, spectra and cyclicvoltammetric measurements. The structural assessment of the complexes has been carried out based on electronic, infrared and molar conductivity values.

The synthesis and characterization of a novel iminooxime Schiff base ligand and its complexation with copper (II), nickel (II), zinc (II), cadmium(II), and cobalt (II)**(104)** was investigated. All of the structures were characterized by using spectroscopic techniques.

The Co(II), Ni(II), Cu(II), Zn(II), and Hg(II) complexes of Schiff base 2-hydroxy-5-methylbenzaldehyde N-(4´-phenyl-1´,3´-thiazol-2´-yl) semicarbazone**(105)** were studied. The complexes are characterized by elemental analysis, conductivity measurements, magnetic susceptibility, UV visible, IR, NMR and mass spectra data. It is found that Zn(II), Cd(II), and Hg(II) complexes exhibited tetrahedral geometry whereas Co(II), Ni(II), Cu(II) complexes exhibited octahedral geometry.

The transition metal complexes of thiosemicarbazone and semicarbazone derived from pyrrole-2-carboxaldehyde**(106)** were investigated. All the complexes reported here had been characterized by elemental analysis, molar conductance, magnetic moment, IR and spectral studies. The molar conductance measurements of the complexes in DMSO corresponds to non electrolytic nature.

Spectral characterization and electrochemical behaviour of seven new cobalt(III) complexes of the type cis-b-[Co(trine)(RC 6H4NH$_2$)Cl] Cl

2,where R= H, p-Me, p-OMe, p-Et, p-Oet, P–F and m-Me (107) was studied.The elemental analysis, UV-Vis, IR and HNMR techniques are carried out. Molar conductance measurements support the 1:2 natures of these complexes.

The synthesis and characterization of Ni(II), Pd(II) and Cu(II) complexes of Schiff base derived from amino-1,2,3,6-oxatrizaine and salicylaldehyde(108) was studied. Square planar complexes of Ni(II), Pd(II) and Cu(II) of Schiff base were obtained in a 2:1 mol ratio in refluxing ethanol for 4 hours.

5-hydroxysalicylide-p-aminoacetophenoneoxime (LH)(109 was synthesized from p-aminoacetophenoeoxime and 5-hydroxysalicylaldehyde. Complexes of this ligand with Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} salts were prepared. With this ligand, complexes were synthesized using Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} salt with a metal : ligand ratio of 1:2. Their structures were elucidated on the bases of elemental analysis, IR and NMR, electronic spectra, molar conductivity and thermogravimetric analyses.

The structure and electrochemical behaviour of bis [N-(4-methylphenyl)salicylaldimine] copper (II) N,N'dimethylformamide solvate(110) was studied. The molecular model of mononuclear complex formed, through a reaction between N- (4-methylphenyl) salicylaldimine and Cu(II) ion was determined using x-ray diffraction method. The Cu(II) coordination was found to have a distorted square-planar structure and a cis coordination geometry was observed within the surrounding of the copper.

The synthesis and characterization of two new zinc (II) and cadmium (II) complexes of the tetradentate dissymmetric Schiff base ligand 2(E)-(2-(2-(pyridine-2yl) ethylthio) ethylimino)methyl)-4-bromophenol(111) was described which 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 1M methanolic solution of NaOH.

The syntheses and characterization of some tetradentate Schiff-base complexes and their heteroleptic analogues(112) were studied. VO(IV),Ni(II) and Cu(II) complexes of the asymmetric Schiff base$[(HOC_6H_3(OCH_3)C(C_6H_5):N(CH_2CH_2)N:C(CH_3)CH:C(C_6H_5)OH)]$, and their heteroleptic analogues with triphenyl phosphine and 2,2'-bipyridine have been synthesized and characterized by elemental analyses, conductance, magnetic, infrared and electronic spectral measurements.

The electrochemical properties of vanadyl (IV) derivatives, namely salen Schiff base complexes of the type [VO(salen)] (5-Br salen, 5-NO_2 salen,5-MeO salen, salpn (bis (salicylaldehyde)-1,3-propanediamine ,5-Br salpn,5-NO_2 Salpn, 5-MeOSalpn, Me2Salen, Salophen, 5-Br salophen, and 5-MeOsalophen)(113) were investigated. The equatorial Schiff base ligands affect the oxidation potentials via interaction with the d-orbitals of the vanadyl metal ion.

Chlorides and nitrates of Zinc(II), nickel(II) and cobalt(II) of the type $[ML_2X_2]$ n H_2O (M = Zn, Ni or Co; L= 2-phenyl-2-imidazoline ; X=Cl or NO_3 ; n = o, 1 or 2)(114) was studied. The complexes were synthesized and characterized by elemental analysis of the metal, molar conductivity, magnetic susceptibility measurements and IR spectra. The molar conductances of the zinc (II) complexes in DMF solutions indicate that the complexes behave as non-electrolytes.

The solvent extraction of metal ions with acyclic and macrocyclic Schiff basees(115) was studied. The phenol groups in the Schiff base moiety led to alarge increase in the percent extraction of manganese(II) and iron (II). The substitution of methoxy groups for phenolic OH ligands resulted in a marked decrease in the extractability of manganese (II) and iron (II). The thiophene groups in the Schiff base moiety exceedingly increased extractability of silver (I), palladium (II) and platinum (II).

Ciprofloxacin-imines and their complexes with Cu(II), Ni(II), Co(II), and Zn(II)**(116)** were studied. The complexes were synthesized and characterized on the basis of physical properties, conductance measurements, elemental analysis, UV/Vis, infrared and nuclear magnetic resonance spectroscopy. These ligands as well as their metal complexes were also evaluated for their antibacterial activity against several bacterial strains.

Two new blue luminescent zinc and beryllium complexes**(117)** investigated with Schiff base calixarene derivative as the ligand. Their luminescent properties were determined, which indicated that they also had good solubility and film formation. These new complexes can be used as blue organic electroluminescent materials in organic electroluminescent devices.

Four kinds of bis(N-alkylsaicyldimino) zinc(II) complexes**(118)** were synthesized and determined their molecular structures by FT-IR and elemental anakysis. Their photoluminescence properties were determined, which indicated that they could emit strong fluorescence varying from blue to yellow to reddish orange depending on their different molecular structures.

New bidentate or tridentate Schiff bases and their VO(II) and Co(II) complexes **(119)** were prepared by the condensation of methyl isobutyl ketone with nicotinamide (mna) / 2-amino-4-chlorophenol (map) and 2-hydroxy acetophenone with nicotinamide (han) / isoniazide (hai). Physiochemical characterization has been carried out to determine the structure of the complexes. Some of the complexes have been screened for their antimicrobial activity by the well diffusion technique using DMSO as solvent on different species of pathogenic bacteria/fungi.

Co^{2+}, Ni^{2+} and Cu^{2+} complexes of Schiff bases **(120)** were synthesized which derived from the condensation of ethanolic solution of benzyl monophenyl hydrazone with aniline and substituted anilines (in presence of H_2O, α,ß,γ picoline and pyridine), the complexes are characterized by elemental analyses, magnetic, IR, electronic , mass spectra and thermal studies. The Schiff base behaves as a tridentate ligand.

New nickel (II), cobalt (II), copper (II), and palladium (II) complexes of a Schiff base ligand **(121)** were studied which formed by condensation of furoin with S-benzyl-dithiocarbazate. These have been synthesized and characterized by elemental analysis, magnetic moment and spectra [IR,Uv-vis and NMR] measurements. The special data show that the ligand behaves in a bidentate and / or tridentate manner.

Several iron (III) complexes of tridentate dibasic salicylidene / substituted salicylidene amino acids**(122)** were prepared and characterized. All iron compounds posses dimeric pseudo-octahedral structure esrablished on the basis of elemental analysis, magnetic moment studies, infrared spectra of these complexes with those of nickel(II), cobalt(II), manganese(II), and zinc(II) complexes, and thermogravimetric analysis.

The Schiff base 2,5-dihydroxyacetophenone isonicotinyl hydrazone (H2L)**(123)** was synthesized by condensation of 2,5-dihydroxyacetophenone with isonicotinyl hydrazide in ethanol. Metal complexes of the Schiff base were prepared from salts of Cr(II),Mn(II),Fe(II), VO(IV), Zn(II) and UO2(IV).Characterization of the ligand and its metal complexes were carried out by elemental analysis, molar conductivity, magnetic susceptibility measurements.

Mixed ligand transition metal complexes of Cu^{2+},Ni^{2+} and Co^{2+} ions with Schiff base ligand **(124)** were studied which derived from the condensation of o-hydroxybenzaldehyde with amino phenols and nitrogen donor amine bases. Their conventional physical and chemical analysis had been done. Their anti-bacterial and anti-fungal activity had been evaluated including toxicological studies.

Homodinuclear complexes of lanthanium (III), zinc(II), cadmium (II) and mercury (II) ions and heterodinuclear complexes of lanthanium (II) and zinc(II) ions**(125)** were prepared containing Schiff base open-chain ligands terminated by two carbonyl groups or one amine and one carbonyl group as a result of the partial Schiff base condensation reaction between 2,6-diacetylpyridine and 4-methyl-1,2-phenylenediamine or 2,6-diaminopyridine in the presence of the appropriate ions acting as templates. The complexes were characterized by spectroscopic methods (IR, ^{1}H NMR, FAB-MS) and elemental analysis.

A new series of symmetric and unsymmetric supramolecular copper (II) complexes**(126)** was proposed which derived from- diketones and aniline derivatives which have been synthesized and characterized by elemental analysis, IR,UV-VIS spectra, magnetic moments, conductances, thermal analyses (DTA and TGA) and ESR measurements. The IR data show that the ligands behave as monobasic bidentate towards copper (II) ion .

A new ligand 5-bromo-2-aminobenzothiazole**(127)** was studied which has been synthesized from 2-aminobenzothiazole and 5- bromosalicylaldehyde by condensation in ethanol.Metal complexes of the ligand were prepared from chloride salts of Co(II), Cu(II) and Ni(II) in ethanol characterization of the ligand and its complexes were carried out by microanalysis, magnetic susceptibility measurements, FT-IR,13C, 1HNMR, and UV-visible spectroscopy.

Complexes of cadmium (II), mercury(II) and lead (II) with quercetin-5-sulfonic acid (QSA)**(128)** were investigated.(QSA)ligand is non-toxic and well soluble in water, forms complex compounds with cations of toxic metals (Cd,Hg,Pb). New complexes compounds with QSA have been synthesized. Some of their physicochemical properties such as UV-VIS and infrared spectra, mass spectra, thermogravimetric analysis, and solubility were studied. It was found that the obtained compounds are sparingly soluble in water, which points out that QSA could be an antidote against cadmium, lead and mercury.

Two novel 8-hydroxyquinoline connected dioxotetraamines**(129)** were designed and synthesized which have been characterized by elemental analysis, IR, mass spectra and ^{1}H NMR. The two ligands L1 and L2 have two chelating groups. Each can react with a transition metal ion forming complexes. The results show that as to Mn^{2+}, Zn^{2+}, and Co^{2+}, 8-hydroxyquinoline is a stronger chelating reagent than dioxo[13] or [14]tetraamine macrocycles and at 1:1 molar ratio (M:L), the former binds in 100 % to the metal ions, while the dioxotetraamines can be only partially or not coordinated.

The synthesis of salicyliden-p-aminoacetophenoneoxime(LH) from p-aminoacetophenoneoxime and salicylaldehyde under reflux in absolute ethanol**(130)** was studied.Mononuclear complexes with a metal : ligand ratio of 1:2 have been prepared with Co^{2+}, Ni^{2+},Cu^{2+} and Zn^{2+} salts.Their structures have been prepared elucidated on the basis of IR, ^{1}H- and ^{13}C-NMR spectra, electronic spectra, elemental analysis, magnetic susceptibility mreasurements.

A series of 18-membered N_6 macrocyclic complexes was studied**(131)** which was synthesized by template condensation stoichiometry of α , α'-dibromo-o-xylene and 2,6-diaminopyridine.The proposed and nature of the macrocyclic complexes have been confirmed on the basis of elemental analysis and conductivity data, respectively.

New neutral Schiff base complexes of Cu(II), Co(II), Ni(II) and Zn(II) were studied**(132)** which derived from 4-aminoantipyrine and N-(1-morpholinobenzyl) acetamide (Mannich base). The structural features of the complexes have been confirmed by microanalytical data IR, UV-Vis., NMR. The antimicrobial activity of the ligand and its complexes has been extensively studied on microorganisms such as Staphylococcus aureus and Baciilus subtilis.

The deprotonation constants of 1-benzyl-4-piperazineglyoxime (BPGO) and 1-methyl-4-piperazineglyoxime have been determined in 0.1 mol dm^{-3} NaCl at 25 ºC potentiometrically**(133)** .The pK_a values have been found as 9.79, 7.04and 3.19 for BPGO and 9.56,7.62 and 3.01 for MPGO in acidic medium. In various pH conditions, the different complexes, which are formulated as, MHsLz, MH_5L_2, MH_4L_2, MH_3L_2, MH_2L_2, MHL_2, ML_2, MHjLz and MH $_2L_2$ have been formed by titration of the transition metal ions (Cu^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}) and ligands mixtures with NaOH.

A new series of transition metal complexes of Cu(II), Ni(II),Co(II) Mn(II), Zn(II), VO(IV),Hg and Cd(II) have been synthesized from the schiff base (L) derived from 4-aminoantipyrine,3-hydroxy -4-nitrobenzaldehyde and o-phenylenediamine**(134)**. Structures features were obtained from their elemental analysis, magnetic susceptibility, molar conductance, mass,IR,UV-Vis, 1H NMR and spectral studies.

New complexes with the Schiff base ligand derived from s-benzyldithiocarbazate**(135)** were studied which have been prepared and characterized by elemental analysis, magnetic, conductometric IR, and electronic spectral studies. The tridentate ONS Schiff base s-benzyl N-(phenyl, phenylhydroxymethyl) methyenedithiocarbazate gave monoligand complexes with Ni(II) and Cu(II) having the general formula [MligandX] (M=Ni(II) and Cu(II) ; XNO,Cl,Br,NCS)

New vic-dioxim N - (glyoxyldioxime) N-(2-hydroxybenzylidene)- 1 , 4-diaminonaphthalene from naphthalene (136) was synthesized. Its complexex of nickel, copper and cobalt were prepared. The vicdioxime and its complexes were characterized by FT-IR, UV, ^{1}H NMR, mass spectrometry, elemental analysis DTA/TG analysis techniques and conductometric measurements.

Modified form of Irving-Rossotti titration technique is used(137) to dermine the formation constants for Cu(II) mixed ligand complexes at 1:1:1 optimum molar concentration of metal, primary ligand (A) and secondary ligand (L). The formation constant values of binary complexes are compared with ternary complexes. Stability constants have been evaluated and discussed in terms of basicity of ligand, statistical and stereochemical phenomenon. A mechanism of protonation in complex formation is suggested.

Mixed ligand complexes of Cu(II) with 2,2’-bipyridylamine and phenols, viz., catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid(138) were studied which have been synthesized and characterized by modern methods like elemental analysis, infrared spectra, thermogravimetric analysis, magnetic moment, electronic spectra and conductivity measurements. All complexes are found to be coloured.

Metal Chelates of Co(II), Ni(II) and Cu(II)(139) were proposed with Schiff bases which have been synthesized by the condensation of 1-oxo-1,2,3,4-tetrahydrocarbazoles with semicarbazide/thiosemicarbazide hydrochloride and characterized by using physico-chemical and spectroscopic methods. The complexes have general composition $[M(OTCS)_3]$ and $[M(OTCTS)_2]$, M= Co(II), Ni(II) and Cu(II). The complexes were found to be non-electrolytic in nature due to low value of electrical conductivity.

Preparation and characterization of some of Co(II), Ni(II) and Zn(II) complexes**(140)** was investigated with diazine ligands including phthalazine, pyridazine and naphthyridines. The complexes $[(NH_3)_4CoL_2](ClO_4)_3$ (L = phthalazine, pyridazine) were prepared by reaction of triflate complex $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ with the appropriate ligand in sulfolane. Also some complexes of naphthyridines with Co(II), Ni(II), Zn(II) were prepared by reaction of ML_2 salt (L = Cl) and the appropriate naphthyridine ligand. However, preparation of $(NH_3)_4CoL_2](ClO_4)_3$ with L = naphthyridines was unsuccessful.

Complexes of Ni(II) and Cu(II)**(141)** were studied with Schiff bases, vanillidene-4 chloroaniline (VCA) and vanillidene-3-nitroaniline (VNA) which have been synthesized and characterized by elemental analysis, molar conductance, magnetic measurement, IR and electronic spectra. Coordination of azomethine nitrogen in the Schiff base of the metal has been proposed. Antimicrobial activities of the complexes have also been evaluated.

Complexes of Mn(II), Fe(III) and Co(II) **(142)** were studied with 2-cis-3,7-dimethyl-2,6-octadiene-1-semicarbazone formed by condensation of semicarbazone hydrochloride and 2-cis-3,7-dimethyl-2,6-octadiene-1-al which have been synthesized and their physico-chemical properties have been investigated by elemental analysis, magnetic measurements, molar conductance, electronic spectroscopy and infrared spectroscopy. The ligand was found to be bidentate chelating agent for the metal ions. All these complexes have been tested in vitro for their antimicrobial activity against bacteria Staphylococcus aureus (gram postitive) and Escherichia coli (gram negative) and fungi Candida albicans and Aspergillus niger.

Two new complexes of Cu(II)**(143)** were prepared with drugs ranitidine (N-[2-[[[5-[(dimethylamino)methyl]-2-furanyl] methyl] thio]ethyl]-N'-methyl- 2-nitro-1,1-ethene diamine) and nizatidine (N-[2-[[[2-(dimethylamino) methyl]-4-thiazolyl] methyl] thio] ethyl]-N'-methyl-2-nitro-1,1-ethenediamine) of the general formula $[Cu(drug)_2](ClO_4)_2$. Elemental analysis, conductometric and magnetic measurements, electronic and IR spectroscopy have been employed to characterize them. The molar conductivity values in ethanol show a behaviour of 1:2 electrolytes.

Two novel Schiff bases**(144)** were synthesized using 1-methyl 2-pyrrolidinone/1-methyl-2-pyridone with o-phenylene diamine along with their Mn(II), Co(II), Ni(II) and Cu(II) chelates and characterized. The IR, electronic thermogravimetric data, antibacterial and antifungal activities are discussed here.

A new vic-dioxime ligand and its Cu(II), Co(II), Ni(II), Pd(II), VO(IV) and Zn(II) complexes**(145)** was studied which have been prepared and characterized by elemental analyses, infrared, electronic spectra, magnetic moment and molar conductance data. The Ni(II), Pd(II) and Zn(II) complexes have a diamagnetic character. The ^1H- and ^{13}C-NMR and GC/MS spectra of the *vic*-dioxime ligand and its Ni(II), Pd(II) and Zn(II) complexes were recorded. In addition, all compounds are non-electrolyte.

Copper(II) complexes of thiosemicarbazone (L1) and semicarbazone (L2) derived from pyrrole -2 - carboxaldehyde**(146)** were developed. All the complexes reported here had been characterized by elemental analysis, molar conductance, magnetic moment, IR, electronic and EPR spectral studies. The molar conductance measurements of the complexes in DMSO correspond to non electrolytic nature.

The reactions of nickel (II) and cobalt (II) complexes, [MCl $_2$(PPh $_3$) $_2$] (M = Ni or Co) with bidentate Schiff base ligands derived from acetylacetone or benzoylacetone with aniline, o -, m-nitroaniline were studied**(147)**. The complexes were characterized by elemental analysis, spectral (IR, electronic) and cyclic voltammetric studies and are formulated as [MCl(PPh $_3$) (L)] (M = Ni or Co; L = bidentate Schiff base ligand.a square planar structure has been tentatively proposed for all the new complexes.

The reaction between ciprofloxacin and $VOSO_4.3H_2O$ in 1:1, 1:2 and 1:3 molar ratio in methanol at 20°C, 0°C and -10°C**(148)** was investigated. In various pH conditions the different complexes which are formulated as $VO(H_2O)3L$, $VO(H_2O)L_2$ and VL_3 have been formed by titration of $VOSO_4.3H_2O$ with ciprofloxacin in the presence of NaOH. These complexes have been characterized by IR spectroscopy. The order of stability is estimated as 1:1 >1:3 >1:2 which is justified by the proposed mechanism.

Acetohydroxamic acid, $CH_3CONHOH$, forms highly stable complexes with vanadium (V) and vanadium (IV) in 1:1, 1:2 and 1:3 mole ratios**(149)**. The stability of these complexes can be determined in terms of thermodynamic parameters;ΔG, ΔH and ΔS. Graphs of ln ß versus 1/T, gave a straight line, with a slope $\Delta H/R$ and intercept $\Delta S/R$. Enthalpy and free energy changes for V(V) complexes were found in the order of ML ›ML_2› ML_3 with a negative sign. Whereas entropy change was found to be in the same order but positive, for vanadium (IV) acetohydroxamic acid complexes, the order of ΔG, ΔH and ΔS was ML›ML3 ›ML2. The ΔS is most positive for a 1:1 complex, while ΔG and ΔH are more negative for the same.

Complexes of Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(I1) with 4'-nitrobenzyiidene-2-hydroxy-3,5-dinitroaniline**(150)** have been prepared and characterized by their microanalyses, molar conductance, magnetic susceptibility, electronic and IR spectra. The donor sites of the ligand have been derived from the results of infrared spectra.

Complexes of Co(II), Ni(II) and Cu(II) with Oxalic (OZ), malonic (MZ) and terephthalic (TPZ) dihydrazides(151) were investigated which have been prepared and characterised from elemental analysis, magnetic moment, visible, IR and ESR Spectra. TGA and DTA results are also reported.

Mixed-ligand complexes of the type MS, (MeBI), (where M = Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II), Hg(II), SH = N-6-methyl benzothiazol-2-ylsalicylaldimine and MeBI = 2-methyl benzimidazole) and VOSz. MeBl were prepared and characterized (152) on the basis of analysis, molar conductances, magnetic moments, electronic and IR spectral data. All the complexes, were found to be nonelectrolyte.

Four neutral complexes of Cu(II), Ni(II), Co(II) and Zn(II)(153) were prepared with a new tridentate Schiff base (HL) derived from anthranilic acid and acetoacetanilide. The analytical data show that the metal to ligand ratio is 1:2. The structural features have been determined from IR, UV-Vis, ^{1}H-NMR, ESR and mass spectral data. Their low electrical conductance values support their neutral nature.

Fe(III), Co(II), Ni(II) and Cu(II) complexes of 4-azomalononitrile antipyrine (L)(154) were studied which have been prepared in ethanol solution and characterized by IR, electronic, and ESR spectra as well as magnetic susceptibilities and molar conductivities. The ligand behaves as a neutral bidentate one and the coordination takes place via the azomethine nitrogen and the carbonyl oxygen atom. Ligand field parameters have been calculated and structures are proposed.

A series of bidentate Schiff base ligands, 5-((4-*n*alkoxyphenyl)azo)-N-(*n*alkyl)-salicylaldimine (*n*alkoxy = octyloxy, dodecyloxy, nalkyl=Butyl, nhexyl) homologues were investigated**(155)**, which have been synthesized and characterized by IR, NMR, mass spectroscopy and elemental analyses. For all the ligands the nickel(II) and copper (II) complexes have been synthesized and characterized by elemental analyses and IR spectroscopy.

The Schiff base complexes derived from Salicylaldehyde and opheneylenediamine have been prepared and characterized using several physical techniques **(156)**, in terms; elemental analysis, molar conductance measurements, thermogravimetric analysis, magnetic moment measurements, infrared, electronic and electron paramagnetic resonance spectra. The elemental analysis data exhibit the formation of 1:1[M:L] complexes. The infrared spectral data display the coordination behavior of the Schiff base towards Cr(VI), Cr(III), Pb(II) and TiO(IV) ions. Schiff base and its new complexes were tested for antibacterial activity against gram positive bacteria; Staphylococcus aureus and gram negative bacteria; Salmonella, Escherichia coli including the resistance bacteria Pseudomonas aeruginosa.

Co(II) and Fe(III) chelates of Schiff bases derived from isatin with α-alanine, valine, ß-phenyl-α-alanine, serine, threonine, aspartic acid, glutamic acid, histidine and tryptophan have been synthesized and identified on the basis of their chemical analysis, IR, UV-Vis. spectra and magnetic moment measurements **(157)**. All the complexes area suggested to possess octahedra structures.

Some Schiff base ligands were prepared from the N-amino rhodanine and each of 2-formylindole and salicylaldehyde, respectively**(158)**. Moreover, the ligands were characterized by elemental analysis, IR, mass, ^{1}HNMR and electronic spectra. The Cr(III), Co(II), Ni(II) and Ag(I) complexes of the ligands were prepared and characterized by the analytical and spectroscopic methods. The free ligands, and their metal complexes were screened for their antimicrobial activities.

The stability constants of M-A-B [M=Ni(II), Cu(II) or Zn(II), A=salicylaldehyde(sal) and B=L-valine(Val), L-phenylalanine(phe) and L-tryptophan(Trp) and AB the corresponding Schiff base] were determined**(159)**. The study indicates preference for formation of Schiff base complexes rather than the ligands binding as such to the metal ions without fusion of rings.The presence of aliphatic or aromatic side chains in the amino acids has no effect on the basicities of the coordinating sites of the Schiff bases.

The tridentate schiff base, salicylinene imino-o-thiolbenzene was synthesized**(160)**, from salicylaldehyde and o-amino thiolbenzene.The Schiff base has been reacted with Cu (II)), Ni(II) and Zn(II, to form new complexes, Cu(II)[$C_{13}H_9ONS$].H_2O, Ni(II)[$C_{13}H_9ONS$].3H_2O, and Zn(II)[$C_{13}H_9ONS$].3H_2O. The mole ratio of tridentate Schiff base ligand to metal was 1:1. The complexes have been identified by infrared spectra, visible spectra, TGA, DTA and elemental analysis .

Complexes of Mn(II), Co(II), Cu(II) and Zn(II) with Schiff base formed by condensation of cinnamaldehyde and anthranilic acid have been synthesized and their physicochemical properties have been investigated by elemental analysis, magnetic measurement, molar conductance, electronic spectroscopy, infrared spectroscopy and thermal studies**(161)**. The ligand was found to be bidentate chelating agent for the metal ions. Thermal decomposition data of the complexes have been analyzed to obtain the activation energy, entropy of activation and frequency factor based on Coats-Redfern equation. The relative thermal stability of the chelates can be given as $[MnLOAc(H_2O)]_3 \approx [ZnLOAc(H_2O)] < [CoLOAc(H_2O)_3] < [CuLOAc(H_2O)]$.

Cobalt(III) complexes of the type [Co(DH)$_2$LBr] where DH = dimethylglyoximato, anion L = (pyridine, piperidine, quinoline, isoquinoline, triazole, indole, benzimidazole, benzotriazole, carbazole) have been isolated and characterized on the basis of physico-chemical methods **(162)**. The chemical analyses are in complete agreement with the above formula of the compounds. The IR spectra reveal the hydrogen bonding and bonding from nitrogen of the ligand to the cobalt. The NMR spectra indicate the stereochemistry of the compound. The UV spectra indicate the octahedral geometry of the complexes.

2,2-Dithiobenzoic acid (1) metal complexes (1a-4a, 1b-4b, 1c-4c) were synthesized using 1 and metal salts such as copper (II), cobalt (II), manganese (II), nickel (II), zinc (II) acetates and ruthenium (III) chlorides in the absence or in the presence of diamines**(163)**. The analytical and spectroscopic data of all complexes confirmed an octahedral geometry around the central metal ion with water molecules occupying the coordination sphere. Some of the metal complexes display antibacterial activity.

The new macroacyclic Schiff base ligand was prepared by the condensation of 2,5 bis(aminomethyl)-thiophene with 2-formylpyridine, and the relevant Ni^{2+} and Cu^{2+} complexes synthesized simultaneously as well **(164)**. IR, NMR and CHN techniques were used for structural characterization.

Metal polychelates of the type [ML(H$_2$O)$_2$] where M = Mn(II) Ni(II), Cu(II), Zn(II) and H$_2$L = 4,4-dihydroxy-3,3-dipropionyl biphenyl-(3,4-diaminoanisole) were synthesized**(165)**. Their structures have been elucidated on the basis of analytical, magnetic, electric and spectral study as well as elemental analysis. D.C. electrical conductivity has been measured over a temperature range 400-425 K. The ligand and its polychelates have also been screened for their antimicrobial activity using various microorganisms.

Complexes of 2-(4-aminophenyl) benzimidazole with Zn(II), Cd(II) and Hg(II) chlorides and Cd(II) and Hg(II) bromides have been synthesized **(166)**. They have been characterized by elemental analysis, conductivity measurements, IR and ^{1}H NMR spectral studies. The results show that the complexes are non-electrolytes, four coordinated and the ligand acts as a monodentate.

Complexes of Fe(II), Co(II), Ni(II) and Cu(II) with o-vanillin-L-histidine were investigated**(167)**. Physical and spectral data of the chelates were determined by elemental and spectral analysis. The synthesized complexes were screened against microorganisms isolated from prawn and soil for antibacterial activity.

The interaction of Cu(II) and Th(IV) with 1-(3-chlorophenyl)-3-(2-hydroxy-5-methylphenyl)-5-phenylpyrazoline (1), 1-(3-chlorophenyl)-3-(2-hydroxy-3-bromo-5-methylphenyl)-5-phenyl-pyrazoline (2) and 1-(3-phenylsulphonyl)-3-(2hydroxy3bromo5methylphenyl)5(4methoxyphenyl) pyrazole (3) was studied **(168)**. The stability constants of complexes of Cu(II) and Th(IV) have been studied at constant temperature (27 ± 0.1 ^{o}C) and 0.1 M ionic strength in 70% DMF-water mixture. It was observed that as the colour changes from light brown to darker shade there is complex formation between ligand and metal ion.

Transition metal dialkyldithiocarbamates [$\{R_2NCS_2)_nM\}$; R_2 = Me_2 or Et_2 and M = V, Mo, W and Pt] complexes were prepared by the reaction of metal chloride $\{MCl_n$; n = 3, M V, W and n = 4, M Mo, Pt$\}$ with sodium dialkyldithiocarbamate, [$\{R_2NCS_2Na\}$; R_2 = Me_2 or Et_2] in dichloromethane/water (1:1) mixture**(169)**. The metal complexes were characterized by elemental analysis, solubility, conductance and infrared spectral studies. The various synthesized complexes along with their parent salts were screened for their fungitoxicity under in vitro conditions against the three phytopathogenic fungi viz. Alternaria alternata, Fusarium oxysporum and Colletotrichum capsici by spore germination inhibition technique. All the complexes exhibit antifungal activity to varying extents.

Anodic oxidation of Co, Ni, Cu, Zn, Cd and Sn metal ions in an anhydrous acetone solutionof poly(azomethinethiosenicarbazone)(PATS) yields the PATS-metal complexes**(170)**. Chemical and thermal analyses as well as FTIR and electronic spectral data are presented to confirm the formulation of the isolated materials. The spectral datd show that the ligand polymer is coordinated to the metal ions via the thiol sulfur atom and the nitrogen of the azomethine group. Thermogravimetric measurements (TGA) and differential thermal analyses (DTA) were used to obtain the energy of decomposition of PATS and its metal polymer complexes.

A series of metal complexes of Zn(II) have been synthesized with newly synthesized biologically active 1,2,4-triazole Schiff bases derived from the condensation of 3-substituted-4-amino-5- mercapto-1,2,4-triazole with 8-formyl-7-hydroxy-4- methylcoumarin**(171)**. The structure of the complexes has been proposed in the light of elemental analyses, spectroscopic data (IR, UV-Vis and ^{1}H NMR), thermal studies. Electrochemical study of the complexes is also reported. All the complexes are soluble to limited extent in common organic solvents but soluble to larger extent in DMF and DMSO and are non-electrolytes in these two solvent.

Cu(II)-complexes of N-salicylideneaniline and its derivatives were not light sensitive in most solvents such as acetonitrile. A photo-decomposition occurred upon irradiation in halocarbon solvents such as

$CHCl_3$. It has been suggested that such photoreactivity is attributed to the reactivity of charge-transfer to solvent (CTTS) excited state attained upon irradiation. The complexes have been thermally analysed in nitrogen and static air using thermogravimetry (TG) and derivative thermogravimetry (DTG)**(172)**. The thermal degradation of the complexes proceeds in two or three stages. The kinetic parameters obtained from the Coats-Redfern and Horowitz-Metzger equations show the kinetic compensation effect.