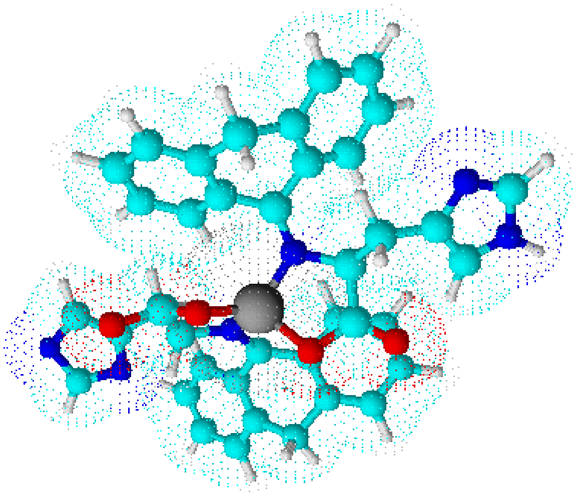
# PART I
# SYNTHESIS AND CHARACTERIZATION

Shaju. K. S. “Evaluation of metal evaluation binding capacity of azomethine class of compounds, electrochemical investigations on corrosion and their biological studies ” Thesis. Department of Chemistry, St. Thomas College Thrissur, University of Calicut, 2014



# PART I

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# CHAPTER 1

## INTRODUCTION AND REVIEW

Coordination chemistry is a widely developed branch of inorganic chemistry and the chemistry of coordination compounds has always been a challenge to the inorganic chemists as it has more branches. A coordination compound contains a central metal atom or ion linked to a number of oppositely charged ions or neutral molecules called ligands. Coordination compounds play a very significant role in our lives; the study of them has contributed to the highest degree of understanding the chemical bond in inorganic chemistry.

The applications of coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological function system, industry and medicine. Coordination compound contains single or additional organized bonds, which is a connection among a couple of electrons in which the electrons are donated by one of the atoms.

Importance and applications of coordination compounds find use in many qualitative and quantitative chemical analyses. Similarly purification of metal can be achieved through formation and subsequent decomposition of their coordination compounds. Inflexibility of water is predictable by simple titration with $Na_2EDTA$. The $Ca^{2+}$ and $Mg^{2+}$ ions form stable complex with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes. Some important extraction processes of metals like those of silver and gold make use of complex formation. Importance and applications of coordination compounds are of great importance in biological system. The pigment responsible for photosynthesis, chlorophyll, is a coordinated compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Coordination compounds are used as catalysts for many industrial processes.

Articles can be electroplated with silver and gold much more smoothly and evenly from the solution of the complexes. In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the unrecompensed AgBr to from a complex ion $[Ag_9S_2O_3)_2]^{3-}$.

There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problem caused by the presence of metal in toxic proportion in plant and animal. Thus, excess of copper and iron are removed by chelating ligands D-penicillamine and desferrioxime B via the formation of the coordination compounds. EDTA is used in the conduct of poisoning (EDTA binds to heavy metals and minerals in the blood so that they can be excreted in the urine). Some coordination compounds of platinum effectively inhibit the growth of tumours.

Metals play a vital role in an immense number of extensively differing biological processes. Some of these processes are quite specific in their metal ion requirements, in that only certain metal ions in specified oxidation states can accomplish the necessary catalytic structural requirement. Metal ion dependent processes are found throughout the life science and vary tremendously in their function and complexity.

The chemistry of metal complexes with multidentate ligands having delocalized π-orbitals, such as Schiff bases or porphyrins has recently gained more attention because of their use as models in biological systems. Transition metal complexes with Schiff bases as ligands have occupied a central role in the development of coordination chemistry.

**Azomethines (Schiff base) ligands**

A Schiff base, named after Hugo Schiff, is a compound with a functional group that contains a carbon-nitrogen double bond (>C=N) with the nitrogen atom connected to an aryl or alkyl group, not hydrogen. Schiff base was first reported by Hugo Schiff in 1864[1]. Schiff bases are formed by the condensation reaction of aliphatic or aromatic carbonyl compounds with aliphatic or aromatic primary amines in different conditions and in different solvents with the elimination of water molecules.

$$\underset{\text{Primary amine}}{R\text{-}NH_2} \quad + \quad \underset{\text{Aldehyde / Ketone}}{>C=O} \quad \rightarrow \quad \underset{\text{Schiff Base}}{>C=N\text{-}R} + H_2O$$

Schiff bases have the general structure R-N=C-R' where R and R' are aryl, alkyl, cycloalkyl or heterocyclic groups which may be variously substituted. Schiff bases that contain aryl substituents are substantially more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable. Often Schiff bases are also referred to as anils, imines or azomethines.

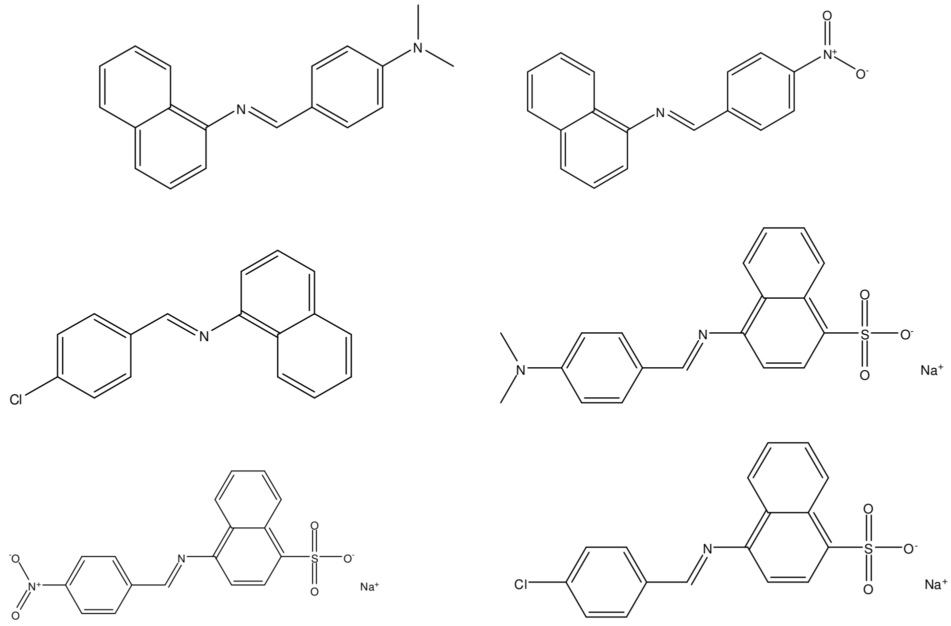
"Schiff bases are used, e.g., in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhanced selectivity and sensitivity"[2-4]. "Among the organic reagents actually used, Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties”[5,6]. “Schiff bases are widely applicable in analytical determination, using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed (determination of compounds with an amino or carbonyl group); using complex formation reactions (determination of amines, carbonyl compounds and metal ions); or utilizing the variation in their spectroscopic characteristics following changes in pH and solvent”[7]. “Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions”[8,9]. In organic synthesis, Schiff base reactions are useful in making carbon-nitrogen bonds.

Schiff bases are used as substrates in the preparation of a number of industrial and biologically active compounds via closure, cyclo addition and replacement reactions. Moreover, “Schiff bases are also known to have biological activities such as antimicrobial, antifungal, antitumor and as herbicides”[10]. “Schiff bases have been employed as ligands for complexation of metal ions”[11]. On the industrial scale, they have a wide range of application such as dyes and pigments[12].

L-amino acid Schiff bases with N,O donor system have been reported by Taqui Khan et. al[13] and are used as catalyst of enantioselective epoxide of 1,2-dihydronaphthalene. Nitro substituted benzaldehyde Schiff bases were used in organic catalytic reactions[14].

Schiff bases of N-methyl and N-acetyl isatin derivatives with different aryl amines have been prepared and screened for anticonvulsant activities[15]. Antibacterial screening of monobasic bidentate Schiff base complexes with N, O donor have been reported[16]. "Schiff bases of ethylenediamine/ triethylene tetramine (salen) with benzaldehyde/ cinnamic aldehyde/ salicylaldehyde as corrosion inhibitors of zinc in sulphuric acid have been reported" by Desai et. al[17].

Many of the Schiff bases[18] (Scheme I) are shows fluorescence properties. These compounds can be used for spectrofluorimetric monitoring of small pH ranges.



**Scheme I**

Several Schiff bases with heteroatoms and π electrons have been previously reported as effective corrosion inhibitors for steel, copper and aluminum in acid mediums like hydrochloric acid, sulphuric acid, acetic acid, formic acid etc[19-29].

## Application of metal complexes of Schiff bases

Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas. Presence of a lone pair of electrons in an $sp^2$ hybridised orbital of nitrogen atom of the azomethine group is of considerable chemical importance and impart excellent chelating ability especially when used in combination with one or more donor atoms close to the azomethine group. The chelating ability of the Schiff bases combined with the ease of preparation and flexibility in varying the chemical environment about the C=N group makes it an interesting ligand in coordination chemistry.

A large number of Schiff bases and their complexes are of significant interest and attention because of their biological activity including anti-tumor, antibacterial, fungicidal and anti-carcinogenic properties[30-35] and catalytic activity[36-42]. Few of them are explained below.

Sivagamasundari and Ramesh reported that[37] naphthylideneimine Schiff base complexes possessing luminescence property, catalyze oxidation of primary and secondary alcohols into their corresponding carbonyl compounds in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as the source of oxygen.

Four coordinate cobalt(II) Schiff base complexes catalyze efficiently, in primary or secondary alcohols under atmospheric pressure at 60°C, the oxygenation of alkenes substituted with an aromatic or an electron-withdrawing group, which results in ketonization without carbon-carbon bond cleavage[43].

Some copper complexes derived with amino acids, enhances hydrolysis rate[44] more than simple copper (II) ion. Synthetic iron (II) Schiff base complex exhibits catalytic activity towards electron-reduction of oxygen[45]. Some metal complexes of a polymer based Schiff base show catalytic activity on decomposition of hydrogen peroxide and oxidation of ascorbic acid[46]. Cyanohydrins cobaltate complexes exhibit marked catalytic activity[47].

The metal chelates such as tris (8-hydroxy quinolinate) aluminium have excellent electroluminescent properties and used in the fabrication of electroluminescent devices[48]. Wei et. al prepared blue luminescent zinc and beryllium complexes of the Schiff bases derived from calixarene[49]. Yet another Schiff base complex reported by Xie et. al[50] was bis salicylidene[(4-dimethylamino) aniline]zinc(II). This complex exhibits very good light emission and charge transporting performance in organic light emitting diodes (OLEDs). Metal complex films are finding increased use in energy conversion devices such as dye sensitized photo electrochemical solar cells, intercalation batteries, optical display and optical sensors[51]. Schiff base complexes play a vital role of nonlinear optical materials because of its various excited states and also organo metallic interactions[52-57].

Murray et. al[58] has been paid much interest to the rapid thermal decomposition of metal complexes to create metals and metal oxides. Metal complexes with pyruvic acid oxime were studied as precursors to variety of nano metal oxides[59-61]. Saravanan et. al synthesised nano crystal of ZnO and ZnS by the thermal decomposition of cupferon complex[62].

Schiff base complexes of copper have been used as catalysts for oxidation of alcohols and widely studied for the DNA-binding and DNA-cleaving properties and mimic of galactose oxidase[63]. Copper complexes of semicarbazones and phenolic hydrazones have been used as herbicides, insecticides, nematocides, and redenticides[64-66]. Popova and Berova reported that copper and its complexes are good for liver function, its level in blood and urine has influence in pregnancy disorders, nephritis hepatitis, leprosy, anemia and leukemia in children[67]. Semicarbazone Cu(II) complexes mimic superoxide dismutase activity and used as hypnotic [68-69]. Copper complex with isatin (1H-indole-2,3-dione) and its derivatives have shown a variety of biological effects, including inhibition of monoamine oxidase[70]. Copper(II) N-salicylidene amino acidates, copper(II) complexes derived from salicylaldehyde, α- or β-alanine and its thiourea derivatives and copper(II) complexes derived from pyruvic acid and β-alanine have been studied by *in vitro* and *in vivo* methods for antiradical activity[71-72]. “Plasticized membranes using Schiff’s base complex derived from 2,3- diaminopyridine and o-vanilin act as copper (II) selective electrochemical sensors”[73].

Many manganese complexes with double Schiff base ligands have been reported[74-76]. Manganese complexes of Schiff bases are known to be involved in the catalytic epoxidation of olefins and other substrates and in the design of artificial metalloproteins[77,78]. Furthermore, tetradentate Schiff base complexes of manganese(III) act as catalyst in the oxidation of organic substrates[76- 80].

Cobalt complex[81] of a Schiff base (salicylaldehyde with diamine) has excellent light resistance and storage ability and does not degrade even in acidic gases ($CO_2$). Cobalt octanoates and naphthenates have been investigated as driers for linseed oil on paper[81]. Both bis(acetylacetonato)cobalt(II) and tris(acetylacetonato) cobalt(III) have been found to possess fungicidal activity[82]. Besides, bis(salicyladehyde)diimine complexes of cobalt take up and release molecular oxygen and are used in the purification of oxygen[83].

Cobalt complexes find various applications as additives for polymers. Thus cobalt phthalocyanines act as smoke retardants for styrene polymers. Bis (acetylacetonato) cobalt(II) in the presence of triphenyl phosphate has been found to act as an antioxidant for polyenes.

Nickel complexes are used in heterogeneous catalysis, electroplating, and in making pigments and ceramics. Novel tetradentate Schiff bases act as chromogenic reagents for the determination of Ni in some natural food samples[84]. The Ni(II) complex of benzoic acid derivative acts as a stabilizer against oxidation of polybutadiene[85]. A number of nickel complexes of Schiff bases have been found to possess fungicidal and bacterial activity. Nickel complex of N-benzoyl-N'-(2-aminophenyl) thiocarbamide has been shown to exhibit antifungal activity. N-5- chloro-salicylidiene tauriene Schiff base[86] and its Ni complexes show antibacterial activities to *Colibacillus* and *Pseudomonas aeruginosa*. Fe complexes show[87] antibacterial activity and amido –schiff base forms chelate with Fe(II) and act as thrombin inhibitor[88].

Schiff bases are present as reactants in umpteen synthetic organic processes, as important scaffolds in organometallic chemistry, as backbones of precious catalysts and as pharmaceutical presidiums against a series of different diseases and pathological states. Studies of new kinds Schiff bases and complexes are now attracted the attention of researchers for apply in the field of corrosion and other industrial field.

## Review of metal complexes derived from Schiff bases

A series of preparations are reported by Parekh et. al[89] "representing complexes between a range of ligands [KHL = potassium salt of salicylidene-β-alanine, $A^1$ = 2,2′-bipyridylamine, $A^2$ = bis (benzylidene) ethylenediamine,

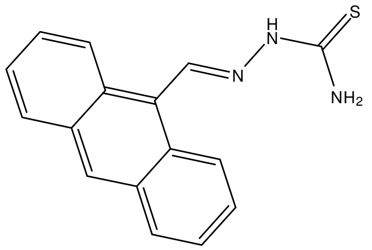
$A^3$ =thiophene-*o*-carboxaldene-aniline, $A^4$ = thiophene-*o*-carboxaldene-*p*-toluidine, $A^5$ =bis(benzylidene)-1,8-diaminonaphthalene, $A^6$ = bis(acetophenone)-ethylenediamine] and oxovanadium(IV) ion". Tümer and coworkers[90] have synthesized the "three Schiff base ligands $H_2L^1$–$H_2L^3$ and their $Co^{II}$, $Fe^{III}$ and $Ru^{III}$ metal complexes. All compounds have been characterized by analytical and spectroscopic methods".

Gölcü et. al[91] reported the synthesis of the "Schiff base ligands, 4-[(4-bromophenylimino)methyl]benzene-1,2,3-triol ($A_1$), 4-[(3,5-di-*tert*-butyl-4-hydroxyphenylimino)methyl]benzene-1,2,3-triol ($A_2$), 3-(*p*-tolyliminomethyl)-benzene-1,2-diol ($A_3$), 3-[(4-bromophenylimino)methyl]benzene-1,2-diol ($A_4$), and 4-[(3,5-di-*tert*-butyl-4-hydroxyphenylimino)methyl]benzene-1,3-diol ($A_5$) and their Cd(II) and Cu(II) metal complexes. Stability constants and potentiometric studies were also performed".

"Complexes of Mn(II), Fe(II), Co(II) and Ni(II) with Schiff base formed by condensation of semicarbazide hydrochloride and anthracene carboxaldehyde have been synthesized and their physico-chemical properties have been investigated"[92]. "Mixed-ligand complexes of copper(II) with 1,10-phenanthroline and various Schiff bases have been prepared by Tümer and coworkers[93] and characterized by elemental analysis, electronic and IR spectra, magnetic moment and molar conductance data".

"Cobalt(II), copper(II), nickel(II) and zinc(II) complexes with 2-hydroxy-1-naphthaldehyde derived N-substituted sulfonamides have been synthesized and the nature of bonding and structure of compounds have been deduced" by Chohan and Supuran[94] from physical, analytical and spectral (IR, $^1H$ NMR, $^{13}C$ NMR, Mass and electronic) data".

The complexes of transition metals with A9CTSC have been prepared and characterized by J. Thomas and G. Parameswaran[95,96] .



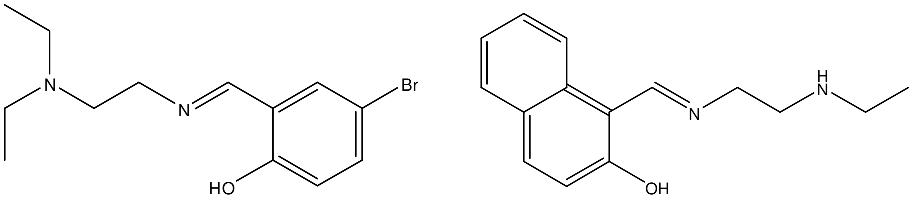
Structure of A9CTSC

A tridentate ONN donor hydrazone ligand, $H_2L$, was synthesized by Khalil et. al[97] by the condensation of 2-amino-4-hydrazino-6-methyl pyrimidine with *o*-hydroxyacetophenone. The structure of the ligand was elucidated by IR and $^1H$ NMR spectra.

"A new series of manganese(II) complexes of amino acid Schiff bases was synthesized from 2-hydroxy-1-naphthaldehyde and L-serine, L-methionine and L-cystein. The structure of their metal complexes was investigated by Sakiyan and Yilmaz[98] using elemental analyses, IR, TGA, magnetic susceptibility and mass spectra". "New complexes of Mn(II) with Schiff bases obtained by the condensation of 2-hydroxy-1-naphthaldehyde with glycine, L-alanine, L-phenylalanine, L-histidine, L-tryptophan and L-threonine have been synthesized" by Sakiyan et. al[99] and characterized by elemental analyses, UV, IR, magnetic susceptibility, thermogravimetry and non-aqueous titration.

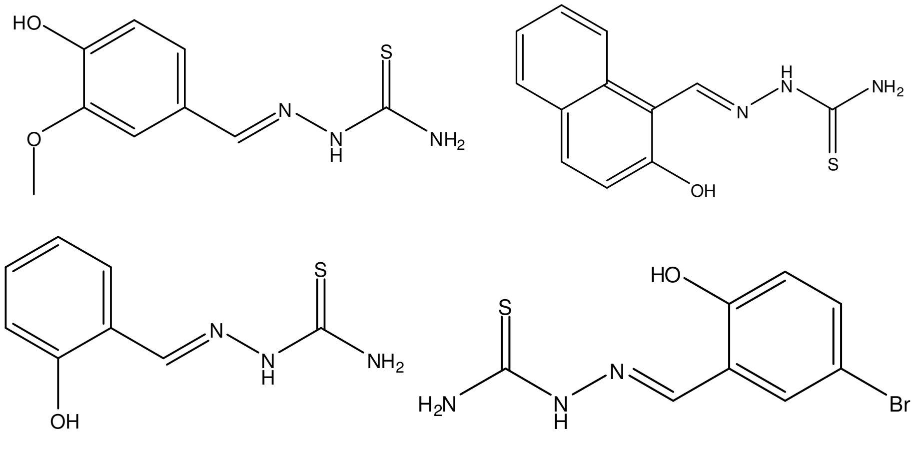
"Two novel asymmetrical Schiff base ligands, $H_2L^1$ and $H_2L^2$, were prepared by Salib et.al[100] by reacting two half-unit Schiff base compounds with 2-methyl-7-formyl-8-hydroxyquinoline. The two half-unit Schiff base compounds were initially prepared by condensing dimedone with either ethylenediamine or p-phenylenediamine, respectively. Twelve metal complexes were obtained by reacting both ligands with Cu(II), Ni(II), Co(II), Mn(II), Fe(III) and VO(IV) cations".

Two Schiff bases (Scheme II) and their copper complexes were prepared by Hui et. al[101]. Each Cu atom in the complexes is five coordinate in a distorted square- pyramidal geometry.



**Scheme II**

Complexes of Ag(I), Pt(II) and Pd(II) with various thiosemicarbazones (Scheme III) have been described by Laly and Parameswaran[102]. The complexes have been characterized on the basis of elemental analysis, infrared, electronic, and nmr spectral and magnetic susceptibility data.

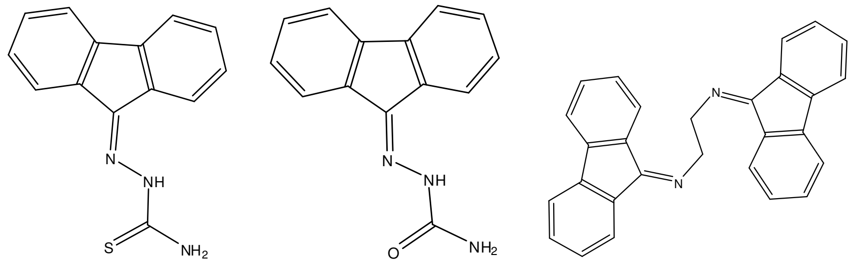


**Scheme III**

"Metal complexes of a Schiff base ligand derived from cefotaxime and salicylaldehyde were prepared" by Anacona et. al[103]. The salicilydene-cefotaxime ligand ($H_2L$) and mononuclear [M(L)] (M = Co(II), Ni(II) and

Cu(II)), dinuclear $[Ag_2(L)(OAc)_2]$ and tetranuclear metal complexes $[M_4(L)(OH)_6]$ (M(II) =Ni(II) and Cu(II)) were characterized on the basis of analytical, thermal, magnetic and spectral studies (IR, UV-visible, $^1$H NMR, $^{13}$C NMR and EPR)".

"New bidendate Schiff base ligands HL1, HL2 and L3 (scheme IV) derived from the condensation of thiosemicarbazide, semicarbazide, and ethylenediamine with 9-fluorenone as polycyclic aromatic compound (PAC) and their complexes of Ag(I), Cu(II), VO(IV), La(III), and Zn(II) have been prepared" by Youssef et. al[104] and characterized by conductance and magnetic measurements, electronic, infrared and $^1$H NMR spectral data.



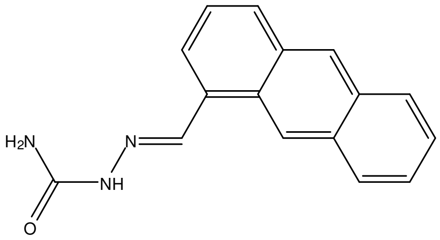
HL1 HL2 L3

**Scheme IV**

"A series of complexes of Co(II), Ni(II), Cu(II), Mn(II) and Fe(III) have been synthesized by Kulkarni et. al[105] with Schiff base derived from isatin monohydrazone and fluvastatin. The complexes have been characterized in the light of elemental analysis, spectral (IR, UV-Vis., FAB-mass and ESR) and magnetic studies". Four new iron(III) complexes were obtained by Herchel et. al[106] by "the reaction of 4-salicylideneamino-1,2,4-triazole (Hsaltrz) and selected dinuclear μ-oxo-bridged iron(III) Schiff base complexes

[{FeL$^4$}$_2$(μ-O)], where L$^4$ represents a terminal tetradentate dianionic Schiff base ligand".

The metal complexes of the type [$CuL_2(H_2O)_2$], [$UO_2L_2$], [$PdL_2$], [$CdL_2$] were synthesized by Marykutty and Parameswaran[107]. The IR data suggest the co-ordination of ligand through O and N atom. The structure of 'L' is given as follows



Structure of L

Schiff base ligands HL$^1$–HL$^6$ have been prepared by Tümer et. al[108] from the reaction of 2,6-diformyl-4-*t*-butylphenol and 2,6-di-formyl-4-methylphenol with various aromatic amines in ethanolic solution. TG, DTG and DTA curves of [$PdL_2$] and [$Pt(LH)_2Cl_2$] (LH= flurenone thiosemicarbazone) in air are studied by Laly et. al[109].

Co(II), Ni(II) and Cu(II) complexes of the Schiff base anthracene carboxaldehyde L-histidine were prepared by Indiradevi et. al[110] and characterized by elemental analysis, magnetic measurements, conductivity experiments and spectral studies.

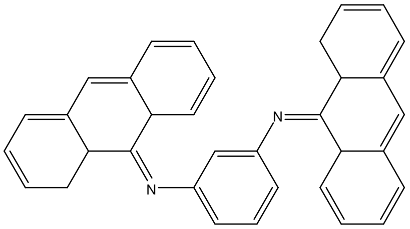
"The zinc(II), copper(II), nickel(II) and cobalt(II) complexes of Schiff bases obtained by the condensation of cefixime with furyl-2-carboxaldehyde, thiophene-2-carboxaldehyde, salicylaldehyde, pyrrol-2-carboxaldehyde, and 3-hydroxynaphthalene-2-carboxaldehyde, were reported" by Arif et.al[111] and characterized by their elemental analyses, molar conductances, magnetic moments, IR and electronic spectral measurements.

"Cu(II), Co(II), Ni(II) and Zn(II) metal complexes with new heterocyclic Schiff base derived from 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one and 3-methoxysalicylaldehyde have been synthesized by Sonmez et. al[112] and characterized on the basis of elemental analysis, electronic, IR and $^1$HNMR spectra and also by aid of molar conductivity measurements, magnetic moment measurements and thermogravimetric analyses".

A new series of lanthanide chloride complexes with the ligands fluorenone semicarbazone (FSC) and fluorenone thiosemicarbazone (FTSC) were synthesised and characterized by Laly and Parameswaran[113]. Cd(II) and Ni(II) complexes with FTSC were also prepared and characterized[114] .

"Several new binuclear and polynuclear dioxomolybdenum(VI) Schiff base complexes have been synthesized" by Ngan et. al[115]. "The reaction of bis(acetylacetonato)dioxomolybdenum with 5-dichlorosalicylaldehyde 4-ethylthiosemicarbazide (L1/L2) in the presence of 4,4′-bipyridine (4,4′-bpy) or 4,4′-bipyridine *N*,*N*′-dioxide (4,4′-dpdo) gave a binuclear *cis*-dioxomolybdenum complex $[(MoO_2)_2L_2(D\text{-}D)]$, in which the bidentate ligand, 4,4′-bipyridine or 4,4′-bipyridine *N*,*N*′-dioxide (D-D), formed a bridge between the two molybdenum atoms. The synthesis of polynuclear dioxomolybdenum(VI) $[(MoO_2)L'(D\text{-}D)]_n$ complexes were achieved by the reaction of the second type of dinuclear dioxomolybdenum(VI) complex, $[(MoO_2)_2L'D_2]$, with the bidentate ligand 4,4′-bipyridine (D-D)".

“A new Schiff base N,N’-di(9-anthrylidene)-1,3-phenylenediamine and a bis (aminophosphonate) 1,3-bis[N-methyl (diethoxyphosphonyl)-1-(9-anthryl)] diaminobenzene have been synthesized by Karicheva”[116].



Structure of N,N’-di(9-anthrylidene)-1,3-phenylenediamine

“The complexes formed from the interaction of Cu(II) and Schiff base derived from salicylaldehyde and 2-amino benzoic acid has been prepared” by Aliyu and Ado[117] and characterized by gravimetry, potentiometry, molar conductance and infrared analyses.

**Review of metal complexes derived from amino acid Schiff bases**

“New modified chiral auxiliaries (*S*)-*N*-(2-benzoylphenyl)-1-(2-chlorobenzyl) pyrrolidine-2-carboxamide and (*S*)-*N*-(2-benzoylphenyl)-1-(3,4-dimethylbenzyl)pyrrolidine-2-carboxamide and their Ni(II) complexes of Schiff’s bases with glycine and alanine have been synthesized by Saghiyan et. al[118]. They were tested in asymmetric C-alkylation and aldol condensation reactions of amino acid moieties”.

Stability of Schiff bases from Pyridoxal-5′-phosphate and *α*-& non *α*-amino acids have been studied by Vázquez et. al[119] in a wide range of pH. Furthermore the transamination process for the PLP-serine Schiff base and the cyclization reaction of PLP-histidine Schiff base have also been studied.

A relationship between antimicrobial activities and the formation constants of amino acid-Schiff bases and their Cu(II) and Ni(II) complexes was studied Sari et. al[120]. For this purpose, a series of Schiff bases were prepared from DL-amino acids (DL-glycine, DL-alanine) and halo aldehydes (5-chloro-2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde).

MacDonald and co-workers[121] reported that "amino acid Schiff base copper complexes of either salicylaldehyde or 2-hydroxy-1-naphthaldehyde wth L-serine, L-histidine, histamine and L-tryptophan were prepared. Schiff bases of salicylaldehyde or 2-hydroxy-1-naphthaldehyde with cysteine or penicillamine were also prepared and characterised".

"Iron (III) complexes $[Fe(L)_2]Cl$ where L is monoanionic *N*-salicylidene-arginine, hydroxynaphthylidene-arginine and *N*-salicylidene-lysine were prepared and their DNA binding and photo-induced DNA cleavage activity were studied" by Mohammed et. al[122].

"Ni(II) complexes with Schiff bases obtained by condensation of arginine with salicylaldehyde; 2,3-; 2,4-; 2,5-dihydroxybenzaldehyde and o-hydroxynaphthaldehyde have been synthesized by Sallam and Abbas[123] using the template method in ethanol or ammonia media. They were characterized by elemental analyses, conductivity measurements, magnetic moment, UV, IR and $^1$H NMR spectra as well as thermal analysis (TG, DTG and DTA). The Schiff bases are dibasic tridentate donors and the complexes have diamagnetic square planar and octahedral structures".

The structural study of five Schiff bases derived from "L-arginine and 2-hydroxy carbonyl" compounds were performed by Kołodziej et al.[124] in both solution and solid state using NMR and X-ray methods. Both analytical methods applied to the solid state samples showed a significant difference in molecular structures of unsubstituted and 7-$CH_3$ substituted compounds. This effect was explained as a steric interaction of methyl group”.

In the study by Çakır et. al[125], a novel Schiff base of “cysteine and saccharin was synthesized and characterized by UV–Vis, FT-IR, $^1$H NMR and elemental analysis. The voltammetric behaviour of Schiff base was investigated on the static mercury drop electrode (SMDE) by using square-wave voltammetry (SWV) and cyclic voltammetry (CV)”.

“Six new complexes of the Schiff base ligand (HL) derived from benzoin and cysteine with Ln=La(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) of the type $LnLCl_2(H_2O)_2$ have been synthesized by Ma et. al[126] and characterized by elemental analyses, molar conductance, XPS, IR, thermal analysis, $^1$H NMR and electronic spectra”.

Zhang and coworkers[127] reported that the “Mg(II) complex of Schiff base derived from vanillin and L-tryptophan could bind with herring sperm DNA. The binding behaviours between them in physiological pH environment (pH 7.40) have been studied by spectroscopy, cyclic voltammetry and viscosity methods”.

“Five novel Schiff base complexes of tin with histidine analogues (derived from the condensation reaction between L-histidine and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde) have been synthesized and charecterised by Ortiz et. al[128]. Characterization has been completed by IR and high resolution mass spectroscopy, 1D and 2D solution NMR ($^1$H, $^{13}$C and $^{119}$Sn), as well as solid state $^{119}$Sn NMR”.

“New complexes of Ti(III), Cr(III) and Ni(II) with Schiff bases (synthesised by condensation of anthracene-9-carboxaldehyde with L-histidine, L-tryptophan, L-valine, L-methionine & L-glycine) have been synthesised by Prakash and Ahmad[129] and characterised by elemental analyses, molar conductance, magnetic susceptibility measurement, thermogravimetric analysis, I.R and electronic spectral studies. These complexes have been found to posses 1:2 stoichiometry between the metal and ligand. The ligands and their corresponding complexes were screened for their antimicrobial activities".

"Three new salicylidene Schiff base nickel(II) complexes $[Ni(L(1))(CH_3COOH)_2]_2$ (1), $[Ni_2(L(1))_2(CH_3OH)]$ (2), $[Ni(L(2))_2]\cdot 3H_2O$ (3) {H2L(1)=N,N'-bis(salicylidene)-3,6-dioxa-1,8-diaminooctane, HL(2)=2-ethyl-2-(2-hydroxybenzylideneamino)propane-1,3-diol} were synthesized by Li et. al[130] and characterized fully by structural, analytical, and spectral methods. The single-crystal X-ray structures of complexes 1 and 2 exhibit the symmetrical ligands coordinated to the nickel(II) ion in a tetradentate fashion via ONNO donor atoms, while the unsymmetrical ligand L(2) presented a ONO tridentate coordination mode in complex 3. The nickel(II) ions lie in the six-coordinated octahedral environment for the mononuclear complexes 1 and 3, along with dinuclear complex 2".

"Neutral tetradentate $N_2O_2$ complexes of Cu(II), Ni(II), Co(II), Zn(II) and VO(II) have been synthesized by Kavitha et. al[131] using the 1-phenyl-2,3-dimethyl-4-imino-(2-hydroxybenzylidene)-pyrozol-5-(α-imino)-indole-3-propionic acid ($H_2L$). All the complexes were characterized by elemental analysis, molar conductivity, magnetic susceptibility data, IR, $^1H$ NMR, UV-Vis, FAB-Mass and EPR spectral studies".

Lovely and Christudhas investigated[132] the "Schiff base complexes of Co(II), Ni(II), Cu(II) and Zn(II) derived from 3-pyridine carboxaldehyde and L-tryptophan. They have been synthesized and investigated by different physicochemical techniques. The resulting complexes were characterized by elemental analysis, molar conductance, IR, XRD and SEM".

"New zirconium(IV) complexes were synthesized with bidentate ligands and characterized by elemental analysis, molar conductance measurements, molecular weight determinations, IR, electronic, NMR ($^1$H and $^{13}$C), fluorescence and molecular modeling studies by Singh[133]. All the complexes are 1: 2 electrolytes in nature and may be formulated as [$ZrL_2Cl_2$] (where L is Schiff bases of amino acids glycine, alanine, valine, methionine, phenylalanine, tryptophan and substituted isatin). The analytical data showed that the Schiff base ligand acts as bidentate toward zirconium ion via the azomethine nitrogen and carboxylate oxygen".

Azzouz and Ali[134] reported the "synthesis of some Schiff bases derived from benzaldehyde and salicylaldehyde with some amino acids as glycine, DL-alanine, ß-alanine and L- methionine, with a new alternative method. The structures of these Schiff bases are confirmed by using physical methods, namely, melting points or boiling point, UV and IR spectra".

"New dibutyltin(IV) complexes of Schiff base derived from 5-chloroindoline-2,3-dione, indoline-2,3-dione with amino acids (tryptophan, alanine and valine) were synthesized by Singh[135] and characterized by elemental analysis, IR, electronic spectra, conductance measurements, and biological activity".

"Three new Schiff bases derived from the condensation reaction of thiophene-2-carbaldehyde and DL-alanine, DL-valine and DL-phenylalanine have been synthesized and their Co(II), Ni(II) and Cu(II) complexes have been prepared by Sarı and G¨urkan[136]. The Schiff bases and the complexes have been characterized by their analytical and spectral data".

Sleema et. al[137] reported that "o-vaniline-L-histidine forms 1:1 complexes with the transition metals like Mn, Co, Ni, Cu and Zn. All the complexes are found to be non-electrolytes in distilled water and octahedral structures were assigned to them based on electronic, ESR and room-temperature magnetic measurements".

"A new Schiff base ligand as salt (KL) was synthesized by Fan et. al[138] using potassium salt of DL-β-phenylalanine and 2-hydroxy-1-naphthaldehyde. Cu(II) and Ni(II) binuclear complexes of this ligand, $[M_2L_2(CH_3COO)_2]$ have been synthesized and characterized by elemental analyses, IR, UV spectra and molar conductance".

"Co (II) complexes of Schiff base 2-amino-4-nitrophenol-N-salicylidene with some amino acids (viz. alanine, phenylalanine, valine, cysteine, leucine and glutamic acid) were synthesized by Patil et. al[139]. The structural characterization of Schiff base and cobalt complexes were done on the basis of their melting point, solubility, elemental analyses, conductivity measurements, GC-MS, FTIR, NMR, UV-Visible spectroscopy, magnetic susceptibility, and X-ray diffraction studies".

"The structure of a Schiff base containing phenylalanine derived from curcumin has been studied by Deng et. al[140] using computational simulations using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at B3LYP/6-311G** level".

M. A. Neelakantan et. al[141] has derived the Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and VO(II) Schiff base complexes from indole-3-aldehyde and amino acids like L-alanine, L-phenylalanine and L-histidine. Biological studies were also done in this work.

## Significance of study

The starting materials proposed for the present research study are anthracene-9(10H)-one, β-alanine, L-arginine, L-phenyl alanine, L-tryptophan, L-histidine, L-cysteine. These compounds are relatively inexpensive, ecofriendly and have special characteristic required to form Schiff bases due to the presence of carbonyl and amino group. Also the formed Schiff bases have lone pair of electrons and poly nuclear rings containing π- bonds. This enables the Schiff base to act as a chelating agent, corrosion inhibitors and antimicrobial agents. This research may contribute to corrosion science by the discovery of new Schiff bases with potential ability for preventing corrosion in acidic environment. Moreover, the structural information of the newly synthesized molecules and their antimicrobial abilities may be useful for other researchers for further investigations.

## Scope of present investigation

From the above literature survey it becomes evident that, systematic studies on metal complexes of polynuclear carbonyl Schiff bases were carried out. Investigations also reported on metal complexes of Schiff base derived from essential & nonessential amino acids. There are only few reports available for metal complexes of Schiff base derived from polynuclear carbonyl compounds and essential& nonessential amino acids. However no work has been reported on metal complexes of Schiff base derived from anthracene-9(10H)-one and various biologically important essential& nonessential amino acids. The observation is that many such ligands and their metal complexes have ample applications and demand detailed investigation.

In the present investigation, the focus is mainly on the synthesis and characterization of Schiff bases derived from various essential & nonessential amino acids with anthracene-9(10H)-one. The metal complexes of these Schiff bases with transition metal ions are also proposed to be synthesized and characterized by various physicochemical methods.

# CHAPTER 2

# MATERIALS AND METHODS

Reports of the general reagents employed for the present investigation are specified in this chapter. Also the details of the analytical and physical methods used for the characterization of ligands and complexes synthesized are also briefly described.

## Materials

In preparation of reagents, chemicals of analytical grade purity were used. The polynuclear carbonyl compound anthracene-9(10H)-one was from Fluka as synthetic material and used directly without further purification. The amino acids β-alanine [3-amino propanoic acid], L-arginine [(S)-2-amino-5-guanidinopentanoic acid], L-phenyl alanine [(S)-2-amino-3-phenylpropanoic acid], L-tryptophan [(S)-2-amino-3-(1H-indole-3-yl)propanoic acid], L-histidine [(S)-2-amino-3-(1H-imidazol-4-yl)propanoic acid], L-cysteine [(R)-2-amino-3-mercaptopropanoic acid] procured from E-Merck were used. Analar grade metal acetates from Qualigens were used as source of metal for synthesis of the complexes Co(II), Ni(II), Cu(II) and Zn(II). In order to prepare iron complexes, analar grade ferric chloride sample from Ranbaxy was used. The distilled ethanol was used as the solvent. Mineral acids like hydrochloric acid, nitric acid and sulphuric acid, sodium acetate, potassium hydroxide used in the present investigations were of analar grade. The remaining chapters in this part illustrate the procedure for the preparation of ligands and complexes.

## Analytical methods

The following measures were employed to test the characterization of ligands and their metal complexes.

### *C H N S analysis*

CHNS analysis is a form of elemental analysis concerned with determination of only Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) in a sample. The technology behind the CHNS analysis is combustion analysis where the sample is first fully combusted and then the products of its combustion are analyzed. Carbon, hydrogen nitrogen and sulphur content of the ligands and their metal complexes were determined by microanalysis using Elementar make Vario EL III model CHNS analyzer.

### *Estimation of metals*

The metal content in the synthesized complex was determined by using the standard procedures[142] available. In these procedures, volumetric, gravimetric, colorimetric and pyrolytic methods are included.

"A common method was adopted for decomposing the metal complexes and the residue solution used for the volumetric, gravimetric and colorimetric estimations. For this a known amount of complex was digested with concentrated nitric acid-perchloric acid mixture followed by concentrated HCl. The digestion process was repeated three times by adding fresh amounts of hydrochloric acid. The resultant solution was then quantitatively made up to 100 ml. The metal content in the complex was estimated using a definite volume of this solution.

Amount of copper was determined iodometrically by the addition of KI and subsequent titration of liberated iodine by standard sodium thiosulphate. Manganese and zinc were estimated volumetrically by complexometric titration using standard EDTA with eriochromeblack–T as indicator and aq. $NH_3/NH_4Cl$ buffer solution of pH 10. At the end point the color changes from red to blue.

The amount of cobalt was estimated volumetrically also by complexometric titration using standard EDTA solution and xylenol orange indicator and hexamine buffer solution of pH 6. At the end point color changes from red to yellow. Gravimetrically, nickel was estimated by precipitating as dimethyl glyoxymate. From the mass of nickel dimethyl glyoxime complex [$Ni(C_4H_7O_2N_2)_2$], the mass of nickel is calculated.

Estimation of iron and chromium was conducted by colorimetric analysis. For the estimation of chromium, 1,5-diphenylcarbazide $CO(NH.NHC_6H_5)_2$ used for developing the color and chromium acquires a violet color with this reagent. A green filter having the transmission maximum at 540nm is used. The iron in the metal complexes was estimated by thiocyanate method using the filter 480 nm (blue-green filter).

The complexes were also subjected to pyrolysis method for the estimation of metals. About 0.2g complex was accurately weighed out in a silica crucible and heated strongly. During heating, all the organic particles in the complex were burnt off and the metal oxide left behind was weighed. From the weight of the metal oxide, the metal percentage was calculated".

## Physicochemical technique used for the characterization

Physicochemical techniques such as solution conductance, magnetic susceptibility measurements and spectral studies like UV-Visible, infra red, $^1$H NMR, $^{13}$C NMR and mass spectra have been used to elucidate the structure and geometry.

### *Molar conductance measurements*

The metal complexes were dissolved in DMSO and prepare the solutions at a concentration of $10^{-3}$M. Then the molar conductivities of the solutions at room temperature were measured to establish the charge of the metal complex using a ELICO conductivity meter.

***Magnetic susceptibility***

The measurement of magnetic moment is a very useful method for studying the electronic structure of a transition metal complex. It gives fundamental information about the bonding and stereochemistry of metal complexes. Magnetic susceptibilities of the complexes were determined at room temperature by Gouy method. It consists of a suspension of a uniform rod in a nonhomogeneous magnetic field of about 5000 Oersteds and measuring the force exerted on it by a conventional weighing technique. $Hg[Co(SCN)_{4]}$ is used as the calibrant[143] which are easy to prepare, do not decompose or absorb moisture and pack well in the sample tube.

"The molar susceptibility, a measure of magnetic field, of a substance is an algebraic sum of the susceptibilities of the constituent atoms, ions or molecules. The susceptibility per gram atom of a paramagnetic metal ion in a particular compound is determined by measuring the molar susceptibility of the compounds and applying diamagnetic corrections for the other ions or molecules in the compound. Diamagnetic corrections were applied using Pascal constants taking into consideration, the magnetic contribution by various atoms and structural units[144,145]. The effective magnetic moments were calculated from the corrected susceptibilities using the equation

$$\mu_{\mathrm{eff}} = 2.84\sqrt{\Psi_{\mathrm{M}}.\mathrm{T}} \qquad (1)$$

where $\Psi_M$ is the molar susceptibility corrected for diamagnetism and T is the absolute temperature in K. The theoretical magnetic moments were calculated using the formula

$$\mu_{\text{eff}} = g\sqrt{S(S+1)} \qquad (2)$$

where ‘g’ is the Lande splitting factor and ‘S’ is the total spin quantum number”. Magnetic susceptibility was measured by Sherwood, UK (Mark 1).

### *Electronic spectra*

Electronic spectrum is concerned with the transition of electrons from one energy level to another higher energy level with the absorption of light radiation in the UV and visible region. In transition metal complexes transitions may occur between the split d-levels of the central atom. The transitions are affected by the effect of ligands on the energies of the d orbital of the metal ions. The splitting of d orbitals are different in different geometries, the geometry will have a pronounced effect on the d-d transitions in a metal complex. Thus UV-Vis spectral data of transition metals provide useful information about the structure of complexes.

The UV-visible spectra of the ligands and complexes were recorded on a Shimadzu UV-visible-1800 Spectrophotometer using DMSO as solvent. Electronic spectral studies were carried out mainly in a structural diagnostic perspective so as to supplement any information obtained from magnetic studies.

### *Infrared spectra*

This is one of the most widely used tools for the detection of functional groups in the synthesized ligands and complexes. The importance of IR spectroscopy lies in the fact that characteristic infrared absorption of a group occurs at about the same frequency irrespective of the molecules in which the group is present. By studying the shift in the IR frequencies of ligands with corresponding complexes, the presence of metal–ligand bonds can be interpreted.

The infrared spectra of the ligands and metal complexes were recorded using KBr disc technique in the range 4000-400cm$^{-1}$ on a Shimadzu model FT-IR Spectrometer (Model IR affinity).

### $^{1}$H NMR and $^{13}$C NMR Spectroscopy

NMR spectroscopy involves the change of the spin state of a nuclear magnetic moment when the nucleus absorbs electromagnetic radiation in a strong magnetic field. The chemical shift values provide clues to the chemical environments of the different types of protons and also the number of principal signals gives the number of types of protons. In $^{13}$C NMR spectrum each magnetically nonequivalent carbon gives a single unsplit peak

$^{1}$H NMR and $^{13}$C NMR spectra were recorded at 300 and 75 MHz, respectively, in DMSO-$d_6$ for all compounds on a Bruker AMX-400 NMR spectrometer. The chemical shifts are reported in part per million (ppm) downfield from internal tetramethylsilane (TMS) (chemical shift in $\delta$ values).

### Mass spectra

Mass spectroscopy is used to measure exact molecular weights and from this, exact molecular formulae can be determined. Also used to indicate within a molecule the points at which it prefers to fragment; from this, the presence of certain structural unit in the compound can be recognized.

The mass spectra were run at 70 eV with HP Model MS.5988A and / or GCMS. Cap 1000 EX SHIMADZU spectrometer using Electron Impact Ionization Technique.

# CHAPTER 3

## STUDIES ON Mn(II), Fe(III), Co(II), Cu(II) AND Zn(II) COMPLEXES OF 3-(ANTHRACEN-9(10H)-YLIDENEAMINO) PROPANOIC ACID

Compounds which contain amino acids and its derivatives or Schiff bases as ligands have occupied a central role in the development of coordination chemistry and biochemistry. Schiff base ligands form stable complexes with different transition metal ions. The chemotherapeutic importance of Schiff bases, particularly those derived from different amino acid precursors against tuberculosis, small pox, influenza and certain kinds of tumor are well documented. Furthermore they act as chelating agents for transition and inner transition metal ions and their ability to chelate with trace metals have been considered as one of the reasons for their pharmacological activity.

However, little information is available on metal complexes of Schiff bases derived from anthracene-9(10H)-one and amino acids. Therefore it was considered to be worthwhile and interesting to investigate the donor properties of six different monovalent bidentate Schiff base ligands of anthracene-9(10H)-one with six different amino acids, which is well documented in the following sections of this Part I.

3-(Anthracen-9(10H)-ylideneamino)propanoic acid [A9Y3APA], a potential bidentate Schiff base ligand, has been synthesized for the first time. The ligand can be complexed with different transition metal salts to form different complexes. Detailed investigations on the synthetic and structural aspects of these metal complexes are presented in this chapter.

**Preparation of 3-(anthracen-9(10H)-ylideneamino) propanoic acid**

Anthracene-9(10H)-one (0.38g, 2mM) was dissolved in hot ehanol and refluxed on a water bath. To the refluxing solution added β-alanine (0.18 g, 2mM) in ethanol-water mixture. The mixture was refluxed for 6 hours. The reaction mixture was kept overnight and needle shaped yellow crystals of the ligand were obtained. It was then filtered using a vacuum pump, washed with dilute alcohol, dried in a desiccator over anhydrous calcium chloride (yield 90%, melting point 240$^{0}$C).

**Characterization of the ligand**

The characterization of the ligand was carried on the basis of different analytical tools such as elemental analysis and spectral analysis like infrared, electronic, $^{1}$H NMR, $^{13}$C NMR and mass spectra.

From the elemental analysis the percentage of carbon, hydrogen and nitrogen were obtained. The theoretically calculated values and experimentally found out values were in good agreement. The values are presented in the table 1.1.

The prominent characteristic peaks of IR spectrum are tabulated in the table 1.2. A strong peak at 1595 cm$^{-1}$ can be attributed to characteristic C=N stretching vibration in the ligand. The aromatic, CH stretching vibrations were observed in the region 3064-3015cm$^{-1}$. The absorption of stretching vibration of –OH group of the carboxylic acid part appeared in the region 3380cm$^{-1.}$ The peaks at 1672 cm$^{-1}$ and 1498cm$^{-1}$ were assigned to the asymmetric and symmetric stretching vibrations of the carboxylate group [$\upsilon_{COO^{-}(assy)}$ and $\upsilon_{COO^{-}(sym)}$]. A strong peak at 1740 cm$^{-1}$ may be assigned due to the stretching of carbonyl bond.

The π→π* and n→π* transition bands were shown by the ligand in its electronic spectrum at 28600cm$^{-1}$ and 26400cm$^{-1}$ respectively.

The proton magnetic resonance spectrum of the ligand exhibited the characteristic carboxylic acid proton peak, as a singlet, at δ 12.19. A peak at δ 2.44 corresponds to the $CH_2$ proton (α-carbon) attached to carboxyl carbon. The methylene proton attached to azomethine nitrogen showed a chemical shift value at δ 4.95. Chemical shift value at δ 7.96 corresponds to the $CH_2$ proton in the anthracene ring. The aromatic protons of anthracene-9(10H)-one rings appeared in the regions at δ 7.3- 7.89. The $^{13}C$ NMR spectrum in DMSO-$d_6$ of the Schiff base, A9Y3APA, showed the carboxylic acid carbon signal at 182.11ppm. The azomethine carbon atom showed a peak at 150.8 ppm. The aromatic carbon signals were appeared in the $^{13}C$ NMR spectrum in the region 125-134 ppm. The methylene carbon signal near to azomethine nitrogen appeared at 52.60 ppm.

The peak due to molecular ion was absent in the high resolution mass spectrum of the ligand which establishes the instability of the compound. The loss of fragment $[C_4H_6NO_2]^+$ from the ligand gave a cation at m/z 165 as base peak. The base peak is due to the formation of the cation fragment $[C_{13}H_9]^+$. Other prominent peaks shown in the mass spectrum are at m/z 180, 194 and 208, which can be assigned due to the fragment ions $[C_{14}H_{12}]^+$, $[C_{14}H_{12}N]^+$ and $[C_{15}H_{14}N]^+$ respectively. All these fragments are derived from carbonyl moiety. The $^1H$ NMR, $^{13}C$ NMR and mass spectra are shown in the figures 1.3, 1.4 and 1.5.

The elemental data presented in the table 1.1 were found to be in good agreement with the empirical formula of the ligand. On the basis of the above results, the structure of the ligand A9Y3APA was confirmed and shown in the figure 1.1.

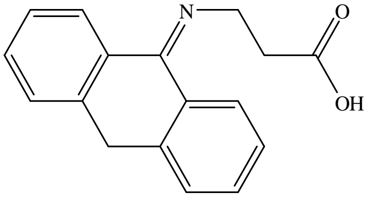


**Fig. 1. 1:** Structure of Schiff base A9Y3APA

**Synthesis of complexes**

Mn(II), Fe(III), Co(II), Cu(II) and Zn(II) complexes of A9Y3APA were prepared by mixing ethanolic solutions of metal acetate (1mM), anthracene-9(10H)-one in ethanol (1mM) and β-alanine in aqueous/ethanol (1mM) in the presence of sodium acetate (1g). The resulting solution was refluxed for about 6 hours, concentrated and kept overnight at room temperature. The complex formed was filtered using a vacuum pump and washed with ethanol, dried in a desiccator over anhydrous calcium chloride. Ferric chloride solution was used for the synthesis of Fe(III) complex.

**Characterization of the complexes**

The complexes were characterized on the basis of elemental analysis, molar conductivity measurements, magnetic measurements, electronic, infrared, $^{1}$H NMR, $^{13}$C NMR and mass spectral data.

All the complexes are coloured, photostable and non hygroscopic. They are soluble in DMSO and in other common organic solvents. On the basis of elemental analysis, Mn(II), Co(II) and Cu(II) complexes can be represented by the general formula $[ML_2(H_2O)_2]$, where M is the metal and L is the ligand moiety. The other metal complexes are represented as $[FeL_2AcH_2O]$ and $[ZnL_2]$, where Ac is acetate moiety. The analytical data of these complexes are also presented in the table 1.1. The room temperature magnetic moments and molar conductivities of the complexes are also given in the same table. Important IR spectral bands of the ligand and complexes are given in the table 1.2.

### ***Elemental analysis***

The complexes were analyzed for metals by standard methods. Percentage of carbon, hydrogen and nitrogen were determined by microanalytical methods. The observed values of the elemental analysis establish that there is 1:2 stoichiometry between the metal and ligand in all the synthesized complexes and are in close agreement with the calculated values.

### ***Molar conductance***

Conductance measurements of these complexes in DMSO at a concentration of $10^{-3}$M at room temperature resulted in molar conductance values in the range of 4-11 ohm$^{-1}$cm$^{2}$mol$^{-1}$. The very low values indicate that these complexes behave as non-electrolytes and are neutral in nature[146].

### ***Magnetic measurements***

The values of the magnetic moments of the complexes are tabulated in table 1.1. The Mn(II) complex possesses a magnetic moment value of 5.92BM. It is reported that if the measured value is in the range of 5.9-6.5BM, Mn(II) complexes can be assigned an octahedral geometry[147]. The $\mu_{eff}$ value of Fe(III) complex at room temperature was 5.84BM. This indicates $d^5$ configuration and an octahedral geometry around the metal ion[148].

The Co(II) complex showed an effective magnetic moment of 4.60 BM. It is reported that octahedral geometry can be assigned to Co(II) complexes, if the measured $\mu_{eff}$ value is in the range of 4.3-5.2 BM[148]. The magnetic moment value of Cu(II) complex was 1.81 BM as expected for an octahedral geometry which corresponds to a $d^9$configuration ($t_{2g}^6e_g^3$) with one unpaired electron[149,150]. Zn(II) complex was found to be diamagnetic as expected due to the $d^{10}$ configuration.

***Infrared spectral studies***

The infrared spectroscopic results provide support for the molecular constitution of these complexes. The assignments are made on the basis of comparison with the spectra of similar type of compounds. The selected infrared absorption frequencies of the ligand and complexes are given in the table 1.2.

On complex formation most of the bands in the IR spectrum of the ligand A9Y3APA undergo frequency shift and in many cases intensity changes. A strong intense band at 1595cm$^{-1}$ in the spectrum of the ligand may be assigned to $\upsilon_{(C=N)}$ stretch. This band showed a downward shift by about 24-29cm$^{-1}$ in the spectra of all the metal complexes, indicating the participation of the azomethine nitrogen in coordination with metals[151]. The depression in stretching frequency may tentatively attributed to a lowering of the C=N bond order as a result of the M-N bond formation in the complexes[152]. The shifted band in many cases is coincident with the C=C band, which then shows greater intensity or broadening. Further evidence for bonding by nitrogen and oxygen atoms is provided by far IR spectra of complexes. Due to interference of skeletal vibrations of ligands with M-N and M-O vibrations, definite assignments of bands are difficult. Therefore only tentative assignments are made on the basis of information available in literature. Spectra of all complexes showed bands at 546-552cm$^{-1}$ and 447-453cm$^{-1}$ which may be assigned to the $\upsilon_{M-O}$ and $\upsilon_{M-N}$ stretching vibrations[153-155].

A broad band at 3425-3444cm$^{-1}$ in the spectra of complexes except zinc complex was attributed to the hydroxyl stretching mode of water molecule[156,157]. In addition, a medium band approximately at 860-930cm$^{-1}$ suggests that water molecules are coordinated. The aromatic out of plane vibration[156] was seen near 940cm$^{-1}$ and in-plane vibrations at 745cm$^{-1}$ and 710cm$^{-1}$.

***Electronic spectra***

The electronic spectrum depends on the energy of metal'd' orbital, their degeneracy and the number of electrons distributed. These features are in turn controlled by the oxidation state of the metal, number and kind of the ligand and the geometry of the complex[158]. The electronic spectral data obtained were found to agree with conclusions arrived from magnetic susceptibility measurements.

In Mn(II) complex, central metal atom in the octahedral environment was confirmed by the presence of electronic spectral bands at 13200, 14800 and 25700cm$^{-1}$. In agreement with the magnetic moment values, these spectral bands can be assigned to the transitions $^6A_{1g}\rightarrow{}^4T_{1g}(G)$, $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ and $^6A_{1g}\rightarrow{}^4E_g(G)$ respectively.

An intense band at 28000cm$^{-1}$ in the electronic spectrum of Fe(III) complex may be attributed to the L→M charge transfer band. Another shoulder peak at 18790cm$^{-1}$ exhibited by the iron complex may be due to $^5T_{2g}\rightarrow{}^5E_g$ transition, confirming its octahedral geometry. Since ground state

Fe(III) in high spin[159] complex is $^6A_1$, all the d-d transitions are weak and obscured with the intense charge transfer bands.

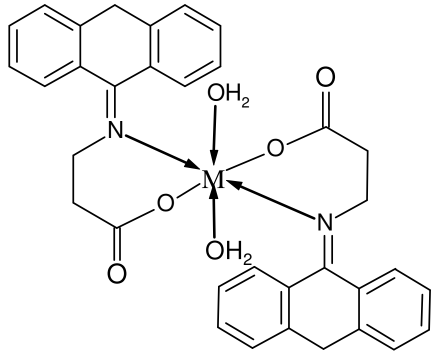
The expected octahedral transitions of Co(II) are $^4T_{1g}$ (F) → $^4T_{2g}$ (F), $^4T_{1g}$ (F) → $^4A_{2g}$ (F) and $^4T_{1g}$ (F) → $^4T_{1g}$(P)[160,161]. The middle band was due to the transition of two electron which is forbidden and gave a weak band, moreover, $^4A_{2g}$(F) and $^4T_{1g}$(P) were very close in octahedral geometry. Due to these factors detection of middle band was very difficult. The electronic spectrum of Co(II) exhibited two peaks at 17500cm$^{-1}$ and 21230cm$^{-1}$ due to $^4T_{1g}$ (F) → $^4T_{2g}$ (F) and $^4T_{1g}$ (F) → $^4T_{1g}$(P) transitions respectively corresponding to octahedral geometry**.**

The electronic spectrum of Cu(II) complex exhibited two bands at 13750cm$^{-1}$ and 15600cm$^{-1}$; the former may be assignable to $^3E_g \rightarrow {}^3T_{2g}$ transition[162] and the later may be attributed to L→M charge transfer band, suggesting thereby the octahedral geometry. The Zn(II) complex does not show any characteristic d-d transition bands.

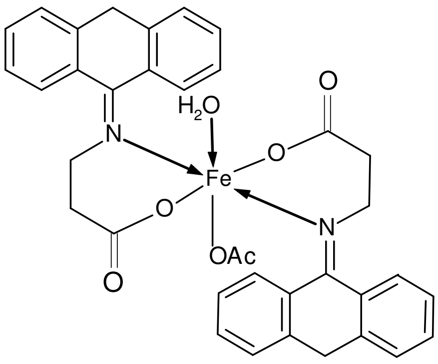
***NMR spectra***

The $^1$Hnmr spectra of the complexes exhibited significant difference from the spectrum of the ligand A9Y3APA mainly in two regions. In the $^1$H NMR spectra of chelates, the disappearance of the signal at δ 12. 19 due to the acid proton in the ligand, it is a clear indication of the coordination of the ligand through the carboxylate group. Similarly, the $^{13}$C NMR spectrum of complexes showed downward shift in the signals due to carboxylic acid and azomethine carbon atoms. This downward shift can be attributed due to the lowering of electron densities as a result of coordination to the metal ion.

From the above detailed discussions, the following geometries can be assigned to the transition metal complexes of A9Y3APA (figure 1.2).



M= Mn(II), Co(II), Cu(II)



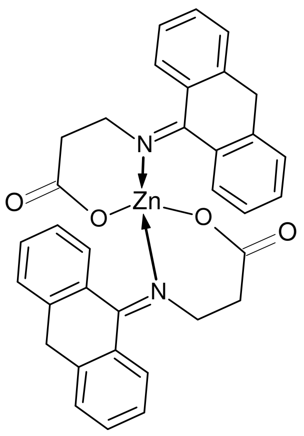


**Fig. 1.2:** Structures of the metal complexes of Schiff base A9Y3APA

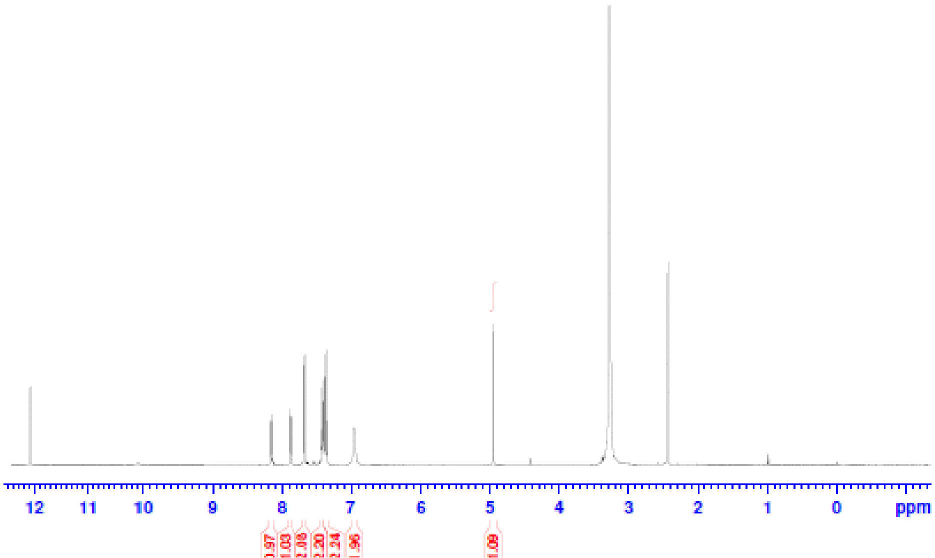


**Fig. 1.3:** $^{1}$H NMR spectrum of Schiff base A9Y3APA

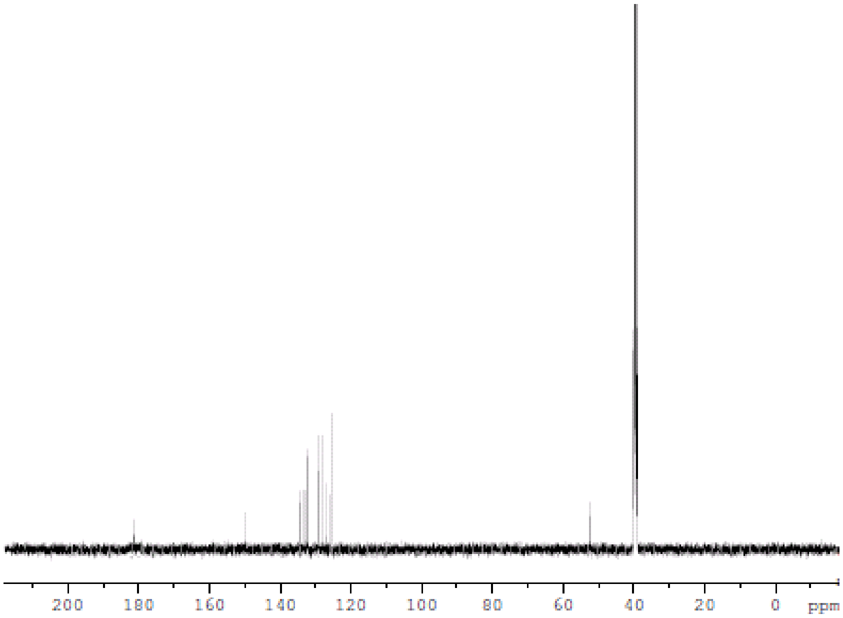


**Fig. 1.4:** $^{13}$C NMR spectrum of Schiff base A9Y3APA

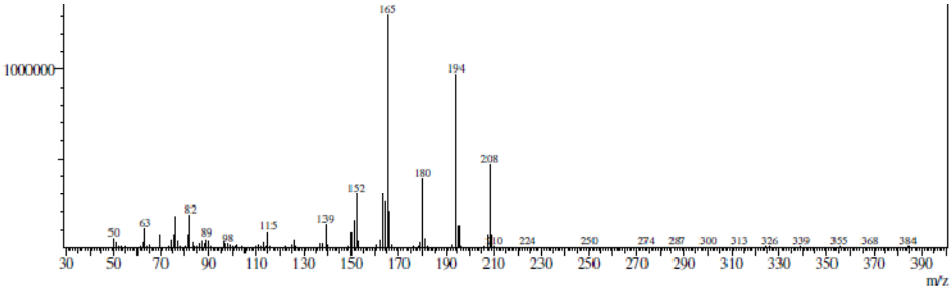


**Fig. 1.5:** Mass spectrum of Schiff base A9Y3APA

**Table. 1.1.** Micro analytical, magnetic and conductance data of transition metal complexes of 3-(anthracen-9(10H)-ylideneamino)propanoic acid [A9Y3APA]

| **Complex** | **Colour** | **Yield (%)** | **Mol.wt.** | **M.P ($^0$C)** | **Metal % Found (Calculated)** | **Elemental Analysis Found (Calculated)** | | | **$\mu_{eff}$ (BM)** | **Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)** | **Geometry** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **C %** | **H %** | **N %** | | | |
| A9Y3APA | Pale Yellow | 90 | 265 | 240 | - | 75.96<br>(76.88) | 6.13<br>(5.65) | 4.95<br>(5.28) | - | - | - |
| $[MnL_2(H_2O)_2]$ | Brown | 74 | 619 | >300 | 8.62<br>(8.87) | 65.48<br>(65.85) | 5.05<br>(5.16) | 4.32<br>(4.52) | 5.92 | 8.63 | Octahedral |
| $[FeL_2AcH_2O]$ | Reddish Brown | 71 | 661 | >300 | 8.15<br>(8.44) | 65.14<br>(65.31) | 4.79<br>(4.99) | 4.11<br>(4.23) | 5.84 | 10.82 | Octahedral |
| $[CoL_2(H_2O)_2]$ | Yellow | 74 | 623 | >300 | 9.28<br>(9.45) | 65.27<br>(65.43) | 5.02<br>(5.13) | 4.27<br>(4.49) | 4.60 | 7.24 | Octahedral |
| $[CuL_2(H_2O)_2]$ | Blue | 70 | 628 | >300 | 9.94<br>(10.11) | 64.72<br>(64.95) | 4.98<br>(5.09) | 4.26<br>(4.46) | 1.81 | 5.92 | Octahedral |
| $[ZnL_2]$ | Yellow | 69 | 594 | 280 | 10.78<br>(11.00) | 68.17<br>(68.68) | 4.11<br>(4.71) | 4.12<br>(4.71) | D | 4.73 | Tetrahedral |

Ac = Acetate L = Ligand

**Table. 1.2.** Characteristic infrared absorption frequencies of A9Y3APA and its transition metal complexes

| **Complex** | $\upsilon_{H_2O}$ | $\upsilon_{COO(asym)}$ | $\upsilon_{C=N}$ | $\upsilon_{COO(sym)}$ | **In plane bending** | **Out of plane bending** | $\upsilon_{M\text{-}O}$ | $\upsilon_{M\text{-}N}$ |
|---|---|---|---|---|---|---|---|---|
| A9Y3APA | - | 1672 | 1595 | 1498 | 952 | 758,715 | - | - |
| $[MnL_2(H_2O)_2]$ | 3425 | 1664 | 1566 | 1433 | 943 | 745, 708 | 547 | 447 |
| $[FeL_2AcH_2O]$ | 3444 | 1658 | 1570 | 1428 | 940 | 744, 706 | 552 | 452 |
| $[CoL_2(H_2O)_2]$ | 3426 | 1662 | 1567 | 1432 | 942 | 748, 709 | 550 | 451 |
| $[CuL_2(H_2O)_2]$ | 3429 | 1660 | 1571 | 1428 | 939 | 744, 707 | 546 | 453 |
| $[ZnL_2]$ | - | 1663 | 1569 | 1431 | 941 | 742, 711 | 552 | 449 |

Ac = Acetate L = Ligand

# CHAPTER 4

## STUDIES ON Mn(II), Fe(III), Co(II), Cu(II) AND Zn(II) COMPLEXES OF (S)-2-(ANTHRACEN-9(10H)-YLIDENEAMINO)-5- GUANIDINOPENTANOIC ACID [A9Y5GPA]

The literature survey showed that there have been numerous studies on the Schiff bases and metal complexes derived from amino acids. However little information is available on metal complexes of poly nuclear Schiff bases derived from anthracene-9(10H)-one and L-arginine [(S)-2–amino-5-guanidino-pentanoic acid]. Hence it is considered to be valuable and interesting to investigate the properties, structures and geometries of the ligand (S)- 2-(anthracen-9(10H)-ylideneamino)-5-guanidinopentanoic acid [A9Y5GPA] and its complexes with metal ions such as Mn(II), Fe(III), Co(II), Cu(II) and Zn(II).

### Synthesis of the ligand

For the preparation of the ligand A9Y5GPA an ethanolic solution of anthracene-9(10H)-one (2mM) was refluxed with an ethanolic/water solution of L-arginine (2mM) for about 6 hours on a water bath. The resulting solution was concentrated, cooled and kept overnight. The separated crystals were collected through filtration using a vacuum pump and washed with ethanol, dried over anhydrous $CaCl_2$ (yield 84%, melting point $235^0C$).

### Characterization of the ligand

CHN analysis and spectral techniques were adopted for the characterisation of the ligand A9Y5GPA. The obtained analytical results are given in the table 1.3 and found to be in good agreement with the empirical formula.

The percentage of elements such as carbon, nitrogen and hydrogen, determined by CHN analysis, has been found to be in good agreement with the calculated percentages of the elements using the molecular formula $C_{20}H_{22}N_4O_2$. The IR spectral data of the ligand A9Y5GPA contain a significant absorption frequency at 1595cm$^{-1}$ and it can be attributed due to the stretching frequency of C=N group. The absorption of stretching vibration of $NH_2$ group appeared in the region 3425cm$^{-1}$ as doublet. The NH absorption frequency was appeared at 3304cm$^{-1}$. The asymmetric and symmetric stretching frequencies of the carboxylate groups exhibited respectively at 1656cm$^{-1}$ and 1456cm$^{-1}$. The aromatic, CH stretching vibrations were observed in the region 3064-3026cm$^{-1}$.

The $^1$H NMR spectrum of the ligand showed a singlet peak displayed in its pmr spectrum at highly deshielded region ($\delta$ 12.2) can be assigned to the carboxylic acid proton. All aromatic protons showed their characteristic resonance peaks between $\delta$ 7.40 and 8.35 in the $^1$H NMR spectrum. A broad peak at $\delta$ 6.97 can be attributed to free $NH_2$ proton in the ligand. The methylene proton attached to NH group showed a peak at $\delta$ 2.45. The CH proton attached to -N=C< (azomethine) exhibited a peak at $\delta$ 4.46. The $^{13}$C NMR spectra of the chelates exhibited signals correspond to carbon atoms in different chemical environment. Due to overlapping of the aromatic carbon signals, it is difficult to distinguish each peak corresponding to each carbon atom. The $^{13}$C NMR spectrum of the ligand exhibited a peak at 182.1 ppm due to the presence of highly electron withdrawing oxygen atoms on the carboxylic group and also due to the $\pi$-electron anisotropic effect. The methylene carbon attached to NH group showed a peak at $\delta$ 37.66 ppm. The carbon atom of the azomethine moiety resonated at 140.05 ppm. The $^1$H NMR and $^{13}$C NMR spectrum of the ligand are provided in figures 1.8 and 1.9 respectively.

The high resolution mass spectrum of the ligand A9Y5GPA is shown in the figure 1.10. The molecular ion peak was absent in the mass spectrum, which shows that the molecular radical cation is quite unstable. A base peak observed at m/z 194 is due to the fragment $[C_{14}H_{12}N]^+$. A significant peak at m/z 165 can be assigned to the fragment $[C_{13}H_9]^+$. Other prominent peak shown in the mass spectrum was at m/z 180, which is due to the fragment $[C_{14}H_{12}]^+$, derived from carbonyl moiety. Mass peaks at 208 can be assigned due to the fragment ion $[C_{15}H_{14}N]^+$.

The electronic spectrum of the Schiff base A9Y5GPA showed three specific bands around 26400, 33200 and 40616cm$^{-1}$, characteristic of n→π*, π→π* and n→σ* transitions respectively. From the spectral studies and elemental analysis, the following structure (figure 1.6) can be assigned to the ligand A9Y5GPA

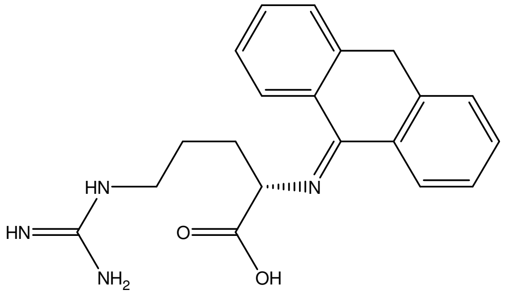


**Fig. 1.6:** Structure of Schiff base A9Y5GPA

**Synthesis of complexes**

The hot ethanolic solution of anthracene-9(10H)-one (1mM), and L-arginine were refluxed for 2 hr. To this added corresponding metal acetate (1mM ) and refluxed for about 6-7 hours in the presence of sodium acetate

(1.0 g) to get the Mn(II), Fe(III), Co(II), Cu(II) and Zn(II) metal complexes of A9Y5GPA. The refluxed solution was concentrated, cooled at room temperature for overnight and filtered. The metal complexes were dried in a desiccator over anhydrous calcium chloride. In the case of Fe(III) complex, the metal salt used was ferric chloride .

## Characterisation of the complexes

The metal complexes were subjected to magnetic and conductivity measurements, elemental, electronic, IR, NMR and mass analysis.

The complexes are coloured and non hygroscopic in nature. They are insoluble in water but slightly soluble in organic solvents like ethanol, methanol and DMSO.

### *Elemental analysis*

Percentage of carbon, hydrogen and nitrogen was determined by micro analytical methods. The analytical data and physical appearance are summarised in table 1.3.

### *Molar conductance*

The very low molar conductance values (4.86-9.53 ohm$^{-1}$cm$^{2}$mol$^{-1}$) of the complexes in DMSO at a concentration of 10$^{-3}$M at room temperature were indicative of their non electrolytic nature.

### *Magnetic measurements*

The values of the magnetic moments of the complexes are tabulated in table 1.3. The Mn(II) complex has a magnetic moment value of 5.96BM which indicate an octahedral geometry. Again an octahedral geometry is suggested around the metal ion Fe(III) complex and has a magnetic moment value of 5.88BM. Co(II) has a magnetic moment 4.98BM, which is suggestive of octahedral configuration. The Cu(II) chelate exhibited the magnetic moment 1.38B.M which is a low value compared to the spin only value 1.73B.M. This suggests a dimeric square planar configuration facilitating anti-ferro-magnetic exchange. Zn(II) complex was diamagnetic as expected.

***Infrared spectral studies***

The characteristic IR absorption bands of the ligand and the complexes are summerised in table 1.4. The comparison of the infrared spectra of the chelates and the ligand revealed that the spectra of chelates differ from that of the ligand in some characteristic frequencies. A strong intense band appeared at 1595cm$^{-1}$ in the spectrum of the ligand due to C=N vibrations, has undergone a frequency shift to lower region of about 22-30cm$^{-1}$ in all metal complexes. This shift indicates the coordination of azomethine nitrogen to metal ion. The aromatic in plane vibration was seen near 915cm$^{-1}$ and out of plane vibration at about 734cm$^{-1}$ and 705cm$^{-1}$. The asymmetric and symmetric stretching vibrations of COO$^-$ of ligand shifted to lower frequency upon complexation and were appeared at ≈ 1650cm$^{-1}$ and ≈ 1430cm$^{-1}$. The Δυ value ($\upsilon_{COO^-(asym)}$-$\upsilon_{COO^-(sym)}$) ≈ 220cm$^{-1}$ are consistent with monodentate carboxylate moiety.

Conclusive evidence of bonding of the ligand to the central metal ion is provided by the appearance of bands at the region 520 – 552cm$^{-1}$ and 442-467cm$^{-1}$, which can be assigned to $\upsilon_{M\text{-}O}$ and $\upsilon_{M\text{-}N}$ bands respectively. The presence of coordinated water molecules in the complexes was confirmed by the appearance of band at the region 3435-3444cm$^{-1}$ and was followed by a sharp rocking mode of vibration at 830-845cm$^{-1}$.

### *Electronic spectra*

The electronic spectral data were found to be in agreement with the conclusions arrived from magnetic susceptibility measurements.

In Mn(II) complex, central metal atom in the octahedral environment, was confirmed by the presence of electronic spectral bands at 13300, 14700 and 25600cm$^{-1}$ and these spectral bands can be assigned to the transitions $^6A_{1g}\rightarrow{}^4T_{1g}(G)$, $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ and $^6A_{1g}\rightarrow{}^4E_g(G)$ respectively.

The Fe(III) complex showed two intense bands at 27000cm$^{-1}$ and 12820cm$^{-1}$ indicating octahedral geometry. The first band is due to charge transfer and second band is due to $^5T_{2g}\rightarrow{}^5E_g$ transition. The electronic spectrum of Co(II) complex was characterised by two peaks at 17400cm$^{-1}$ and 21430cm$^{-1}$ due to $^4T_{1g}$ (F) → $^4T_{2g}$ (F) and $^4T_{1g}$ (F) → $^4T_{1g}$(P) transitions respectively.

Electronic spectrum of the Cu(II) chelate gave a single broad and poorly resolved absorption band around 13880cm$^{-1}$, characteristic of Cu(II) with $D_{4h}$ symmetry[163]. Since this complex exhibited relatively low magnetic moment value compared to spin only value and were four-coordinate, the Cu(II) complex was assumed to have a dimeric square planar geometry. Zn(II) complex exhibited strong charge transfer bands at about 24500cm$^{-1}$.

### *NMR spectra*

The proton nmr spectra of the complexes were very much complex and peak detection was difficult with respect to each characteristic protons. The $^1$H NMR spectra of the complexes exhibited significant difference from the spectrum of the ligand A9Y5GPA mainly in two regions. The disappearance of the signal at δ 12. 2 due to the acid proton in the ligand, is a clear indication of the coordination of the ligand through the carboxylate group. Similarly, the $^{13}C$ NMR spectra of complexes showed downward shift in the signals due to carboxylic acid and azomethine carbon atoms. This downward shift can be attributed to the lowering of electron densities as a result of coordination to the metal ion.

From the above discussions, the following geometries can be assigned to the transition metal complexes of A9Y5GPA and the structures are shown in the figure 1.7.

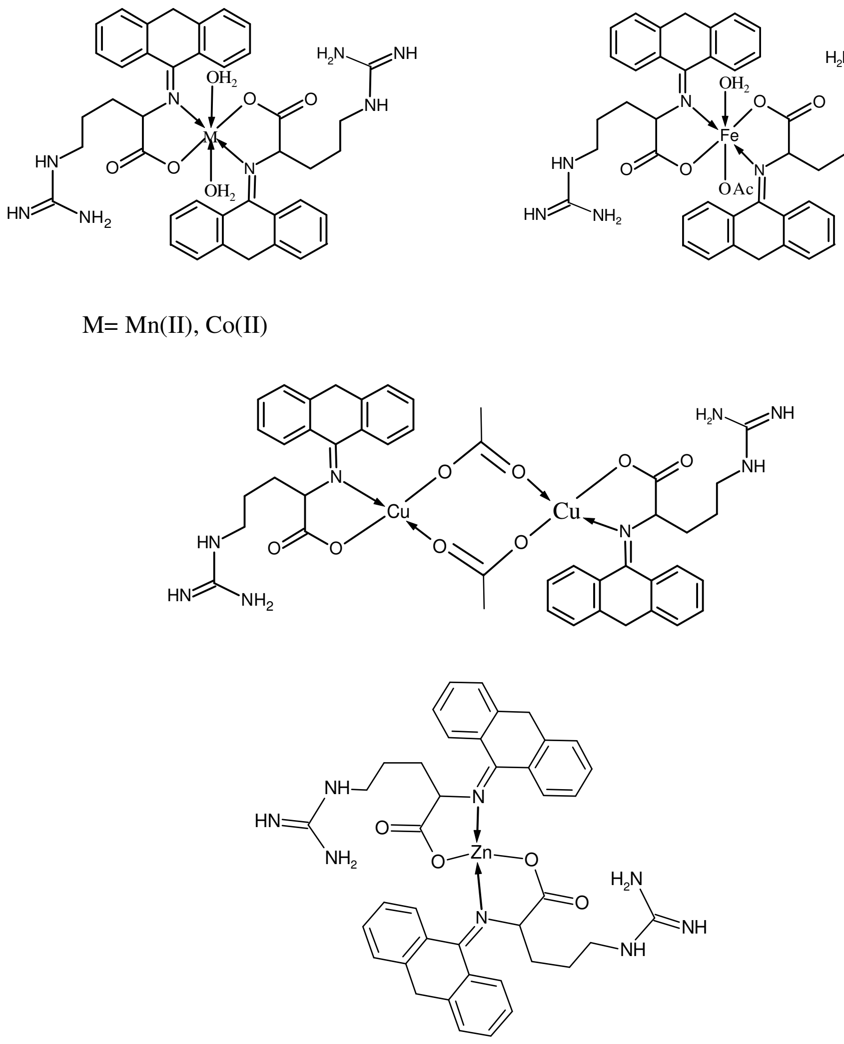

M= Mn(II), Co(II)

**Fig. 1.7:** Structures of the metal complexes of Schiff base A9Y5GPA

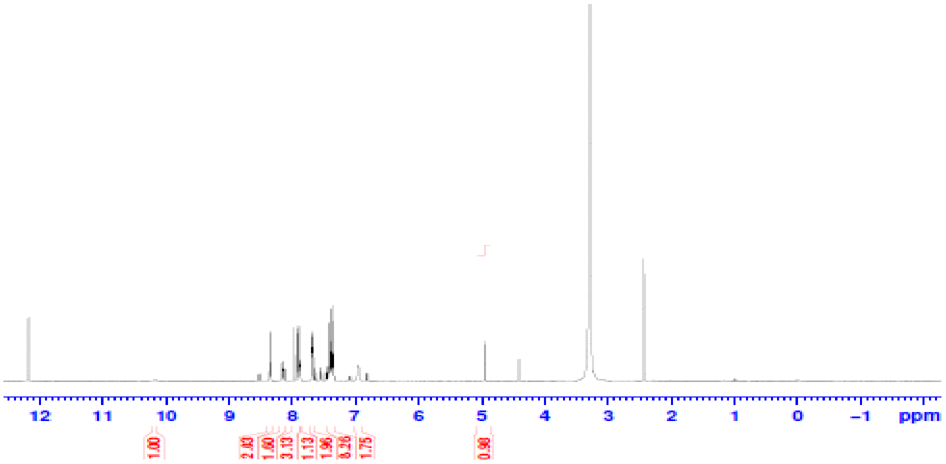


**Fig. 1.8:** $^1$H NMR spectrum of Schiff base A9Y5GPA

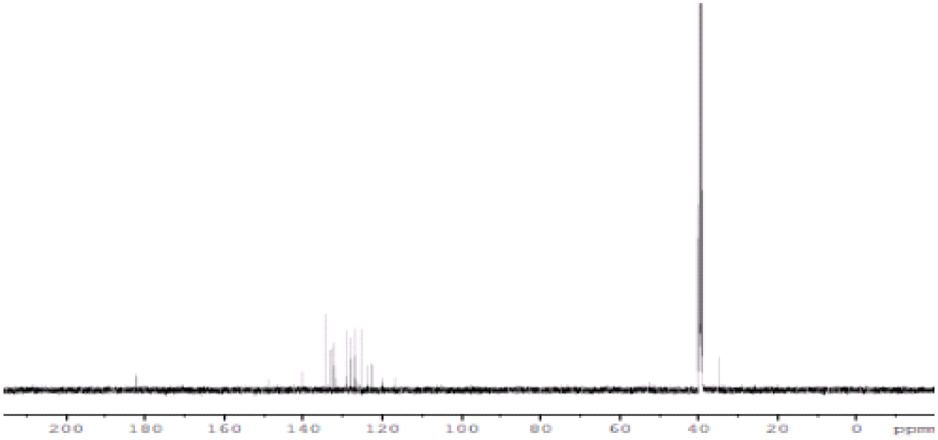


**Fig. 1.9:** $^{13}$C NMR spectrum of Schiff base A9Y5GPA

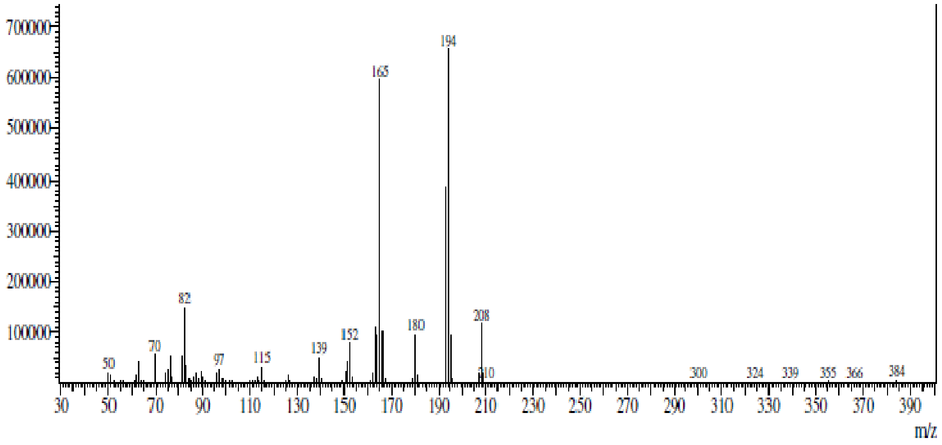


**Fig. 1.10:** Mass spectrum of Schiff base A9Y5GPA

**Table. 1.3.** Micro analytical, magnetic and conductance data of transition metal complexes of (S)- 2- (anthracen-9(10H)- ylidene amino)-5-guanidinopentanoic acid [A9Y5GPA]

| **Complex** | **Colour** | **Yield (%)** | **Mol.wt** | **M.P ($^0$C)** | **Metal % Found (Calculated)** | **Elemental Analysis Found (Calculated)** | | | **$\mu_{eff}$ (BM)** | **Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)** | **Geometry** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **C %** | **H %** | **N %** | | | |
| A9Y5GPA | Dark | 85 | 265 | 235 | - | 68.18<br>(68.48) | 6.03<br>(6.27) | 15.48<br>(15.97) | - | - | - |
| $[MnL_2(H_2O)_2]$ | Brown | 72 | 790 | >300 | 6.52<br>(6.96) | 60.48<br>(60.77) | 5.16<br>(5.82) | 13.92<br>(14.18) | 5.96 | 7.92 | Octahedral |
| $[FeL_2AcH_2O]$ | Reddish Brown | 74 | 832 | >300 | 6.17<br>(6.71) | 60.16<br>(60.60) | 5.28<br>(5.65) | 13.12<br>(13.47) | 5.88 | 9.53 | Octahedral |
| $[Co L_2(H_2O)_2]$ | Yellow | 69 | 794 | >300 | 7.18<br>(7.42) | 60.14<br>(60.47) | 5.36<br>(5.80) | 13.92<br>(14.11) | 4.98 | 4.86 | Octahedral |
| $[CuLAc]_2$ | Bluish Green | 72 | 944 | >300 | 6.44<br>(6.73) | 55.62<br>(55.94) | 4.88<br>(5.09) | 11.26<br>(11.86) | 1.38 | 7.18 | Square Planar (Dimeric) |
| $[ZnL_2]$ | Yellow | 64 | 764 | >300 | 8.28<br>(8.55) | 62.52<br>(62.80) | 5.18<br>(5.50) | 14.22<br>(14.65) | D | 6.24 | Tetrahedral |

Ac = Acetate L = Ligand

**Table. 1.4.** Characteristic infrared absorption frequencies of A9Y5GPA and its transition metal complexes

| **Complex** | $\upsilon_{H_2O}$ | $\upsilon_{COO(asym)}$ | $\upsilon_{C=N}$ | $\upsilon_{COO(sym)}$ | **In plane bending** | **Out of plane bending** | $\upsilon_{M-O}$ | $\upsilon_{M-N}$ |
|---|---|---|---|---|---|---|---|---|
| A9Y5GPA | - | 1656 | 1595 | 1456 | 938 | 758,715 | - | - |
| $[MnL_2(H_2O)_2]$ | 3435 | 1645 | 1569 | 1428 | 913 | 735, 702 | 527 | 467 |
| $[FeL_2AcH_2O]$ | 3444 | 1649 | 1564 | 1432 | 910 | 734, 706 | 542 | 442 |
| $[Co\ L_2(H_2O)_2]$ | 3438 | 1652 | 1567 | 1431 | 912 | 738, 704 | 520 | 456 |
| $[CuLAc]_2$ | - | 1650 | 1561 | 1431 | 915 | 734, 701 | 536 | 443 |
| $[ZnL_2]$ | - | 1648 | 1563 | 1426 | 911 | 732, 709 | 552 | 452 |

Ac = Acetate L = Ligand

# CHAPTER 5

## STUDIES ON Mn(II), Fe(III), Co(II), Cu(II) AND Zn(II) COMPLEXES OF (S)-2-(ANTHRACEN-9(10H)-YLIDENEAMINO)-3- (1H – IMIDAZOLE – 4-YL) PROPANOIC ACID [A9Y3IMPA]

(S)-2-(anthracen-9(10H)-ylideneamino)-3-(1H-imidazole-4-yl) propanoic acid (A9Y3IMPA), a potential bidendate Schiff base ligand, has been synthesised for the first time. This ligand was complexed with five transition metals. Detailed investigation on synthetic and structural aspects of metal complexes derived from anthracene-9(10H)-one and L-histidine [(S)-2-amino-3-(1H-imidazol-4-yl) propanoic acid] are rare. In this chapter, therefore, the results of investigations of the coordination compounds of Schiff base derived from anthracene-9(10H)-one and L-histidine are discussed.

**Preparation of (S)-2-(anthracen-9(10H)-ylideneamino)-3- (1H – imidazole – 4-yl) propanoic acid (A9Y3IMPA)**

A hot 1:1 ethanolic solution (10ml) of l-histidine (0.32 g, 2 mM) was mixed with a refluxing solution of anthracene-9(10H)-one (0.38g, 2 mM) in ethanol (10 ml) and the mixture was further refluxed for six hours on a water bath. The resulting solution was concentrated and kept overnight. The yellowish crystals separated was collected through filtration using a vacuum pump and washed with ethanol and dried over anhydrous $CaCl_2$. The melting point of A9Y3IMPA was found to be $245^0C$ (yield 82%).

## Characterization of the ligand

The ligand was characterized on the basis of different analytical tools such as elemental analysis and spectral analysis like infrared, electronic, $^{1}$H NMR, $^{13}$C NMR and mass spectra.

From the elemental analysis, the theoretically calculated values and experimentally found out values of percentages of CHN are in good agreement. The values are presented in the table 1.5. Data clearly establish that the metal- ligand ratio in all the complexes is 1:2.

The selected characteristic peaks of IR spectrum are shown in the table 1.6. A strong peak at 1610cm$^{-1}$ can be attributed to characteristic C=N stretching vibration in the ligand. The absorption frequency in the region 3090-3035cm$^{-1}$ can be assigned to the aromatic CH stretching vibrations. The band due to stretching vibration of –OH group of the carboxylic acid part appeared in the region 3400-3300cm$^{-1.}$ A medium peak at 1720cm$^{-1}$ may be attributed to the stretching of C=O bond. The peaks at 1664 cm$^{-1}$ and 1488cm$^{-1}$ assigned to the asymmetric and symmetric stretching vibrations of the carboxylate group [$\upsilon_{COO^{-}(asym)}$ and $\upsilon_{COO^{-}(sym)}$].

In the $^{1}$H NMR spectrum of the ligand A9Y3IMPA, proton of the carboxylic acid appeared as a singlet at δ 11.1. The NH proton of the imidazole ring observed at δ 6.96. A pmr signal at δ 4.95 ppm indicates the CH proton linked to azomethine nitrogen. A peak at δ 4.4 corresponds to the $CH_2$ proton near to imidazole ring. The peak of $CH_2$ proton in the anthracene ring appeared at δ 7.97. The aromatic protons of anthracene-9(10H)-one rings appeared in the regions at δ 7.34- 7.88. The CH protons in the imidazole ring appeared in the region δ 8.12-8.34. The $^{13}$C NMR spectrum in DMSO-$d_6$ of the Schiff base, A9Y3IMPA exhibited fourteen distinguished peaks for fourteen carbon atoms in different chemical environment. The $^{13}C$ NMR spectrum of A9Y3IMPA showed the carboxylic acid carbon signal at 182.11 ppm. A peak at 148.80 ppm can be assigned to the azomethine carbon. The aromatic carbon signals were appeared in the $^{13}C$ NMR spectrum in the region 119-140ppm. The methylene carbon signal in the anthracene-9(10H)-one ring appeared at 116.62 ppm. The methylene carbon signal near to imidazole moiety appeared at 52.60 ppm. The signal at 65.20 ppm assigned to CH carbon signal (α-carbon) near to carboxylic acid.

In the high resolution mass spectrum of the ligand, the peak due to molecular ion was absent which establishes the instability of the compound. The loss of imidazole moiety from the ligand gave a cation at m/z 194(100%) as a base peak. The base peak is due to the formation of the cation fragment $[C_{14}H_{12}N]^+$. Other prominent peaks found in the mass spectrum are m/z 165 and 82 which can be assigned due to the fragment ions $[C_{13}H_9]^+$ and $[CH_3NO_2]^+$ respectively. The mass peak at m/z 139 and 152 are due to the formation of cation fragment from histidine moiety and the corresponding moieties are $[C_6H_7N_2O_2]^+$ and $[C_6H_6N_3O_2]^+$ respectively. The figures 1.13, 1.14 and 1.15 represent the corresponding $^1H$ NMR, $^{13}C$ NMR and mass spectra of the ligand A9Y3IMPA, respectively.

The A9Y3IMPA showed three bands in its electronic spectrum. This is due to the transitions of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ and the bands were observed at 32400cm$^{-1}$ and 29900cm$^{-1}$ respectively.

On the basis of the above results, the structure of the ligand A9Y3IMPA was confirmed and shown in the figure 1.11.

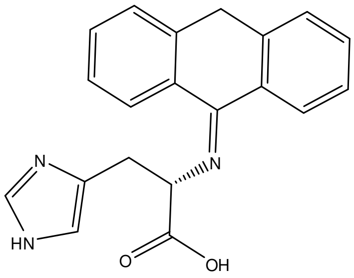


**Fig. 1.11:** Structure of Schiff base A9Y3IMPA

## Synthesis of complexes

To prepare the Mn(II), Fe(III), Co(II), Cu(II) and Zn(II) complexes of A9Y3IMPA, L-histidine (1mM) in Et-OH/water mixture was first refluxed for 2 hr with ethanolic solution of anthracene-9(10H)-one . To this clear solution, 1mM hot ethanolic solution of corresponding metal acetates was added slowly along with 0.5-1g of sodium acetate. The above solution was refluxed for 6 hours, and then concentrated, cooled by kept overnight and filtered. The obtained complexes were dried in a desiccator over anhydrous calcium chloride.

## Characterisation of the complexes

The complexes were characterized on the basis of elemental analysis, magnetic measurements, molar conductance measurements, electronic, IR, NMR and mass spectrum analysis.

The complexes were stable and coloured. They were insoluble in water but slightly soluble in organic solvents like ethanol, methanol and DMSO.

### *Elemental analysis*

Percentages of CHN were determined by micro analytical methods. The results are tabulated in the table 1.5. The ligand A9Y3IMPA act as a bidentate ligand in the reaction with common transition metal ions. All the complexes possess 1:2 metal to ligand stoichiometry.

***Molar conductance***

The molar conductance values of the complexes in DMSO were carried out at a concentration of $10^{-3}$M at room temperature and found to be non electrolytic nature.

***Magnetic moment measurements***

The values of magnetic moments are given in table 1.5. The octahedral geometry of the Mn(II) complex was confirmed from the measured magnetic moment value of 6.09BM. The room temperature magnetic moment of Fe(III) complex was 5.85BM. This indicates an octahedral geometry. The magnetic moment value of Co(II) complex was 4.78BM which is in agreement with its octahedral geometry. Cu(II) complex of A9Y3IMPA registered magnetic moment value of 1.76BM, therefore octahedral structure can be assigned to Cu(II) complex. As expected the Zn(II) complex was found to be diamagnetic due to the absence of unpaired electrons.

***Infrared spectral studies***

The selected characteristic infrared absorption frequencies of the ligand and complex are represented in the table 1.5.

The IR spectra of Mn(II), Fe(II), Co(II) and Cu(II) complexes showed a broad peak in the frequency region 3421-3434 and this can be attributed to the hydroxyl stretching mode of water molecules. In addition, a medium band approximately at 840-920cm$^{-1}$ suggests that water molecules were coordinated to the metal.

The characteristic frequency in the region (1645-1658) and (1444-1458) were attributed to the asymmetric and symmetric stretching vibrations respectively of carboxylate ion. Further the separation value, $\Delta\upsilon_{COO^-}$ value

($\upsilon_{COO^-(asym)}$ - $\upsilon_{COO^-(sym)}$) ≈ $200cm^{-1}$ rules out the possibility of a bridged or multi coordinated carboxylate group.

The azomethine band of ligand showed a downward shift by about 22-$28cm^{-1}$ in the spectra of all the metal complexes indicating the participation of the azomethine nitrogen in coordination with metal ions.

The aromatic in plane vibration was seen near $945cm^{-1}$ and the other in plane vibrations at near $765cm^{-1}$ and $725cm^{-1}$. The band near $540cm^{-1}$ and $486cm^{-1}$ can be due to M-O and M-N vibrations respectively indicate the bonding of the ligand to central metal atom.

***Electronic spectra***

The shift of ligand bands exhibited in the spectra of complexes can be taken as a proof of coordination of the ligands to metal ions. Mn(II) complex, showed three electronic spectral bands at 13400, 14800 and $25700cm^{-1}$due to the transitions $^6A_{1g} \rightarrow ^4T_{1g}(G)$, $^6A_{1g} \rightarrow ^4T_{2g}(G)$ and $^6A_{1g} \rightarrow ^4E_g(G)$ respectively.

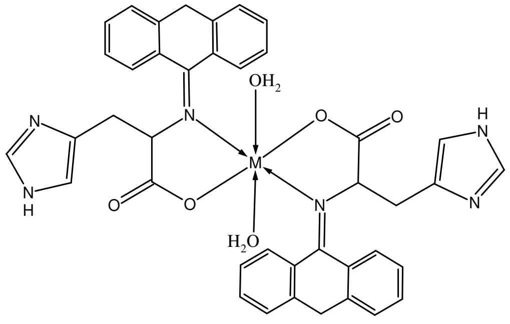
The Fe(III) complex showed two intense bands at $27300cm^{-1}$ and $12620cm^{-1}$ indicating octahedral geometry. The peaks at $17600cm^{-1}$ and $21630cm^{-1}$ were assigned to the transition $^4T_{1g}$ (F) → $^4T_{2g}$ (F) and $^4T_{1g}$ (F) → $^4T_{1g}$(P) respectively of Co(II) complex.

Cu(II) complex showed two bands at $13790cm^{-1}$ and $15630cm^{-1}$; due to $^3E_g \rightarrow ^3T_{2g}$ transition and L→M charge transfer band, suggesting thereby the octahedral geometry. The remaining Zn(II) complex does not show any characteristic d-d transition bands.

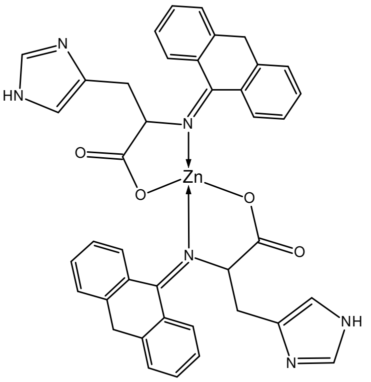
***NMR spectra***

A peak due to δ 11.1 was disappeared in the $^1H$ NMR spectra of the complexes which suggest that the carboxylate oxygen take part in the complex formation. Also the downward shift of the –COOH carbon peak at 182.11ppm confirms the coordination, through carboxylate group. Again there is decrease in the electron density around the azomethine carbon which confirms the coordination through nitrogen atom of C=N group.

From the results, it is evident that in the complexes, the Schiff base, A9Y3IMPA act as a monovalent bidentate ligand binding to the metal ion through carboxylate oxygen and azomethine nitrogen. The complexes of Mn(II), Fe(III) and Cu(II) possess octahedral geometry and the Zn(II) complex possesses tetrahedral geometry. The derived structures of the complexes are given in the figure 1.12.



M= Mn(II), Co(II), Cu(II)



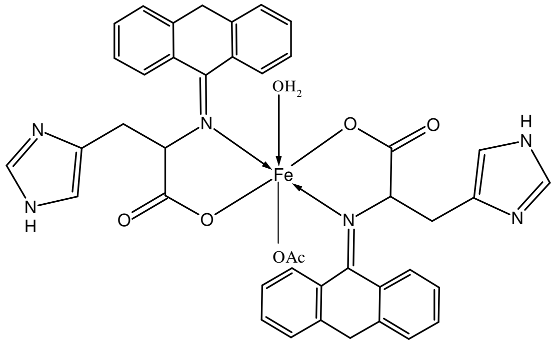


**Fig. 1.12:** Structures of the metal complexes of Schiff base A9Y3IMPA

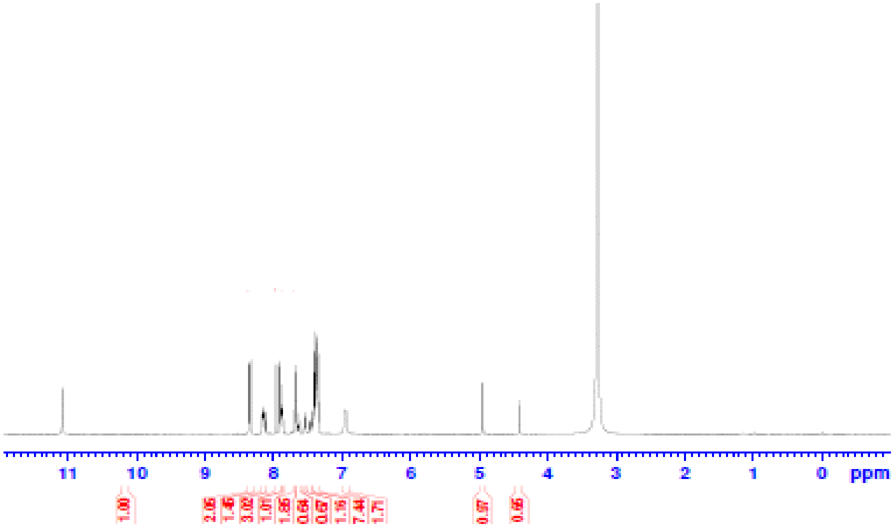


**Fig. 1.13.** $^{1}$H NMR spectrum of Schiff base A9Y3IMPA

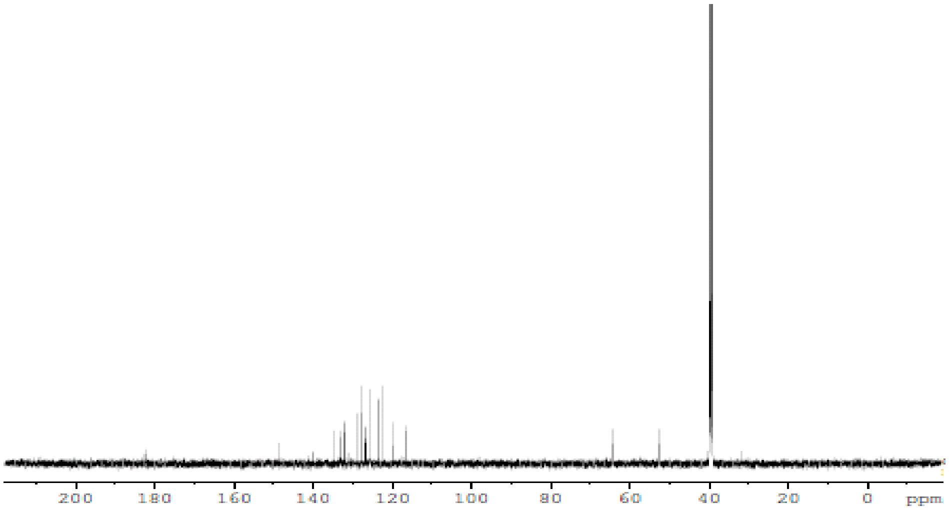


**Fig. 1.14.** $^{13}$C NMR spectrum of Schiff base A9Y3IMPA

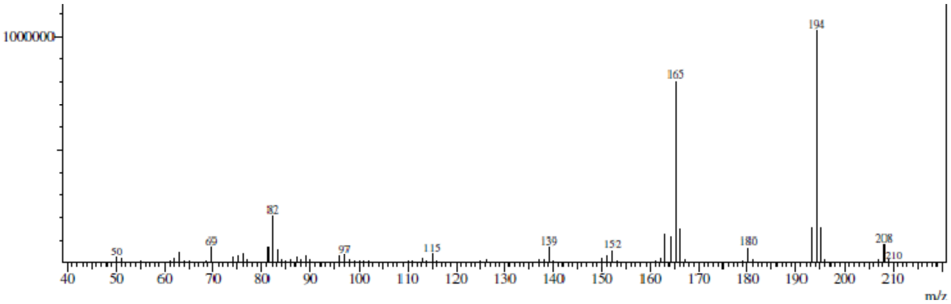


**Fig. 1.15.** Mass spectrum of Schiff base A9Y3IMPA

**Table. 1.5.** Micro analytical, magnetic and conductance data of transition metal complexes of (S)-2-(anthracen-9(10H)-ylideneamino)-3- (1H – imidazole – 4-yl)propanoic acid (A9Y3IMPA)

| **Complex** | **Colour** | **Yield (%)** | **Mol.wt** | **M.P ($^0$C)** | **Metal % Found (Calculated)** | **Elemental Analysis Found (Calculated)** | | | **$\mu_{eff}$ (BM)** | **Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)** | **Geometry** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **C %** | **H %** | **N %** | | | |
| A9Y3IMPA | Yellow | 85 | 330 | 245 | - | 72.18<br>(72.42) | 5.03<br>(5.13) | 12.38<br>(12.67) | - | - | - |
| [$MnL_2(H_2O)_2$] | Brown | 72 | 752 | >300 | 7.10<br>(7.30) | 63.48<br>(63.85) | 4.16<br>(4.79) | 11.07<br>(11.17) | 6.09 | 16.94 | Octahedral |
| [$FeL_2AcH_2O$] | Reddish Brown | 74 | 794 | >300 | 6.87<br>(7.04) | 63.16<br>(63.50) | 4.38<br>(4.66) | 10.12<br>(10.59) | 5.85 | 12.58 | Octahedral |
| [$CoL_2(H_2O)_2$] | Yellow | 69 | 756 | >300 | 7.28<br>(7.80) | 63.14<br>(63.52) | 4.36<br>(4.76) | 11.02<br>(11.12) | 4.78 | 6.38 | Octahedral |
| [$CuL_2(H_2O)_2$] | Bluish Green | 72 | 760 | >300 | 8.04<br>(8.35) | 63.02<br>(63.13) | 4.58<br>(4.73) | 10.92<br>(11.05) | 1.76 | 8.42 | Octahedral |
| [$ZnL_2$] | Yellow | 64 | 726 | >300 | 8.88<br>(9.00) | 66.01<br>(66.10) | 4.18<br>(4.41) | 11.23<br>(11.57) | D | 7.54 | Tetrahedral |

Ac = Acetate L = Ligand

**Table. 1.6.** Characteristic infrared absorption frequencies of A9Y3IMPA and its transition metal complexes

| **Complex** | $\upsilon_{H_2O}$ | $\upsilon_{COO(asym)}$ | $\upsilon_{C=N}$ | $\upsilon_{COO(sym)}$ | **In plane bending** | **Out of plane bending** | $\upsilon_{M-O}$ | $\upsilon_{M-N}$ |
|---|---|---|---|---|---|---|---|---|
| A9Y3IMPA | - | 1664 | 1610 | 1488 | 956 | 772,728 | - | - |
| [Mn$L_2(H_2O)_2$] | 3421 | 1652 | 1588 | 1450 | 942 | 765, 723 | 542 | 484 |
| [Fe$L_2$Ac$H_2O$] | 3434 | 1658 | 1582 | 1458 | 944 | 768, 728 | 538 | 489 |
| [Co$L_2(H_2O)_2$] | 3423 | 1648 | 1587 | 1449 | 949 | 764, 725 | 535 | 486 |
| [Cu$L_2(H_2O)_2$] | 3427 | 1645 | 1584 | 1444 | 945 | 766, 723 | 537 | 485 |
| [Zn$L_2$] | - | 1655 | 1586 | 1455 | 943 | 765, 726 | 540 | 487 |

Ac = Acetate L = Ligand

# CHAPTER 6

## STUDIES ON Mn(II), Fe(III), Cu(II) AND Zn(II) COMPLEXES OF (S)-2-(ANTHRACEN-9(10H)-YLIDENEAMINO)-3-(1H–INDOLE–3-YL) PROPANOIC ACID (A9Y3INPA)

The analytical and commercial applications of transition metal complexes are immense and novel ligands and their metal complexes have been synthesized for potential applications. From Literature survey it is reveals that Schiff bases and their transition metal complexes generally serve as potent corrosion inhibitors and antibacterial agents. But detailed investigation on Schiff bases derived from anthracene-9(10H)-one and their metal complexes are the short comings in this area. Therefore in continuation to our studies on anthracene-9(10H)-one derivatives, in this chapter, a brief study on the synthetic and physicochemical analysis of a Schiff base derived by the condensation of anthracene-9(10H)-one and L-tryptophan [(S)-2-amino-3-(1H-indole-3-yl)propanoic acid], and its transition metal complexes are described.

**Preparation of (S)-2-(anthracen-9(10H)-ylideneamino)-3-(1H–indole–3-yl) propanoic acid (A9Y3INPA)**

To the hot refluxing solution of anthracene-9(10H)-one (0.38g, 2mM) in ethanol (10 ml) added hot 1:1 ethanolic solution (10 ml) of L-tryptophan ( 0.40g, 2mM) and the mixture was left for reflux on a water bath. After six hours, the contents were cooled and kept overnight. The yellowish crystals were filtered using a vacuum pump and washed with ethanol. Then it was further recrystallized from methanol and dried over anhydrous $CaCl_2$. The melting point of A9Y3INPA was found to be $260^0$C (86%).

## Characterization of the ligand

The ligand A9Y3INPA was found soluble in organic solvents like DCM, DMSO etc. The structure of the ligand was formulated on the basis of elemental analysis and spectral data.

The infrared, electronic, $^1$H NMR, $^{13}$C NMR, mass spectra and elemental analysis studies confirm the structure of the ligand A9Y3INPA. The IR spectrum showed the characteristic C=N stretching vibration at 1595cm$^{-1}$. The absorption band at 3400cm$^{-1}$ is attributed to the N-H stretching vibration of the indole ring. The aromatic, olefinic and aliphatic CH stretching vibrations were observed in the region 3062-2897cm$^{-1}$. The absorption of stretching vibration of –OH group of the carboxylic acid part appeared as a scalloped band in the region 3062cm$^{-1}$, overlapping with the absorption of CH stretching band. The asymmetric and symmetric stretching vibrations of the carboxylate group were observed at 1656cm$^{-1}$ and 1468cm$^{-1}$ respectively. A strong peak at 1315cm$^{-1}$ may be assigned to the stretching of C-O bond. In the electronic spectrum, the absorption bands because of the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, were observed at 36800 and 32300cm$^{-1}$ respectively.

The $^1$H NMR (DMSO-d$_6$) signals for proton of the carboxylic acid appeared as a singlet at δ 10.8. The NH proton of the indole ring appeared as a broad singlet at δ 6.95 which can be explained by quadruple broadening. A peak at δ 4.95 corresponds to the CH$_2$ proton near to indole ring. The CH proton linked to azomethine group showed a pmr signal at δ 4.4ppm. Again CH$_2$ proton in the anthracene ring appeared at δ 7.96. The aromatic protons of both indole and anthracene-9(10H)-one rings appeared in the regions at δ 7.3-7.6 and 8.1-8.3 respectively. The $^{13}$C NMR spectrum in DMSO-d$_6$ of the

Schiff base, A9Y3INPA, showed the carboxylic acid carbon signal at 182.12ppm. A peak at 148.82ppm can be assigned to the azomethine carbon. The aromatic carbon signals were appeared in the $^{13}C$ NMR spectrum in the region 119-140ppm. Methylene carbon signal in the anthracene-9(10H)-one ring appeared at 116.60 ppm. The $sp^3$ carbon signal near to indole moiety appeared at 52.59 ppm. The signal at 63 ppm assigned to CH carbon signal (α-carbon) near to carboxylic acid.

In the high resolution mass spectrum of the ligand, the peak due to molecular ion was absent which establishes the instability of the compound. The loss of L-tryptophan part from the molecular ion gave a cation at m/z 193(100%) as a base peak. The base peak was due to the formation of the cation fragment $[C_{14}H_{11}N]^+$. Other prominent peaks shown in the mass spectrum are m/z 165 and 139 which can be assigned due to the fragment ions $[C_{13}H_9]^+$ and $[C_7H_9NO_2]^+$ respectively. The figures 1.18, 1.19, and 1.20 represent the NMR and mass spectra of the Schiff base, A9Y3INPA.

The analytical data obtained are shown in the table 1.7 and were found to be in good agreement with the empirical formula of the ligand. On the basis of the above results, the structure of the ligand A9Y3INPA was confirmed and shown in the figure 1.16.

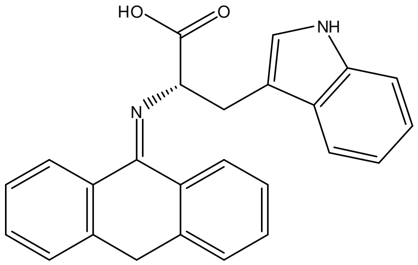


**Fig. 1.16:** Structure of the Schiff base A9Y3INPA

## Synthesis of complexes

Mn(II), Fe(III), Cu(II) and Ni(II) chelates of A9Y3INPA were prepared by mixing ethanolic solution of the anthracene-9(10H)-one, aqueous/ethanol solution of L-tryptophan and aqueous/ethanol solution of metal acetate in 1:1 ratio. Ferric chloride solution was used for the synthesis of Fe(III) complex. Sodium acetate (1 g) in ethanol was added and refluxed for 6 h. The precipitated complex was kept overnight, filtered, washed with ethanol and dried over anhydrous calcium chloride in a desiccator.

## Characterization of the complexes

The complexes were characterized by elemental analysis, conductance and spectral data (table 1.7 & 1.8.). The spectral results provide support for the molecular constitution of these complexes. The assignments are made on the basis of comparison with the spectra of similar type compounds.

The complexes were stable and colored. All the chelates are insoluble in methanol, ethanol, petroleum ether, diethyl ether etc, but they are moderately soluble in DMF and DMSO. The analytical data, physical appearance, magnetic moments and molar conductance of Mn(II), Fe(III), Cu(II) and Ni(II) complexes with A9Y3INPA are presented in the table 1.7. Important IR spectral bands of the ligand and the complexes with their assignments are given in the table 1.8.

### *Elemental analysis*

Percentage of carbon, hydrogen and nitrogen were determined by micro analytical methods. A9Y3INPA act as monovalent bidentate ligand in the reaction with common transition metal ions. All the prepared complexes possess 1:2 metal to ligand ratio.

***Molar conductance***

The molar conductance measurements in DMSO were performed at a concentration of $10^{-3}$M at room temperature. Molar conductances of the studied complex were in the range of 6-12 $ohm^{-1}cm^{2}mol^{-1}$. The low conductance values indicate their non ionic nature in DMSO.

***Magnetic moment measurements***

Mn(II) complex showed a magnetic moment of 5.83BM indicating $d^5$octahedral geometry. The $\mu_{eff}$ value of Fe(III) complex at room temperature was 5.61BM. This also indicates an octahedral geometry around the metal ion.

In regular octahedral Cu(II) complexes ground term is $^2E_g$ and hence no orbital contribution is expected. The spin only magnetic moment value corresponding to one unpaired electron is 1.73BM, but the observed magnetic moment values of Cu(II) complex was 1.88 BM which explains octahedral geometry. The slight higher value is due to the spin orbit coupling. Magnetic susceptibility measurements reveal that Zn(II) complex is diamagnetic.

***Infrared spectral studies***

Characteristic infrared bands of the ligand and complexes were subjected to detailed examination and are presented in table 1.8. In the IR spectra, assignment of two bands $\upsilon_{C=O}$ from COOH moiety and $\upsilon_{C=N}$ are much informative.

A broad peak at 3425- 3251$cm^{-1}$ in the spectra of Mn(II), Fe(III) and Cu(II) chelates was attributed to the hydroxyl stretching frequency and it indicates that water molecules were coordinated to metal.

The disappearance of the stretching frequency at 1656$cm^{-1}$ and 1468$cm^{-1}$ assigned to $\upsilon_{C=O}$ from COOH moiety in the ligand and appearance of new $\upsilon_{asym}$ and $\upsilon_{sym}$ modes of the $\upsilon_{(COO)}$ group in the complexes at 1651-1614 $cm^{-1}$ and 1462–1402 $cm^{-1}$ indicate that the Schiff base has chelated to metal ion. $\Delta\upsilon$ value ($\upsilon_{COO(asym)}$-$\upsilon_{COO(sym)}$) ≈ 240$cm^{-1}$ are consistent with monodentate carboxylate and rules out the possibility of a bridged or coordinated carboxylate group.

From the table it is clear that the $\upsilon_{C=N}$ stretching vibration of the complexes undergoes downward shift by about 30-40$cm^{-1}$ in the spectra of all the metal complexes. This indicate that the involvement of azomethine nitrogen in coordination with metal ions. The shifted band in many cases is coincident with the C=C band, which then shows greater intensity or broadening. In all the IR spectrum of the complexes, the N-H stretching frequency of indole ring is not altered in the complex. Hence the indole nitrogen of tryptophan is not involved in binding.

Further evidence for the nature of the metal-ligand bonding is given by far IR spectra of the complexes. Due to the interference of skeletal vibrations of the ligands, with $\upsilon_{M\text{-}O}$ and $\upsilon_{M\text{-}N}$ vibrations, definite assignments of band is difficult as a result of metal ligand vibration. Therefore the assignments are made on the basis of information available in literature. Spectra of all complexes prepared in this investigation showed intense broad bands at 518-557$cm^{-1}$ and 452- 478$cm^{-1}$ assignable to $\upsilon_{M\text{-}O}$ and $\upsilon_{M\text{-}N}$. Thus A9Y3INPA behaves as a potentially monovalent bidentate ligand during complex formation. The aromatic out of plane vibration was seen near 940$cm^{-1}$ and in-plane vibrations at 790$cm^{-1}$ and 740$cm^{-1}$.

### *Electronic spectra*

During complex formation, a red shift was detected for the bands of ligands which indicate the involvement of the ligand in coordination. In Mn(II) complex, central metal atom in the octahedral environment was confirmed by the presence of electronic spectral bands at 13100, 14700 and 25600cm$^{-1}$. In agreement with the magnetic moment values, these spectral bands can be assigned to the transitions $^6A_{1g}\rightarrow{}^4T_{1g}(G)$, $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ and $^6A_{1g}\rightarrow{}^4E_g(G)$ respectively.

An intense band at 29000cm$^{-1}$ in the electronic spectrum of Fe(III) complex may be attributed to the L→M charge transfer band. Another shoulder peak at 18890cm$^{-1}$ exhibited by the iron complex may be due to $^5T_{2g}\rightarrow{}^5E_g$ transition, confirming its octahedral geometry. Since ground state Fe(III) in high spin[170] complex is $^6A_1$, all the d-d transitions are weak and obscured with the intense charge transfer bands.

The electronic spectrum of Cu(II) complex exhibited two bands at 13650cm$^{-1}$ and 15700cm$^{-1}$; the former may be assignable to $^3E_g\rightarrow{}^3T_{2g}$ transition[171] and the later may be attributed to L→M charge transfer band, suggesting thereby the octahedral geometry. The remaining Zn(II) complex do not show any characteristic d-d transition bands.

### *NMR spectra*

The resonance signal of carboxylic acid proton of the ligand A9Y3INPA, observed at $\delta$ 10.8, was disappeared in the $^1H$ NMR spectra of the complexes. This confirmed the chelation of the ligand to the metal atom through carboxylate oxygen after deprotonation. Similarly, the –COOH carbon peak at 182.12ppm in the $^{13}C$ NMR spectrum of the ligand undergoes downfield shift in the $^{13}C$ NMR spectra of complexes, which may be due to the deshielding effect by coordination. The decrease in the electron density around the azomethine carbon in the chelate was confirmed by the displacement of the corresponding signal, which was a confirmation of the coordination through nitrogen atom of C=N group, during chelation.

From the above results, it can be concluded that in the present complexes of the Schiff base, A9Y3INPA acts as a monovalent bidentate ligand binding to the metal ion through carboxylate oxygen and azomethine nitrogen. The complexes of Mn(II), Fe(III) and Cu(II) possesses octahedral geometry and the Zn(II) complex possesses tetrahedral geometry. The derived structures of the complexes are given in the figure 1.17.

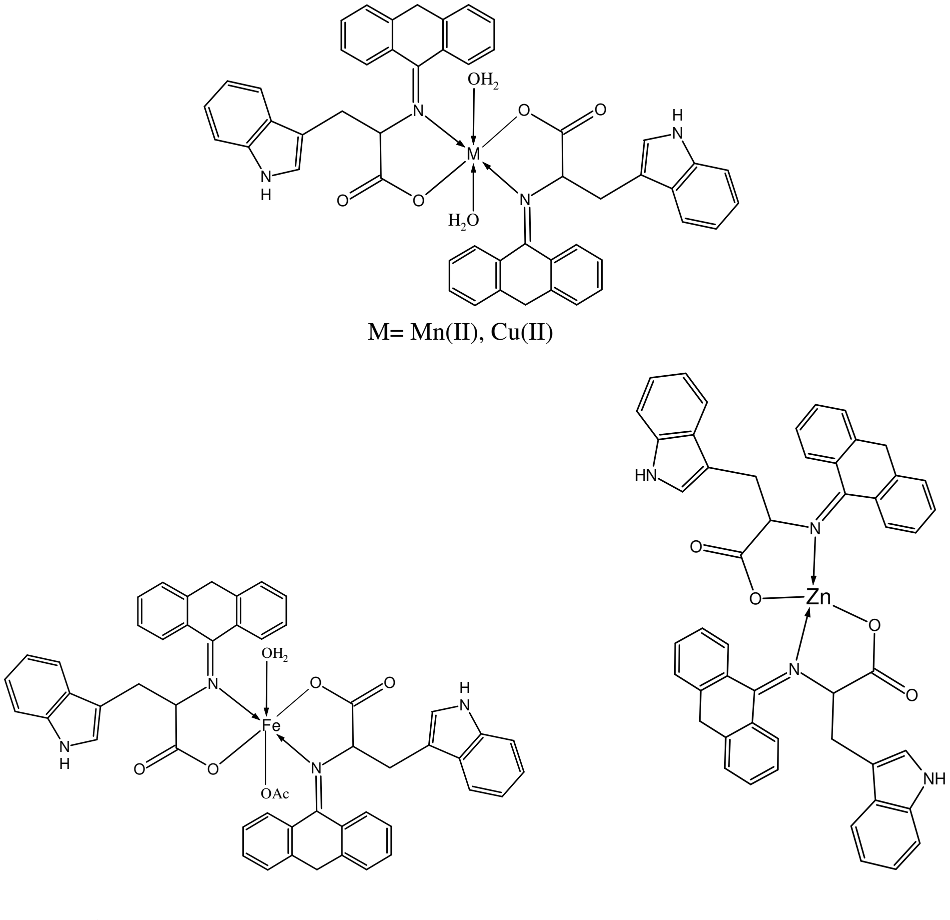


**Fig. 1.17:** Structures of the metal complexes of Schiff base A9Y3INPA

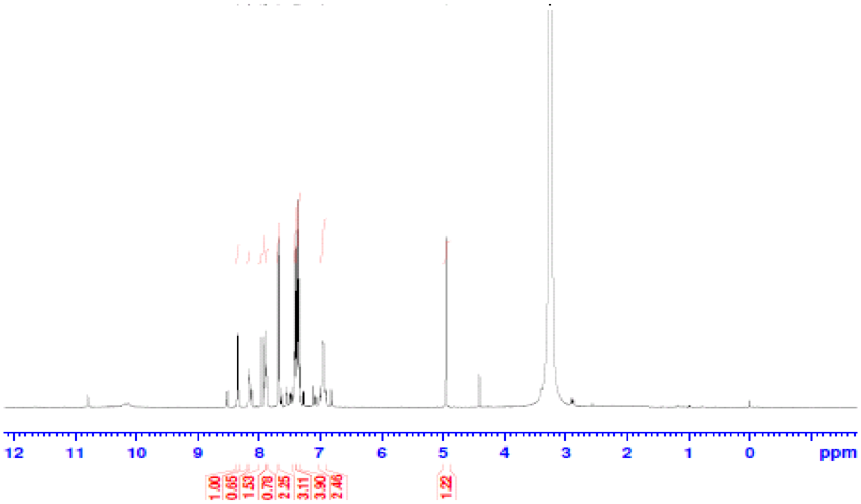


**Fig. 1.18:** $^1$H NMR spectrum of Schiff base A9Y3INPA

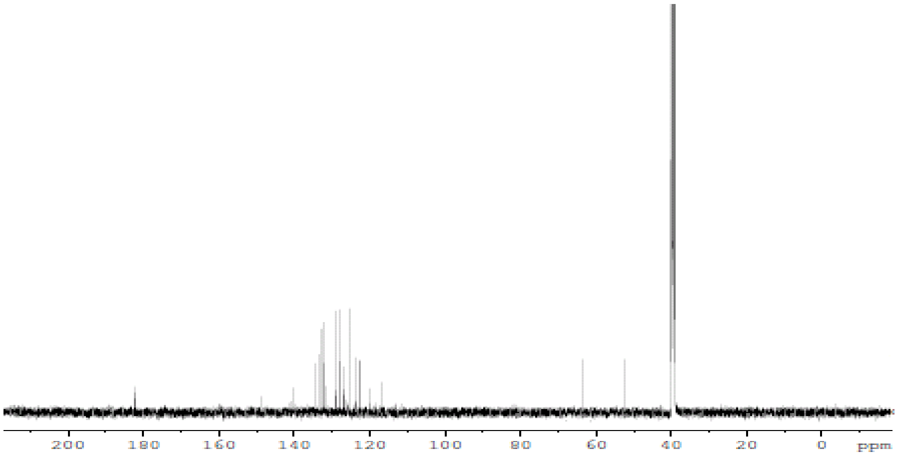


**Fig. 1.19:** $^{13}$C NMR spectrum of Schiff base A9Y3INPA

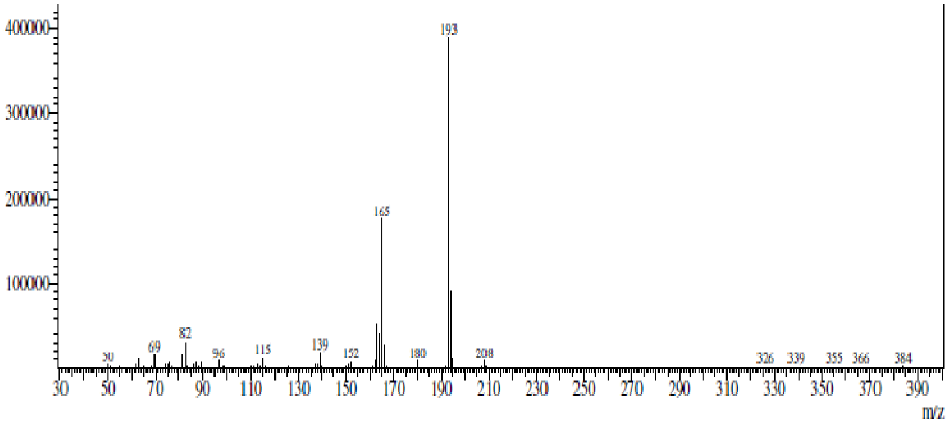


**Fig. 1.20:** Mass spectrum of Schiff base A9Y3INPA

**Table. 1.7.** Micro analytical, magnetic and conductance data of transition metal complexes of (S)-2-(anthracen-9(10H)-ylideneamino)-3-(1H–indole–3-yl)propanoic acid (A9Y3INPA)

| **Complex** | **Colour** | **Yield (%)** | **Mol.wt** | **M.P ($^0$C)** | **Metal % Found (Calculated)** | **Elemental Analysis Found (Calculated)** | | | **$\mu_{eff}$ (BM)** | **Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)** | **Geometry** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **C %** | **H %** | **N %** | | | |
| A9Y3INPA | Yellow | 80 | 380 | 260 | - | 78.66<br>(78.85) | 5.14<br>(5.26) | 7.11<br>(7.34) | - | - | - |
| $[MnL_2(H_2O)_2]$ | Brown | 68 | 849 | >300 | 6.14<br>(6.47) | 70.52<br>(70.65) | 4.81<br>(4.95) | 6.12<br>(6.59) | 5.83 | 7.75 | Octahedral |
| $[FeL_2AcH_2O]$ | Reddish Brown | 75 | 891 | >300 | 6.04<br>(6.26) | 69.67<br>(69.95) | 4.68<br>(4.82) | 6.15<br>(6.27) | 5.61 | 7.19 | Octahedral |
| $[CuL_2(H_2O)_2]$ | Bluish Green | 73 | 858 | >300 | 7.24<br>(7.40) | 69.76<br>(69.94) | 4.79<br>(4.90) | 6.39<br>(6.53) | 1.88 | 11.27 | Octahedral |
| $[ZnL_2]$ | Yellow | 71 | 824 | >300 | 7.78<br>(7.94) | 72.67<br>(72.84) | 4.53<br>(4.61) | 6.62<br>(6.80) | D | 6.79 | Tetrahedral |

Ac = Acetate L=Ligand

**Table. 1.8.** Characteristic infrared absorption frequencies of A9Y3INPA and its transition metal complexes

| **Complex** | $\upsilon_{H_2O}$ | $\upsilon_{COO(asym)}$ | $\upsilon_{C=N}$ | $\upsilon_{COO(sym)}$ | **In plane bending** | **Out of plane bending** | $\upsilon_{M-O}$ | $\upsilon_{M-N}$ |
|---|---|---|---|---|---|---|---|---|
| A9Y3INPA | - | 1656 | 1595 | 1468 | 931 | 788,736 | - | - |
| [$MnL_2(H_2O)_2$] | 3425 | 1651 | 1556 | 1462 | 938 | 782, 734 | 518 | 468 |
| [$FeL_2AcH_2O$] | 3404 | 1649 | 1560 | 1436 | 935 | 790, 738 | 557 | 478 |
| [$CuL_2(H_2O)_2$] | 3251 | 1614 | 1558 | 1402 | 940 | 790, 738 | 538 | 441 |
| [$ZnL_2$] | - | 1648 | 1561 | 1440 | 936 | 786, 740 | 544 | 452 |

Ac = Acetate L = Ligand

# CHAPTER 7

## STUDIES ON Cr(III), Mn(II), Fe(III), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF (S)-2-(ANTHRACEN-9(10H)-YLIDENEAMINO)-3-PHENYL PROPANOIC ACID [A9Y3PPA]

In this chapter the studies on the synthesis and characterization of Cr(III), Mn(II), Fe(III), Ni(II), Cu(II) and Zn(II) complexes of (S)-2-(anthracen-9(10H)-ylideneamino)-3-phenylpropanoic acid [A9Y3PPA] are reported.

### Synthesis of (S)-2-(anthracen-9(10H)-ylideneamino)-3-phenyl propanoic acid [A9Y3PPA]

A mixture of ethanolic solutions of anthracene-9(10H)-one (0.38g, 2mM) and phenyl alanine (0.33 g, 2mM) were refluxed on a water bath for 6 hours. Mixture was concentrated, kept overnight and then the ligand was separated. It was filtered, washed with ethanol and dried in a desiccator over anhydrous calcium chloride.

### Characterization of the ligand

The ligand was characterized on the basis of CHN analysis and spectral data. From CHN analysis, it was confirmed that the calculated and observed percentage values are in good agreement. The values are presented in the table 1.9.

The IR spectral data are tabulated in the table 1.10. A strong peak at 1595cm$^{-1}$ can be attributed to characteristic C=N stretching vibration in the ligand. The peaks in the region 3062-3028cm$^{-1}$ can be assigned to aromatic CH stretching vibrations. The absorption of stretching vibration of –OH group of the carboxylic acid part appeared in the region 3380cm$^{-1}$. The peak at

1658cm$^{-1}$ and 1456cm$^{-1}$ are assigned to the asymmetric and symmetric stretching vibrations of the carboxylate group [($\upsilon_{COO(asym)}$ and $\upsilon_{COO(sym)}$].

In the electronic spectrum the absorption bands at 25700cm$^{-1}$ and 25100cm$^{-1}$ are due to π→π* and n→π* transition respectively.

The proton magnetic resonance spectrum of the ligand exhibited the characteristic carboxylic acid proton signal as a singlet at δ 11.20. A peak at δ 2.80 corresponds to the $CH_2$ proton of amino acid part. The -CH proton attached to azomethine nitrogen showed a chemical shift value at δ 4.95. Chemical shift value at δ 7.89 corresponds to the $CH_2$ proton in the anthracene ring. The aromatic protons of anthracene-9(10H)-one rings appeared in the regions at δ 7.3- 7.8. The $^{13}C$ NMR spectrum of the ligand showed the carboxylic acid carbon signal at 182.11ppm. A peak at 140.05 ppm assigned to be the azomethine carbon atom. The aromatic carbon signals were appeared in the $^{13}C$ NMR spectrum in the region 120-134 ppm. The CH carbon bonded to azomethine nitrogen appeared at 52.59 ppm.

In the mass spectrum analysis, the molecular ion peak was absent which shows the instability of the compound. The base peak was due to the formation of the cation fragment $[C_{14}H_{11}N]^+$ at m/z 193. Other prominent peak shown in the mass spectrum are m/z 165 and 194 which can be assigned to the fragment ions, $[C_{13}H_9]^+$and $[C_{14}H_{12}N]^+$ respectively. All these fragments are derived from carbonyl moiety. The figures 1.23, 1.24 and 1.25 show the $^1H$ NMR, $^{13}C$ NMR and mass spectra of the ligand A9Y3PPA respectively.

On the basis of the above results, the structure of the ligand A9Y3PPA was confirmed and shown in the figure 1.21.

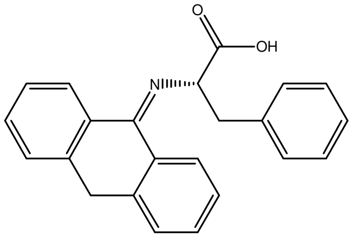


**Fig. 1.21:** Structure of Schiff base A9Y3PPA

## Synthesis of complexes

Metal complexes of A9Y3PPA were prepared by refluxing the ethanolic solutions of appropriate amounts (for 1mM) of anthracene-9(10H)-one, phenyl alanine and metal salts (metal acetate/chloride) in ethanol. After 6 hours the reaction mixture was concentrated and kept overnight. The complex formed was filtered using a vacuum pump and washed with ethanol, dried in a desiccator over anhydrous calcium chloride.

## Characterization of the complexes

The complexes were characterized on the basis of elemental analysis, pyrolytic method, molar conductivity measurements, magnetic measurements, electronic, infrared, $^1$H NMR and $^{13}$C NMR and mass spectral data.

The physical and analytical data of the complexes are presented in the table 1.9. The room temperature magnetic moments and molar conductivities of the complexes are also given in the same table.

### *Elemental analysis*

The observed values of the elemental analysis are in close agreement with the calculated values for the metal complexes. The metal to ligand ratio was found to be 1:2 in all the complexes except Cu(II) complex.

### *Molar conductance*

The conductivity of all the complexes at concentration of $10^{-3}$ M at room temperature was measured in ethanol. All the complexes possess molar conductance in the range 3-9 ohm$^{-1}$cm$^{2}$mol$^{-1}$ in agreement with their non electrolytic nature.

***Magnetic measurements***

The magnetic moment value of Mn(II) complex (5.91BM) was in agreement with their octahedral geometry. Octahedral structure can be attributed to Fe (III) complex based on the magnetic moment value 5.81BM. Ni(II) complex showed magnetic moment value of 3.32BM which suggests an octahedral arrangement around the metal ion. For Cr(III) complex a magnetic moment value of 3.94BM was obtained. This value of Cr(III) complex is suggestive of high spin octahedral geometry. The magnetic moment value of Cu(II) complex was 1.41BM which is very low value compared to the spin only value and this suggest a dimeric square planar configuration. Zn(II) complex was found to be diamagnetic as expected due to the d$^{10}$ configuration.

***Infrared spectral studies***

The selected infrared absorption frequencies of the ligand and complexes are given in the table 1.10. A strong intense band due to $\upsilon_{C=-N}$ stretch in the ligand, upon coordination shift towards lower wave number region by 23-28cm$^{-1}$ indicating the participation of azomethine nitrogen in coordination with metal ion.

The spectra of complexes displayed two additional new bands in the range of 520-528 and 463-469cm$^{-1}$ which were assigned to $\upsilon_{M-O}$ and $\upsilon_{M-N}$ respectively.

In all the complexes, the asymmetric and symmetric stretching vibrations of the carboxylate groups occur at ≈1650 and 1430 cm$^{-1}$ respectively showing a difference of about 220cm$^{-1}$. This indicates the monodentate behaviour of the carboxylate group. All the complexes except Zn(II) and Cu(II) showed broad absorption bands between 3422-3440cm$^{-1}$ due to the presence of coordinated water molecules, which is further supported by the appearance of rocking mode of medium intensity bands at $\approx$ 850cm$^{-1}$.

***Electronic spectra***

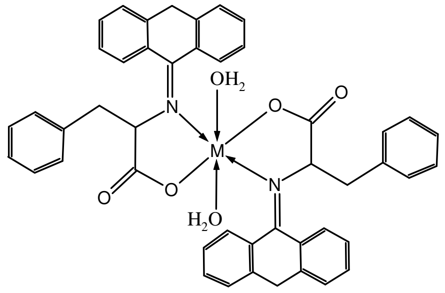
The electronic spectrum of Cr(III) complex showed two bands, one at 16520cm$^{-1}$ and other at 22400cm$^{-1}$. Based on these, the structure of Cr(III) complex can be confirmed to be octahedral. The bands appeared at 13600, 14900 and 25800cm$^{-1}$ in Mn(II) complex was a support for the assigned octahedral geometry. In Fe(III) complexes , weak transitions are masked by strong band seen at 26500cm$^{-1}$.

The Ni(II) complex exhibited three additional bands in the region 13400cm$^{-1}$, 17600cm$^{-1}$ and 23700cm$^{-1}$ attributable to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, which corresponds to octahedral structure. Electronic spectrum of the Cu(II) chelate showed a single broad and poorly resolved absorption band around 13860cm$^{-1}$.

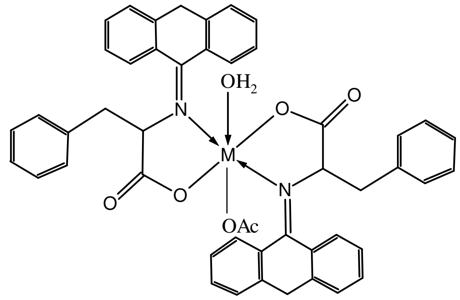
***NMR spectra***

From the comparison between the proton nmr spectra of both ligand and complexes, it can be seen that there is appreciable shift in the peak positions which indicate the chelation. In the $^1$H NMR spectra of chelates, the disappearance of the signal at $\delta$ 11. 2 due to the acid proton in the ligand, it is a clear indication of the coordination of the ligand through the carboxylate group. Similarly, the $^{13}$C NMR spectrum of complexes showed downward shift in the signals due to carboxylic acid and azomethine carbon atoms. This downward shift can be attributed to the lowering of electron densities as a result of coordination to the metal ion.

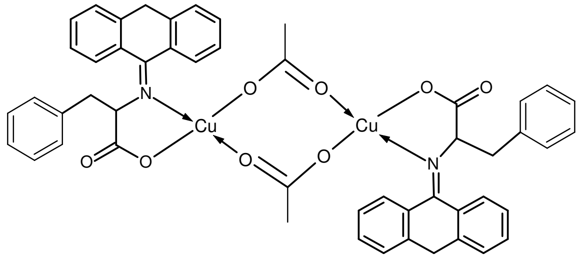
From the above detailed discussions, the following geometries can be assigned to the transition metal complexes of A9Y3PPA.



M= Mn(II), Ni(II)



M= Cr(III), Fe (III)



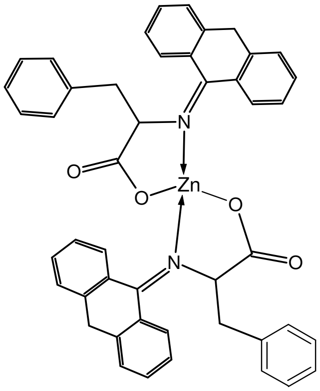


**Fig. 1.22:** Structures of the metal complexes of Schiff base A9Y3PPA

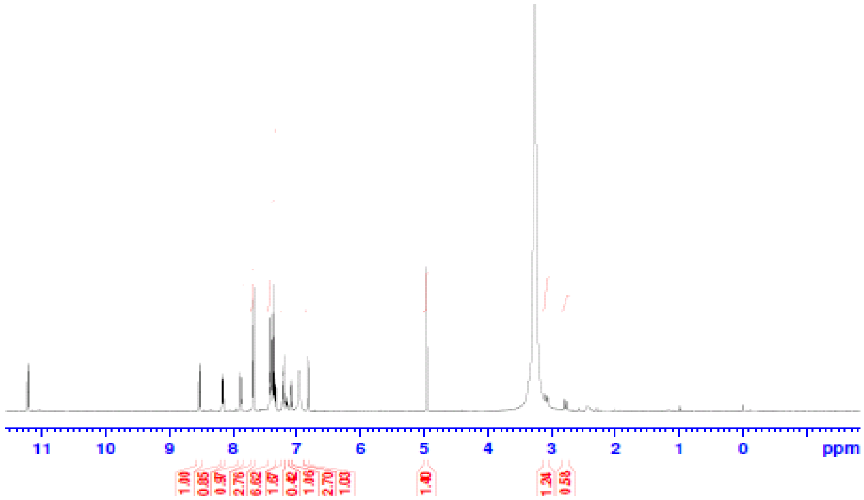


**Fig. 1.23:** $^{1}$H NMR spectrum of Schiff base A9Y3PPA

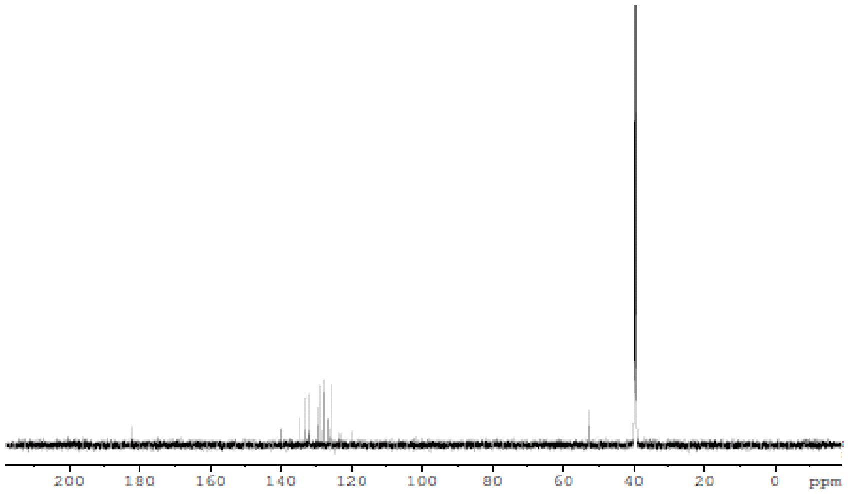


**Fig. 1.24:** $^{13}$C NMR spectrum of Schiff base A9Y3PPA

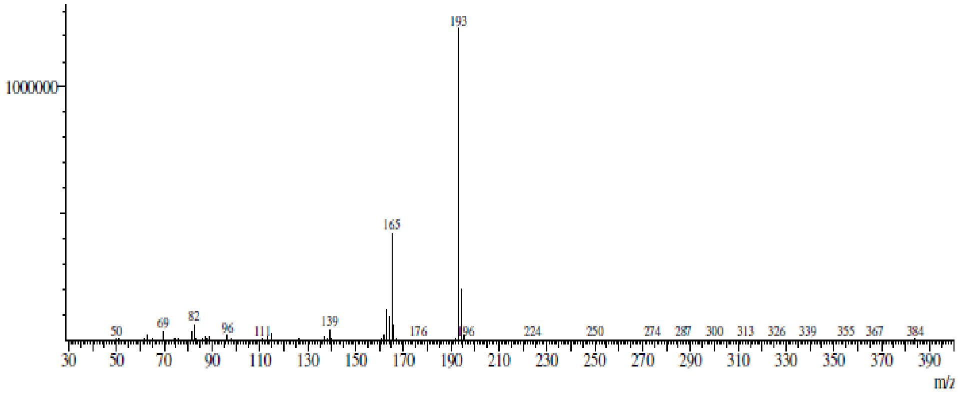


**Fig. 1.25:** Mass spectrum of Schiff base A9Y3PPA

**Table. 1.9.** Micro analytical, magnetic and conductance data of transition metal complexes of (S)-2-(anthracen-9(10H)-ylideneamino)-3-phenylpropanoicacid [A9Y3PPA]

| **Complex** | **Colour** | **Yield (%)** | **Mol.wt** | **M.P ($^0$C)** | **Metal % Found (Calculated)** | **Elemental Analysis Found (Calculated)** | | | **$\mu_{eff}$ (BM)** | **Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)** | **Geometry** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **C %** | **H %** | **N %** | | | |
| A9Y3PPA | Yellow | 83 | 341 | 243 | - | 80.48<br>(80.84) | 5.23<br>(5.56) | 3.98<br>(4.10) | - | - | - |
| [$CrL_2AcH_2O$] | Greenish Yellow | 68 | 810 | >300 | 6.12<br>(6.42) | 71.02<br>(71.12) | 4.93<br>(5.06) | 3.11<br>(3.46) | 3.94 | 3.59 | Octahedral |
| [$MnL_2(H_2O)_2$] | Brown | 70 | 772 | >300 | 6.97<br>(7.12) | 71.28<br>(71.52) | 4.93<br>(5.18) | 3.38<br>(3.63) | 5.91 | 7.68 | Octahedral |
| [$FeL_2AcH_2O$] | Reddish Brown | 72 | 814 | >300 | 6.47<br>(6.86) | 70.26<br>(70.79) | 4.91<br>(5.04) | 3.12<br>(3.44) | 5.81 | 5.84 | Octahedral |
| [$NiL_2(H_2O)_2$] | Yellow | 68 | 776 | >300 | 7.29<br>(7.57) | 71.02<br>(71.17) | 5.04<br>(5.16) | 3.38<br>(3.61) | 3.32 | 7.42 | Octahedral |
| [$CuLAc$]$_2$ | Bluish Green | 73 | 926 | >300 | 6.24<br>(6.86) | 64.58<br>(64.80) | 4.28<br>(4.54) | 2.92<br>(3.02) | 1.41 | 5.38 | Square Planar (Dimeric) |
| [$ZnL_2$] | Yellow | 65 | 746 | >300 | 8.28<br>(8.76) | 73.61<br>(73.97) | 4.38<br>(4.82) | 3.52<br>(3.75) | D | 8.72 | Tetrahedral |

Ac = Acetate L = Ligand

**Table. 1.10.** Characteristic infrared absorption frequencies of A9Y3PPA and its transition metal complexes

| **Complex** | $\upsilon_{H_2O}$ | $\upsilon_{COO(asym)}$ | $\upsilon_{C=N}$ | $\upsilon_{COO(sym)}$ | **In plane bending** | **Out of plane bending** | $\upsilon_{M-O}$ | $\upsilon_{M-N}$ |
|---|---|---|---|---|---|---|---|---|
| A9Y3PPA | - | 1658 | 1595 | 1456 | 890 | 779,738 | - | - |
| [$CrL_2AcH_2O$] | 3429 | 1652 | 1565 | 1430 | 892 | 777,734 | 527 | 464 |
| [$MnL_2(H_2O)_2$] | 3440 | 1648 | 1569 | 1424 | 887 | 775, 733 | 522 | 468 |
| [$FeL_2AcH_2O$] | 3422 | 1651 | 1571 | 1425 | 889 | 778, 738 | 528 | 467 |
| [$NiL_2(H_2O)_2$] | 3432 | 1653 | 1566 | 1428 | 890 | 774, 735 | 525 | 465 |
| [$CuLAc$]$_2$ | - | 1649 | 1572 | 1426 | 887 | 776, 733 | 527 | 463 |
| [$ZnL_2$] | - | 1651 | 1570 | 1426 | 889 | 775, 736 | 520 | 469 |

Ac = Acetate L = Ligand

# CHAPTER 8

## STUDIES ON Mn(II), Fe(III), Cu(II) AND Zn(II) COMPLEXES OF (R)-2-(ANTHRACEN-9(10H)-YLIDENEAMINO)-3-MERCAPTOPROPANOIC ACID (A9Y3MPA)

A potential bidentate Schiff base (R)-2-(anthracen-9(10H)-ylideneamino)-3-mercaptopropanoic acid (A9Y3MPA) was synthesized and complexed with some transition metals ions to form stable metal chelates. The ligand and the corresponding complexes were analyzed for their structural characteristics. This chapter describes with the synthetic and structural aspects of A9Y3MPA and its transition metal chelates of manganese, iron, copper and zinc.

### Preparation of (R)-2-(anthracen-9(10H)-ylideneamino)-3-mercapto propanoic acid (A9Y3MPA)

The ligand A9Y3MPA was prepared by refluxing L-cysteine (0.28 g,) in ethanolic potassium hydroxide (1mM) and anthracene-9(10H)-one (0.38 g) in ethanol in the ratio (1:1). The mixture was refluxed on a water bath for 6 h. On cooling the mixture by keeping overnight, needle shaped dark yellow crystals of potassium salt of the ligand were obtained. It was then filtered, washed with dilute alcohol and dried in a desiccator over anhydrous calcium chloride. The ligand obtained was recrystallized from ethanol (yield 80%, m.p $255^0$C).

### Characterization of the ligand

The ligand A9Y3IMPA was characterized on the basis of elemental analysis and spectral data. The data are presented in the tables 1.11 and 1.12.

The structure of the ligand was formulated from this data. The acid form of the ligand was used for CHNS analysis.

Elemental analysis, infrared, electronic, NMR and mass spectra were used to characterize the ligand A9Y3MPA. The calculated and observed percentages of carbon, hydrogen, nitrogen and sulphur were in good agreement. Detailed examination of the IR spectral data of the ligand A9Y3MPA showed a significant absorption frequency at 1591cm$^{-1}$ and it can be attributed due to the stretching frequency of C=N group. Bands in the region 2640-2690cm$^{-1}$ may be assigned to S-H vibrations. The frequencies at 1642cm$^{-1}$ and 1440cm$^{-1}$ can be assigned to the asymmetric and symmetric stretching frequencies of the carboxylate group respectively. All stretching vibrations of aliphatic C-H bonds of the ligand A9Y3MPA showed their characteristic IR bands between 3040-2980 cm$^{-1}$. The electronic spectrum of the ligand, three absorption bands due to $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, were observed at 35700, 33200 and 30900cm$^{-1}$ respectively.

The $^1$H NMR (DMSO-$d_6$) signals for proton of the carboxylic acid appeared as a singlet at $\delta$ 10.2. A signal at $\delta$ 6.96 appeared due to the presence of thiol proton. A peak at $\delta$ 2.43 corresponds to the $CH_2$ proton attached to thiol group. The methylene proton attached to azomethine nitrogen showed a chemical shift value at 4.95. The $CH_2$ proton in the anthracene ring appeared at $\delta$ 7.96. A multiplet signal at different regions ($\delta$ 7.38, $\delta$ 7.68, $\delta$ 7.88 and $\delta$ 8.15) corresponds to the aromatic protons of anthracene-9(10H)-one moiety. In the $^{13}$C NMR spectrum in DMSO-$d_6$ of the Schiff base, A9Y3INPA, signal at 182.12ppm corresponds to carboxylic acid carbon. CH carbon atom near to carboxyl carbon can be assigned at 52.59ppm. The signal present at 31.58ppm can be attributed to $CH_2$–SH carbon atom. The CMR spectrum showed a signal at 140.05ppm which can be assigned to the azomethine carbon. The aromatic carbons were appeared in the $^{13}C$ NMR spectrum in the region 119-140ppm. $CH_2$ carbon signal in the anthracene-9(10H)-one ring was appeared at 116.62ppm.

The high resolution mass spectrum of the ligand is shown in the figure 1.30. The molecular ion peak was absent in the mass spectrum, which shows that the molecular radical cation is quite unstable. The loss of cysteine part from the molecular ion gave a cation at m/z 194(100%) as a base peak. The base peak is due to the formation of the cation fragment $[C_{14}H_{12}N]^+$ from the original ligand. Other prominent peaks shown in the mass spectrum are m/z 165 and 208 which can be assigned to the fragment ions $[C_{13}H_9]^+$]and $[C_{15}H_{14}N]^+$ respectively. The figures 1.28, 1.29 and 1.30 represent the $^1H$ NMR, $^{13}C$ NMR and mass spectra respectively.

On the basis of the above results, the structure of the ligand A9Y3MPA was confirmed and shown in the figure 1.6.

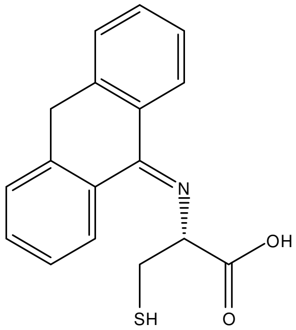


**Fig. 1. 26:** Structure of Schiff base A9Y3MPA

### Synthesis of complexes

Mn(II), Fe(III), Cu(II) and Ni(II) chelates of A9Y3INPA were prepared by refluxing ethanolic solutions of anthracene-9(10H)-one, KOH/ethanol solution of L-cysteine in a R.B. flask. To the refluxing solution added aqueous/ethanol solution of metal acetate. Ferric chloride solution was used for the synthesis of Fe(III) complex. The precipitated complex was kept overnight, filtered, washed with ethanol and dried over anhydrous calcium chloride in a desiccator.

### Characterization of the complexes

The complexes were characterized on the basis of elemental analysis, magnetic moment, conductance, UV, IR spectra etc. The data are presented in the tables 1.11 and 1.12. From the results the molecular constitution of these complexes were found out on the basis of comparison with the spectra of similar type compounds.

#### *Elemental analysis*

The hydrogen, carbon, nitrogen and sulphur percentage were determined by micro analytical methods. The calculated values are good agreement with the experimental values. The results establish that A9Y3MPA acts as a bidentate ligand in reaction with Mn(II), Fe(III), Cu(II) and Zn(II). The complexes found to possess 1:2 stoichiometry between metal and ligand.

#### *Molar conductance*

The molar conductance measurements in DMSO were performed at a concentration of $10^{-3}$M at room temperature. Molar conductance values of the studied complexes were indicative of their non electrolytic nature in DMSO.

#### *Magnetic moment measurements*

The magnetic moment values are tabulated in the table 1.11. Mn(II) complex showed a magnetic moment of 5.72BM and it was consistent with octahedral geometry around the metal ion. The magnetic moment value shown by Fe(III) complex was 5.81BM. This indicates an octahedral geometry around the Fe(III) ion in the complex.

The spin only magnetic moment value corresponding to one unpaired electron in Cu(II) chelate is 1.73BM, and the observed value is 1.79BM. This indicates the octahedral geometry. Zn(II) complex was diamagnetic as expected.

***Infrared spectral studies***

The characteristic infrared bands of the ligand and complexes were compared and revealed that the spectra of chelates were different from that of the ligand in some characteristic frequencies. Selected infrared frequencies of the ligand and the complexes are tabulated in the table 1.12.

The presence of the coordinated water molecules in the complex was confirmed by the appearance of a broad peak at 3419cm$^{-1}$, 3404cm$^{-1}$, 3251cm$^{-1}$ in the spectra of Mn(II), Fe(III) and Cu(II) chelates respectively and is followed by a sharp rocking mode of vibration between 838 and 846cm$^{-1}$.

The aromatic in plane vibrations are found at near to 940 cm$^{-1}$ and out of plane vibration in the range 765cm$^{-1}$ and 715cm$^{-1}$. The appearance of the bands due to asymmetric and symmetric stretching modes of carboxylate groups at lower frequencies, compared to that of ligand (1620 –1638 and 1436-1419 respectively ) and a $\Delta\upsilon_{COO}$ value of > 150cm$^{-1}$ clearly establishes that the carboxylate group is monodentate in nature.

The band appearing in the spectra of ligand due to $\upsilon_{C=N}$, which undergoes shift to lower frequency region in the complexes, indicate coordination through azomethine nitrogen.

Spectra of all complexes prepared in this investigation showed medium bands at 536-542cm$^{-1}$ and 448- 462cm$^{-1}$ assignable to $\upsilon_{M\text{-}O}$ and $\upsilon_{M\text{-}N}$ and this confirms the chelating ability of the ligand.

***Electronic spectra***

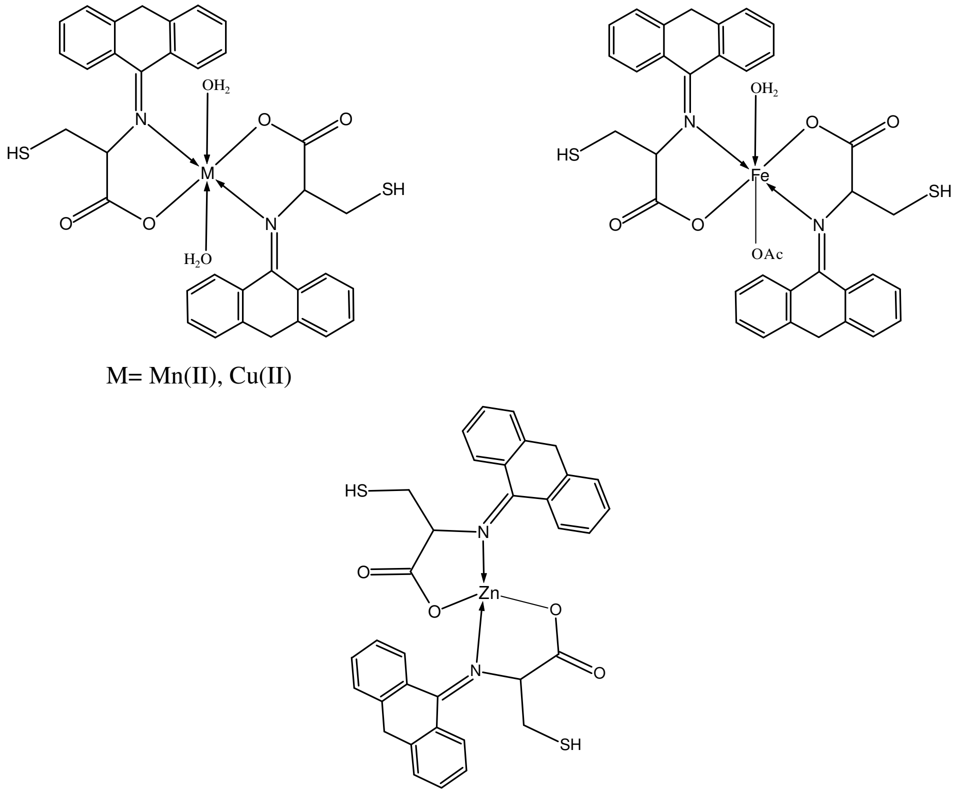
All the electronic bands of the synthesized complexes are shifted to lower region compared the bands of ligand A9Y3MPA, indicates the involvement of the ligand in coordination. In Mn(II) complex, three bands at 13200, 14650 and 25700cm$^{-1}$ can be assigned to the transitions $^6A_{1g}\rightarrow{}^4T_{1g}(G)$, $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ and $^6A_{1g}\rightarrow{}^4E_g(G)$ respectively. This supports the presence of Mn(II) in octahedral environment.

In the case of Fe(III) complex, an intense band at 27000cm$^{-1}$ in its electronic spectrum is due to the charge transfer band. Another shoulder peak at 18680cm$^{-1}$ exhibited by the iron complex may be due to $^5T_{2g}\rightarrow{}^5E_g$ transition, which confirms octahedral geometry. The Cu(II) complex showed two bands at 13450cm$^{-1}$ and 15600cm$^{-1}$; the former may be assignable to $^3E_g\rightarrow{}^3T_{2g}$ transition and the later may be attributed to L→M charge transfer band, suggesting thereby the octahedral geometry.

***NMR spectra***

Though $^1$H NMR spectra of chelates were complex, valuable informations can be deduced regarding the sites of coordination of the ligand to various transition metal ions. On close examination and comparison of the $^1$H NMR spectrum of the ligand and chelates it was understood that the signal corresponds for the carboxylic acid proton ($\delta$ 10.2) was absent in all complexes, suggesting that one of the coordination sites of the ligand is carboxylate moiety. The $^{13}$C NMR spectra of the chelates exhibited signals correspond to carbon atoms in different chemical environment. The carboxylic and azomethine carbon atoms of the ligand in various chelates resonated in the range 178-160ppm and 135-120ppm respectively. In both cases considerable downfield shifts were noted from the signals obtained for free Schiff base i.e., 182.12 ppm for the carboxylic acid carbon and 140.05ppm for azomethine carbon. Thus NMR spectral studies confirmed that the Schiff base interact to the metal ion through the carboxylate part and azomethine part of the molecule

Based on the detailed analysis discussed above, it can be established that A9Y3MPA acts as a monovalent bidentate ligand in the complexes. The complexes of Mn(II), Fe(III) and Cu(II) possess octahedral geometry and the Zn(II) complex has tetrahedral geometry. The derived structures of the complexes are given in the figure 1.27.



M= Mn(II), Cu(II)

**Fig. 1.27:** Structures of the metal complexes of Schiff base A9Y3MPA

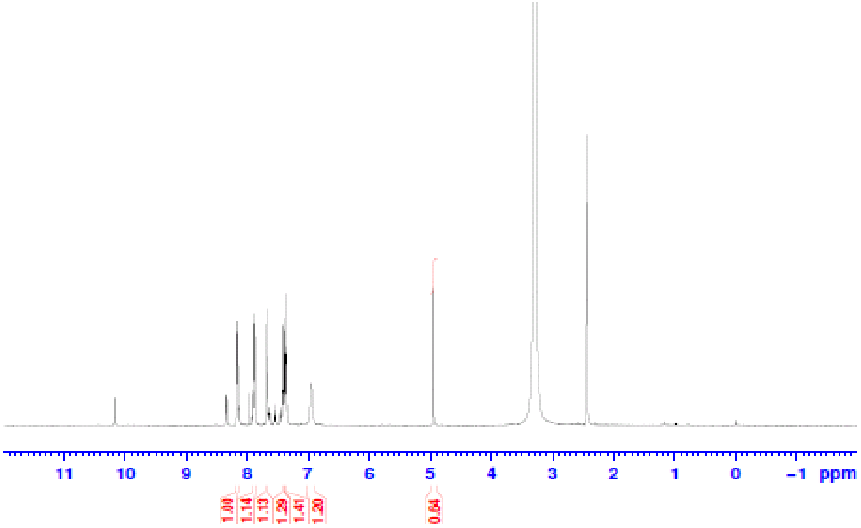


**Fig. 1.28:** $^1$H NMR spectrum of Schiff base A9Y3MPA

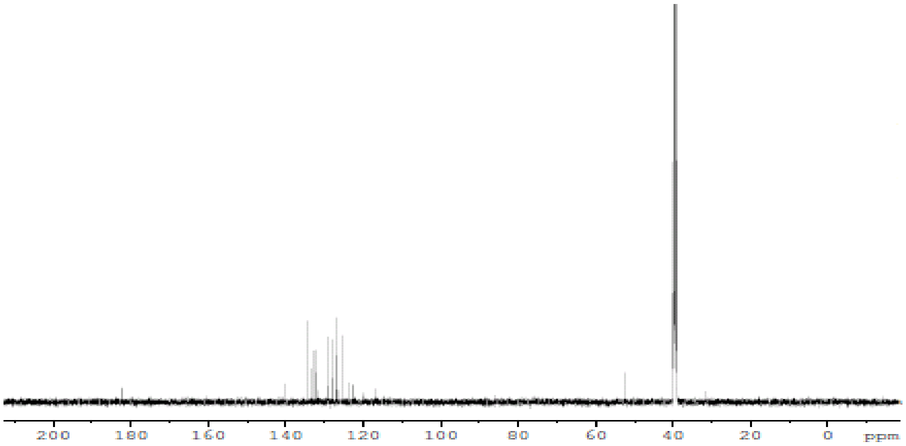


**Fig. 1.29:** $^{13}$C NMR spectrum of Schiff base A9Y3MPA

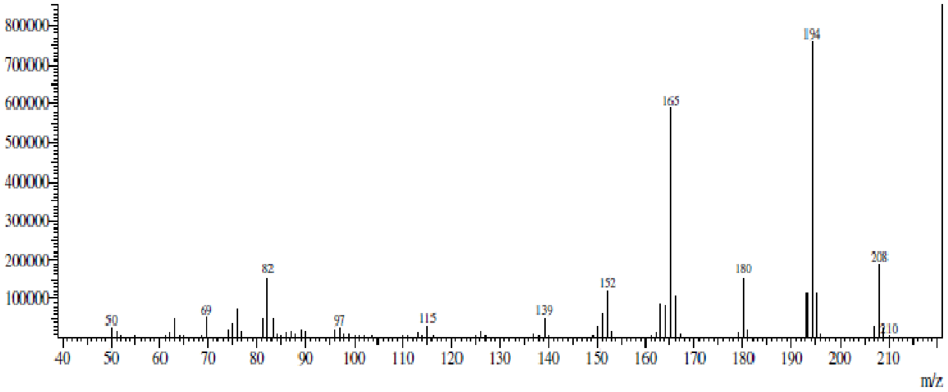


**Fig. 1.30:** Mass spectrum of Schiff base A9Y3MPA

**Table. 1.11.** Micro analytical, magnetic and conductance data of transition metal complexes of (R)-2-(anthracen-9(10H)-ylideneamino)-3-mercaptopropanoic acid (A9Y3MPA)

| **Complex** | **Colour** | **Yield (%)** | **Mol.wt.** | **M.P ($^{0}$C)** | **Metal % Found (Calculated)** | **Elemental Analysis Found (Calculated)** | | | | **$\mu_{eff}$ (BM)** | **Molar conductance ($\Omega^{-1}cm^{2}mol^{-1}$)** | **Geometry** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **C %** | **H %** | **N %** | **S%** | | | |
| A9Y3MPA | Dark Yellow | 80 | 297 | 255 | - | 68.46<br>(68.63) | 4.93<br>(5.05) | 4.50<br>(4.71) | 10.58<br>(10.77) | - | - | - |
| [$MnL_2(H_2O)_2$] | Brown | 70 | 683 | 280 | 7.92<br>(8.04) | 59.48<br>(59.70) | 4.45<br>(4.68) | 4.02<br>(4.10) | 9.12<br>(9.36) | 5.72 | 7.92 | Octahedral |
| [$FeL_2AcH_2O$] | Reddish Brown | 72 | 723 | >300 | 7.05<br>(7.34) | 59.57<br>(59.72) | 4.24<br>(4.56) | 3.57<br>(3.87) | 8.57<br>(8.85) | 5.81 | 8.17 | Octahedral |
| [$CuL_2(H_2O)_2$] | Blue | 72 | 692 | >300 | 9.24<br>(9.17) | 58.76<br>(58.96) | 4.47<br>(4.62) | 3.89<br>(4.05) | 9.19<br>(9.25) | 1.79 | 5.27 | Octahedral |
| [$ZnL_2$] | Yellow | 74 | 658 | 294 | 9.78<br>(9.94) | 61.87<br>(62.02) | 4.11<br>(4.26) | 4.12<br>(4.25) | 9.62<br>(9.73) | D | 4.89 | Tetrahedral |

Ac = Acetate L = Ligand

**Table. 1.12.** Characteristic infrared absorption frequencies of A9Y3MPA and its transition metal complexes

| **Complex** | $\upsilon_{H_2O}$ | $\upsilon_{COO(asym)}$ | $\upsilon_{C=N}$ | $\upsilon_{COO(sym)}$ | **In plane bending** | **Out of plane bending** | $\upsilon_{M-O}$ | $\upsilon_{M-N}$ |
|---|---|---|---|---|---|---|---|---|
| A9Y3MPA | - | 1642 | 1591 | 1440 | 942 | 768,715 | - | - |
| $[MnL_2(H_2O)_2]$ | 3419 | 1638 | 1556 | 1436 | 936 | 762, 712 | 537 | 457 |
| $[FeL_2AcH_2O]$ | 3404 | 1634 | 1560 | 1432 | 934 | 764, 716 | 542 | 462 |
| $[CuL_2(H_2O)_2]$ | 3251 | 1620 | 1558 | 1419 | 937 | 764, 712 | 536 | 451 |
| $[ZnL_2]$ | - | 1635 | 1561 | 1435 | 936 | 766, 714 | 542 | 448 |

Ac = Acetate L = Ligand

# SUMMARY

Six polynuclear Schiff bases 3-(anthracen-9(10H)-ylideneamino) propanoic acid [A9Y3APA], (S)-2-(anthracen-9(10H)-ylideneamino)-5-guanidinopentanoic acid [A9Y5GPA], (S)-2-(anthracen-9(10H)-ylidene-amino)-3-(1H-imidazole-4-yl)propanoic acid (A9Y3IMPA), (S)-2-(anthracen-9(10H)-ylideneamino)-3-(1H-indole-3-yl)propanoic acid (A9Y3INPA), (S)-2-(anthracen-9(10H)-ylideneamino)-3-phenylpropanoic acid [A9Y3PPA], (R)-2-(anthracen-9(10H)-ylideneamino)-3-mercapto-propanoic acid [A9Y3MPA] were synthesized and characterised. Physical measurements such as magnetic susceptibility and molar conductance of the studied metal chelates and also the electronic spectra were very useful in predicting the geometries. CHN analysis and metal percentage determinations using standard analytical techniques like pyrolytic, gravimetric and volumetric estimations were found to be beneficial for predicting the exact ratio between metal and ligand. Spectral analyses like $^{1}$HNMR, $^{13}$CNMR, mass, IR and UV-Vis were performed on the ligands and the complexes for confirming the structure. The data obtained from IR and NMR analysis were very much helpful for predicting the precise sites of coordination of the ligands on the metal ions. From all the above mentioned analytical results clearly established that all the newly synthesized Schiff bases are behaving as monovalent bidentate ligand, coordinating through azomethine nitrogen and carboxylate oxygen. From the mass spectral analysis it is quite clear that molecular ion peak of all the newly synthesized Schiff bases of anthracene-9(10H)-one is absent which unequivocally explains the least stability of $M^+$.

Synthesis and characterization of the Schiff base A9Y3APA and their transition metal chelates with the ions Mn(II), Fe(III), Co(II), Cu(II) and Zn(II) were carried out. The result from elemental analysis and metal content determination shows 1:2 ratio exists between metal and ligand. Molar conductance measurements revealed that all the metal chelates are acting as non-electrolytes in DMSO. The azomethine linkage and presence of water molecule in the complexes confirmed by the broad band in their IR spectra. All the metal complexes except Zn(II) possess octahedral geometry and zinc possesses tetrahedral geometry. Electronic spectral data and molar conductance measurements confirmed the geometries of the complexes.

Transition metal ion such as Mn(II), Fe(III), Co(II), Cu(II) and Zn(II) were used for evaluate the metal binding capacity of the Schiff base A9Y5GPA. The synthesis and characterization of this ligand and complexes were extensively studied and reported. All the synthesized metal chelates were coloured, non hygroscopic and stable to air and light. Molar conductance measurements revealed the non-electrolytic nature of the complexes. Metal content determination and CHN analysis explored the stoichiometry of the complexes. All the complexes except Cu(II) shows 1:2 metal-ligand stoichiomtry. Magnetic moment measurements gave the precise geometry of the complexes. Mn(II), Fe(III) and Co(II) complexes exhibit octahedral geometry, Cu(II) possesses square planar (dimeric) and Zn(II) has tetrahedral geometry. Low value of $\mu_{eff}$ of copper complex obviously establishes its dimeric structure. IR and NMR spectral studies of the metal chelates revealed that the Schiff base is acting as monovalent bidentate ligand having the coordination sites azomethine linkage and caboxylate moiety.

Five transition metal complexes were synthesized by the insitu preparation of the newly synthesized ligand A9Y3IMPA and characterized. The metal percentage determination and CHN analysis recognized that all complex possess 1:2 metal ligand ratio. Magnetic susceptibility measurements revealed that all the complex except Zn(II), possess octahedral geometry and Zn(II) has tetrahedral geometry. The transitions from the electronic spectra also confirm the geometry. The structure of the Schiff base was confirmed by mass, NMR, IR, spectral analysis.

The chelating ability of polynuclear azomethine compound A9Y3INPA was explored by synthesizing the metal chelates of the Mn(II), Fe(III), Cu(II) and Zn(II). The elemental analysis and metal percentage studies supported the structural formulae of the complexes as $[MnL_2(H_2O)_2]$, $[FeL_2AcH_2O]$, $[CuL_2(H_2O)_2]$ and $[ZnL_2]$, where L=ligand and Ac=Acetate. The presence of the water molecules inside the coordination sphere of the metal complexes was obviously verified by the broad band in the IR spectra. Physicochemical methods such as electronic spectroscopy and magnetic susceptibility measurements were very useful in predicting the geometry of metal chelates. All metal chelates, except Zn(II) attained octahedral geometry. The sites of coordination of the Schiff base ligand was established by infrared spectral and NMR spectral studies of the metal chelates.

Six metal complexes with polynuclear Schiff base A9Y3PPA were synthesised and characterized. Various analytical techniques were employed to establish the structure and geometry. The metal content and CHN analysis shows that all the complexes except Cu(II) possess 1:2 metal ligand stochiometry. Magnetic moment values and electronic spectra studies revealed that all the complexes except Cu(II) and Zn(II), possess octahedral geometry. Cu(II) complex has dimeric square planar and Zn(II) hold tetrahedral geometry. IR and NMR data establishes the involvement of azomethine group and carboxylic acid group in chelation with metal ions. Analysis shows that the Schiff base A9Y3PPA behave as monovalent bidentate ligand.

The metal chelates of the Schiff base A9Y3MPA were prepared and characterized using various analytical techniques. Out of the four metal complex prepared only Zn(II) shows tetrahedral geometry. All complexes showed non-electrolytic nature. The presence of coordinated water molecule was established from IR studies. The study shows that the Schiff base ligand is acting as a monovalent bidentate species in the metal complexes having the active probes carboxylate part and azomethine linkage for coordination.

In short six novel potential Schiff base ligands derived from anthracene-9(10H)-one and various essential & non essential amino acids and their twenty nine transition metal chelates were synthesized and characterised.

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