CHAPTER-I

Introduction

Literature Survey

Aim and Significance of the Present Study
"THE EVER INCREASING APPLICATIONS OF METAL COMPLEXES IN VARIOUS FIELDS OF SCIENCE IS THE DRIVING FORCE FOR THE RESEARCH AND DEVELOPMENT IN COORDINATION CHEMISTRY"

Coordination chemistry was founded by Swiss scientist A. Werner (1866-1919), who won the Nobel Prize in 1913. Great contribution was further made by Russian chemist L.A. Chugaev (1873-1922). Coordination (complex) entities consist of a cationic, anionic or neutral complex. Those substances, whose molecules contain a central atom (cation), coordinated with ligands (anions, neutral molecule or radical) can be considered as coordination or complex entities [1] and the area of inorganic chemistry, studying joint behaviour of cations and their ligands was termed as coordination chemistry [2].

The main direction of metal-complex chemistry in 21st century is emphasized as "from biology to nanotechnology" [3]. B-Diketones and their analogues, diketonate complexes [4], azomethinic and heterocyclic ligands remain "eternal". Creation of new hard-soft ligand systems is attractive [5-8]. Creation of hybrid biologically perspective ligating systems is also interesting [9-13]. The principal goal is to work not only for theoretical, but also for practically useful coordination chemistry (competitive coordination), taking into account an operated creation of polyfunctional materials (for instance, selective electrodes). Modern achievements in coordination chemistry are detailed [14]. The list of noble prizes on Coordination chemistry is significant and shows the manifestation of Coordination chemistry into various fields of science.
# Nobel Prizes on Coordination Chemistry

<table>
<thead>
<tr>
<th>Year</th>
<th>Name</th>
<th>Worked on</th>
</tr>
</thead>
<tbody>
<tr>
<td>1912</td>
<td>Victor Grignard</td>
<td>Grignard's reagents.</td>
</tr>
<tr>
<td>1913</td>
<td>Alfred Werner</td>
<td>The area on the nature of bonds of atoms in molecules in inorganic chemistry.</td>
</tr>
<tr>
<td>1915</td>
<td>Rihard Vilshtetter</td>
<td>The area of pigments in plant world especially chlorophyll.</td>
</tr>
<tr>
<td>1963</td>
<td>Karl Ziegler Giulio Natta</td>
<td>Discovery of isotactic polypropylene.</td>
</tr>
<tr>
<td>1964</td>
<td>Doroti Meri Kroufut Hodzkin</td>
<td>Determination of structures of biologically active substances by X-Rays.</td>
</tr>
<tr>
<td>1987</td>
<td>Donald James Cram, Jean-Marie Lehn and Charles J. Pedersen</td>
<td>Elaboration and applications of molecules having structurally-specified interactions of high selectivity.</td>
</tr>
</tbody>
</table>

Coordination chemistry is dominated by the utilization of Schiff bases as ligands [15] due to their chelating and complexing abilities towards transition metal ions. Schiff base compounds containing imine group (-RC=N-) are usually formed by the condensation of a primary amine/diamine with an active
carbonyl compound. The Schiff base ligands and their metal complexes have significant importance in chemistry and every year a number of reports are published on the preparation of these compounds and their application in chemical reactions [16]. The Schiff base compounds and their complexes are widely applied in enantioselective cyclopropanation of styrenes [17], asymmetric addition of cyanide to aldehydes [18], asymmetric aziridination of olefins [19], enantioselective epoxidation [19, 20], regio-selective ring opening of epoxides [21] and as a membrane in ion selective electrode [22–26]. The metal complexes of Schiff bases also finds applications in versatile catalytic reactions for organic synthesis [27–30], degradation of organic substances [31], in radiopharmaceuticals [32], their ability to reversibly bind oxygen [33] and photochromic properties [34]. Schiff base metal complexes have also found greater applications in biological field. Schiff bases have been reported to exhibit a variety of biological actions by virtue of the azomethine linkage, which is responsible for various antibacterial, antifungal, herbicidal, clinical and analytical activities [35–38]. Recently, there has been tremendous interest in studies related to the interaction of transition metal ions with nucleic acid because of their relevance in the development of new reagents for biotechnology and medicine [39]. There has also been substantial interest in the rational design of novel transition metal complexes, which bind and cleave duplex DNA with high sequence and structure selectivity [40–42].

**Thiosemicarbazide**

A compound containing the thiosemicarbazide radical, $\equiv$N-NH-C(S)-NH$_2$. One of the group of tuberculostatic drugs that includes thiosemicarbazide, benzaldehyde thiosemicarbazone, and 4-aminoacetylbenzaldehyde thiosemicarbazone. Thiosemicarbazide-based compounds have been extensively studied. Thiosemicarbazone are well established as an important class of sulphur donor Schiff base ligands particularly for transition metal ions [43–45]. This is due to the remarkable biological activities observed for these compounds, which has been shown to
be related to their metal complexing ability. Thiosemicarbazide Schiff bases are a class of important compounds in medicinal and pharmaceutical field. They show biological activities including a anticancer [46-55] and herbicidal [48] activities. In most of the complexes, thiosemicarbazones behave as bidentate ligands because they can bond to metals through sulphur and the hydrazinic nitrogen atoms, although in a few cases, they behave as unidentate ligands and bond through only sulphur atom [56-58]. Coordination chemistry of mixed hard-soft NS donor ligands is a field of current interest. The most important factor in this objective is probably the design of ligands with an appropriate structural backbone. Thiosemicarbazones that are most widely studied are sulphur and nitrogen consisting ligands [59, 60].

**Coumarin**

Coumarin is a naturally occurring benzopyran found in plants. Many of its derivatives are highly fluorescent. The 7-amino-4-methylcoumarin derivatives were widely studied during the 1970-1980 and were found to be useful for labeling biological molecules. Coumarin (2H-chromen-2-one, 2H-1-benzopyran-2-one) is structurally the least complex member of a large class of compounds known as benzopyrones and also coumarins are among the best known oxygen heterocyclics with a δ-lactone ring which comprise a very large class of compounds found throughout the plant kingdom [61-63]. The biological activities of coumarin derivatives are multiple and include antithrombotic [64], antimicrobial [65], antiallergic [66], anti-inflammatory [67], antitumor [68] and anticoagulants [69]. Coumarin (2H-1-benzopyran-2-one), a naturally occurring plant constituent, has been used in the treatment of cancer [70] and oedemas [71].

Derivatives of coumarin are known to possess significant antifungal as well as antibacterial. Many of the coumarins present in plants, and also their synthetic analogues, have been reported to be good antifungal and antibacterial agents [72-79]. Preliminary structure–activity relationship studies have showed that, the presence of hydroxyl or carboxylic groups on the coumarin nucleus is
necessary for antimicrobial activities[80]. The presence of coumarin nucleus in the antibiotics, such as novobiocin, clorobiocin and coumermycin A, were identified over forty years ago. But, the use of these antibiotics has been limited due to their poor water solubility, low activity against Gram-negative bacteria and the rapid emergence of resistance[81, 65]. However, renewed interest in these antibiotics has arisen following the discovery that, they are potent catalytic inhibitors of DNA gyrase. Additionally, these antibiotics have been shown to be active against Gram-positive bacteria, especially against methicillin-resistant *Staphylococcus aureus* (MRSA) [65]. Further derivatisation of novobiocin, clorobiocin and coumermycin A, has allowed for the production of novel coumarin antibiotics displaying excellent inhibition of DNA supercoiling by DNA gyrase B and good antibacterial activity against vancomycin, teicoplanin and novobiocin resistant *Enterococci* species[65]. In view of such a fascinating structural and biological features of coumarins, in the present study, hydroxy substituted formyl coumarins have been utilized for the synthesis of various Schiff bases.

**Isatin**

Isatin (1H-indole-2, 3-dione) was first discovered in 1842 as a product from the oxidation of indigo[82]. The synthetic versatility of isatin has led to the extensive use of this compound in organic synthesis. Various reviews have been published time to time regarding the chemistry of this compound and on the utility of isatin as a precursor for the synthesis of other heterocyclic compounds[83-85]. Oxindoles usually have a broad range of pharmacological actions such as anxiogenic and sedative agents[86, 87], as antagonists of guanylate cyclase-coupled atrial natriuretic peptide receptor[88, 89] and as potent inhibitors of monoamine oxidase B[90-92]. Schiff bases derived from N-methyl/N-acetyl isatin derivatives and aryl amines were prepared and screened for their anticonvulsant activity. The compounds with bromo substituent in the isatin ring and chloro substituent in the phenyl ring exhibited a broad-spectrum activity and seem to be good prototypes for the development.
of new drugs against epilepsy [93]. Some hydrazones, Schiff and Mannich bases of isatin have also exhibited significant anticonvulsant activity and based on these results some structural features responsible for interaction with the receptor site were established within a suggested pharmacophore [94]. As pharmacological activities started to be demonstrated for isatin and its derivatives, their metal complexes also gained biological relevance and their antibacterial, antiproliferative or mutagenic properties were also investigated. The Cu(II), Co(II), Ni(II) and Zn(II) complexes of isatin-derivatives incorporating thiazole, thiadiazole, benzothiazole and $p$-toluene sulfonylhydrazide moieties were prepared [95]. These compounds exhibit good results as antibacterial and antifungal agents against different strains and most of them had their activity enhanced on complexation. $l$-methylisatin-3-thiosemicarbazone copper(II), cobalt(II) and nickel(II) complexes were isolated and structures were determined by X-ray crystallography and also studied for their biological activities [96].

**Triazole**

Substituted-1,2,4-triazoles are among the large number of heterocyclic compounds, that have received the most attention during the last two decades as potential antimicrobial agents. They are associated with diverse biological activities such as fungicidal, antimicrobial, antiviral activities etc. [97-101]. The 1,2,4-triazole nucleus has been incorporated into a wide variety of therapeutically interesting drugs, including $H_1/H_2$ histamine receptor blockers, cholinesterase-active agents, CNS stimulants, antianxiety agents and sedatives [102]. Mercapto derivatives of substituted 4-amino-1,2,4-triazoles are particularly interesting as complexing agents due to the presence of four potential donor atoms (three nitrogen and one sulphur), consequently many metal derivatives of ligands of this type have been prepared [103-107].

Schiff bases of O-phthalaldehyde and its complexes have a variety of applications including biological [108], clinical [109] and analytical [110]. Earlier work has showed that, some drugs exhibited increased activity when
administered as metal chelates rather than as organic compounds [108, 109] and that, the coordinating possibility of O-phthalaldehyde has been improved by condensing with a variety of carbonyl compounds. Also, the primary amines are known as better condensing agents.

**Survey of the Previous Work**

Recently, Vinod K. Sharma have reported the synthesis of new series of ruthenium(III) and rhodium(III) complexes with two bifunctional tridentate Schiff bases derived from sixteen ring-substituted 4-phenylthiosemicarbazones and 4-nitrophenyl thiosemicarbazones of anisaldehyde, 4-chlorobenzaldehyde, 4-fluorobenzaldehyde and vanillin [111]. Coordination chemistry of mixed hard-soft NS donor ligands is a field of current interest. Their structures were determined on the basis of the elemental analysis, spectroscopic data (IR, electronic, $^1$H and $^{13}$C NMR) along with magnetic susceptibility measurements, molar conductivity and thermogravimetric analysis. Electrical conductance measurement revealed a 1 : 3 electrolytic nature of the metal complexes.

The ligands and their metal complexes have been characterized by elemental analysis, $^1$H-NMR, FT-IR, mass, electronic, ESR spectra, thermal gravimetric analysis and magnetic susceptibility. On the basis of the above studies, three ligands were suggested to be coordinated to each metal atom by thione sulphur and azomethine nitrogen to form low-spin octahedral complexes with ruthenium(III) while forming diamagnetic complexes with rhodium(III). Both the ligands and their metal complexes have been screened for their bactericidal activities and the results indicate that, they exhibit a significant activity.

Sulekh Chandra et al., have reported the synthesis of neutral tetradeutate $\text{N}_2\text{O}_2$ Schiff base formed by the condensation benzil bis(thiosemicarbazone) in alcoholic medium [112]. The Schiff base has been checked for its complexation ability towards Cu(II) and Ni(II) metal ions. All the synthesized metal complexes were characterized on the basis of their microanalytical data, molar conductance, magnetic susceptibility, IR, UV–Vis
\(^1\)H NMR and ESR spectra. The IR spectral data suggests that the involvement of sulphur and azomethane nitrogen atoms in the coordination to the central metal ion. On the basis of spectral studies, an octahedral geometry assigned has been assigned for Ni(II) complexes, whereas but a tetragonal geometry for Cu(II) complexes. The free ligand and its metal complexes have been tested invitro against a number of microorganisms in order to assess their antimicrobial properties.

Eddy *et al.*, have studied the coordination ability of pyridoxal-4-methylthiosemicarbazone with iron(III) ion [113]. The synthesized ligand and its metal complex were characterised by spectroscopic methods (\(^1\)H NMR, IR, and mass spectroscopy), elemental analysis and single crystal X-ray diffraction techniques. The complex crystallises as dark brown microcrystals. The crystal data determined at 100(1) K revealed a triclinic system, space group P (Z = 2). The ONSCl\(_2\) geometry around the iron(III) atom is intermediate between trigonal bipyramidal and square pyramidal (s = 0.40). The temperature dependence of the magnetic susceptibility (5–300 K) is consistent with a high spin Fe(III) ion (S = 5/2) exhibiting zero-field splitting. Interpretation of these data yielded: D = 0.34(1) cm\(^{-1}\) and g = 2.078(3).

The anti-fungal activity and mode of action of a range of silver(I)–coumarin complexes was studied by B. Thati *et al.*, [114]. Amongst all the silver(I)–coumarin complexes, some of the complexes viz. 7-hydroxy coumarin-3-carboxylatosilver(I), 6-hydroxy coumarin-3 carboxylatosilver(I) and 4-oxy-3-nitrocoumarinbis(1,10-phenanthroline)silver(I) exhibited MIC\(_{80}\) values between 69.1 and 4.6 \(\mu\)M against the pathogenic yeast *Candida albicans*. Further, Thati *et al.*, have reported that, a number of the metal complexes disrupted cytochrome synthesis in the cell and induced the appearance of morphological features consistent with cell death by apoptosis. Silver(I)–coumarin complexes demonstrate good anti-fungal activity and manifest a mode of action distinct to that of the conventional azole and polyene drugs thus raising the possibility of their use when resistance to conventional drug has emerged or in combination with such drugs.
Vukadin et al., reported the synthesis and single-crystal X-ray analysis of two sulfato and one thiocyanato copper(II) complex with 2-acetylpyridine S-methylisothiosemicarbazone (HL) of the formulae \([\text{Cu(HL)}-\text{SO}_4(\text{H}_2\text{O})]\text{H}_2\text{O}, [\text{Cu}_2(\text{HL})_2(\text{I-SO}_4)_2]2\text{H}_2\text{O} \text{ and } [\text{Cu(HL)(NCS)(SCN)}] \), as well as the structure of the protonated ligand \(\text{H}_2\text{L}\).

Ana et al., described of palladium (II) complexes of 3,5-diacyl-1,2,4-triazole bis(thiosemicarbazone) \((\text{H}_2\text{L}_2)\), 2,6-diacylpyridine bis(thiosemicarbazone) \((\text{H}_2\text{L}_3)\) and benzyl bis(thiosemicarbazone) \((\text{H}_2\text{L}_4)\). The new complexes \([\text{PdCl}_2(\text{H}_2\text{L}_2\text{L}=)]\) (1), \([\text{PdCl}_2(\text{H}_2\text{L}_3\text{L})]\) (2) and \([\text{PdL}_4]\) DMF (3) have been characterized by elemental analysis and spectroscopic studies (IR, \(^1\text{H}\) NMR and UV-Vis).

Bagihalli et al., have reported the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes of Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and 8-formyl-7-hydroxy-4-methylcoumarin [115]. The elemental analyses, spectroscopic (IR, UV-vis, fluorescence and ESR) studies, magnetic measurements and thermal studies suggested that, all the metal complexes are polymeric in nature. The Schiff bases and their metal complexes were found to possess high antimicrobial activities.

S. U. Rehman et al., have synthesized the Schiff bases derived from 3-formyl-4-chlorocoumarin and heteroaromatic amines/hydrazone (116). The Co(II), Ni(II), Cu(II) and Zn(II) complexes of these Schiff bases have been synthesized, characterized spectroscopically and screened for their in-vitro antibacterial activity against \(E.\ coli, K.\ pneumoniae, P.\ mirabilis, P.\ aeruginosa, S.\ typhi, S.\ dysenteriae, B.\ cereus, C.\ diphtheriae, S.\ aureus\) and \(S.\ pyogenes\) bacterial strains and for in-vitro antifungal activity against \(T.\ longisusus, C.\ albicans, A.\ flavus, M.\ canis, F.\ solani\) and \(C.\ glaberata\).

B. S. Creaven et al., have reported the Cu(II) complexes of bidentate coumarin Schiff bases [117]. The Schiff bases have been synthesized via condensation of 7-amino-4-methylcoumarin with a number of substituted salicylaldehydes and are characterized by IR, \(^1\text{H}\) & \(^{13}\text{C}\) NMR, UV-vis. and
elemental analyses. Subsequently, these ligands are reacted with copper(II) acetate to form Cu(II) complexes. These Cu(II) complexes were characterized by IR, UV-vis., molar conductance, magnetic properties and crystal analysis data. The Schiff bases and their Cu(II) complexes were studied for their anti-candida activities.

Literature also records the synthesis of metal complexes with coumarin derivatives. B.S. Creaven et al., have reported the synthesis, characterization and antimicrobial activity studies of Cu(II) and Mn(II) complexes with coumarin-6,7-dioxyacetic acid and 4-methylcoumarin-6,7-dioxyacetic acid [118]. Metal complexes have been characterized by X-ray crystal structures along with other spectroscopic techniques. The complexes were screened for their antimicrobial activity against a number of microbial species, including methicillin-resistant *Staphylococcus aureus*, *Escherichia coli* and *Candida albicans*. I. Kostova et al., have studied the lanthanide complexes of 4-methyl-7-hydroxycoumarin and their pharmacological activity [119]. Complexes of cerium(III), lanthanum(III) and neodymium(III) with 4-methyl-7-hydroxycoumarin were synthesized by the mixing of equimolar amounts of the respective metal nitrates and 4-methyl-7-hydroxycoumarin sodium salt in water. The complexes were characterized and identified by elemental analyses, conductivities, IR, $^1$H and $^{13}$C NMR spectroscopies and mass spectral data. The newly synthesized compounds were assayed for acute intraperitoneal and per oral toxicity, influence on blood clotting time and for spasmolytic activity.

G.A. Bain et al., have reported the coordination behaviour of Cu(II) complexes of N(4)-substituted thiosemicarbazones of isatin [120]. The Schiff bases have been characterized by crystal studies. The Cu(II) complexes have been characterized by IR, solid state UV-vis., solid state EPR studies.

Some Schiff bases derived from isatin were prepared by the reaction with amino acids or substituted hydrazines and were subsequently metallated with nickel(II), iron(III) or cobalt(II) ions to form respective metal complexes[121]. Zinc(II) and mercury(II) complexes of isatin-3-
thiosemicarbazone were isolated and spectroscopically characterized [122]. Copper(II), chromium(III), manganese(II), cobalt(II), nickel(II), zinc(II), cadmium(II) and lead(II) chelates with tetradeutate Schiff base in the enolic form derived from isatin and $\sigma$-phenylenediamine were reported. In this case, the complexes were obtained as neutral species with divalent ions [123]. Copper(II), nickel(II) and cobalt(II) complexes with pyridyl and quinolylhydrazones of isatin and $N$-methylisatin have also been prepared. In case of the copper complex, spectroscopic results suggested a planar geometry [124, 125].

B. Murukan et al., have conducted a study on synthesis, spectral, electrochemical and antibacterial activities of Cu(II) complexes with isatin derived bishydrazone and different co-ligands [126]. The bishydrazones were prepared via condensation of isatin monohydrazone and salicylaldehyde. The authors have characterized the ligand and their metal complexes on the basis of elemental analysis, molar conductance, magnetic susceptibility data, NMR, UV-visible, IR and EPR spectral studies wherever possible and applicable. The spectral studies revealed that, the bishydrazone is monobasic tridentate coordinating through the deprotonated phenolate oxygen, azomethine nitrogen and carbonyl group of the isatin moiety respectively.

G. Cerchiaro and A.M. da C. Ferreira have reported a review article on the oxindoles and copper complexes with oxindole-derivatives as potential pharmacological agents [127]. The review article illustrates the structural and biological importance of isatin. Various Schiff bases of isatin and their metal complexes have been reported in the article. The importance of Cu(II) complexes along with other transition metal complexes of versatile isatin Schiff bases have been demonstrated. The review records the potential antitumoral activity studies of Cu(II) complexes in comparison to other complexes, based on the proposal of a synergistic effect on adding the metal coordinating and redox properties.
An interesting isatin-Schiff base copper(II) complex was prepared and characterized by different techniques, both in the solid and solution state, and its reactivity towards carbohydrate oxidation was verified [128]. The Schiff base has been derived from 1,3-diaminopropane and isatin. In aqueous solution, this complex undergoes a peculiar keto-enolic equilibrium. This Cu(II) complex was shown to catalyze the oxidation of hexoses (glucose, fructose and galactose) in alkaline medium.

J.G. Hasnoot et al., have reported Cu(II), Ni(II), Co(II) and Fe(II) metal complexes with 3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole ligand system [129]. The metal complexes exhibit very similar spectroscopical and electrical properties. The four compounds appear to be isostructural according to their IR spectra and X-ray powder diffraction data. The crystal structure of Cu complex has been solved.

N.K. Singh et al., have reported the 3d metal complexes with sulfur donor ligands [130]. The metal complexes were characterized by spectroscopic and analytical methods. The ligand and its metal complexes were studied for their in-vitro and in-vivo antitumour studies.

M.H.S.A. Hamid et al., have studied the Cu(II) complexes with tridentate ligand system of NNS donor sequence [131]. The Schiff base is coordinated to the copper(II) ion in its iminothiolate form via the thiolate sulfur atom, the azomethine nitrogen atom and one of the pyrazine nitrogen atoms. The ligand and its Cu(II) complexes have been solved by X-ray crystal structure along with spectroscopic studies.

Very recently, G.B. Bagihalli et al., have studied the synthesis and biological importance of Co(II), Ni(II) and Cu(II) metal complexes of triazole Schiff bases [132]. The Schiff bases have been derived from 3-substituted-4-amino-5-hydrazino-1,2,4-triazole and 8-formyl-7-hydroxy-4-methylcoumarin. The metal complexes were characterized by elemental analyses, spectral (IR, Uv-Vis, ESR, FAB-mass) electrochemical, magnetic and thermal data. The authors have studied all the ligands and their Co(II), Ni(II) and Cu(II)
complexes for their antibacterial (*E. coli*, *S. aureus*, *S. pyogenes* and *P. aeruginosa*) and antifungal (*A. niger*, *A. flavus* and *cladosporium*) activities by MIC method and also the brine shrimp bioassay was carried out to investigate their *in-vitro* cytotoxic properties.

P.G. Avaji and S.A. Patil have reported the Co(II), Ni(II) and Cu(II) metal complexes with hydrazino-1,2,4-triazole Schiff bases [133]. The complexes have been synthesized by template condensation of 2,6-diformyl-4-methylphenol and 3-substituted-4-amino-5-hydrazino-1,2,4-triazole with CoCl$_2$·6H$_2$O, NiCl$_2$·6H$_2$O and CuCl$_2$·2H$_2$O in ethanol. These metal complexes were characterized by elemental analyses, magnetic susceptibility, molar conductance, spectral (IR, Uv-Vis, ESR, $^1$H NMR and FAB-mass), thermal, fluorescence and solid-state DC electrical conductivity studies. The solid state DC electrical conductivity showed that, the complexes were semiconducting. All the Schiff bases and their Co(II), Ni(II) and Cu(II) complexes were evaluated for their antimicrobial properties.

The synthesis, spectroscopic and thermal characterization of Co(II), Ni(II) and Cu(II) complexes of triazole Schiff bases have been reported from our laboratory [134]. The Schiff bases have been derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and indole-3-aldehyde in ethanol which act as bidentate ligands. The authors have proposed octahedral geometry for Co(II) and Ni(II) complexes whereas square-planar geometry for Cu(II) complexes in the light of elemental analysis, magnetic, spectroscopic (IR, UV-Vis, NMR, ESR, FAB-mass) and thermal studies. Further, authors have studied the electrochemical (CV), solid state d.c. electrical conductivities and biological applications of these metal complexes.

Kulkarni *et al.*, have reported the series of Co(II), Ni(II) and Cu(II) complexes which have been synthesized with newly synthesized Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and Isatin [135]. The elemental analyses of the complexes are confined to the stoichiometry of the type ML$_2$ [M=Co(II), Ni(II) and Cu(II)], respectively, where ‘L’ acts as a
deprotonated ligand in which sulphur plays an important role in coordination. In view of analytical, spectroscopic, magnetic and thermal studies, it has been concluded that, the Co(II), Ni(II) and Cu(II) complexes possess octahedral geometry. The redox behaviour of the complexes investigated with the aid of cyclic voltammetry indicated the two-electron transfer process. The antimicrobial studies of Schiff bases and their complexes against various antibacterial (Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa and Bacillus subtilis) and antifungal (Aspergillus niger and Pencillium chrysogenum) species by the minimum inhibitory concentration method revealed that, the Schiff bases and some of their metal complexes possess more healing antibacterial activities.

Kulkarni et al., also reported a series of La(III), Th(IV) and VO(IV) complexes of Schiff bases derived from 8-formyl-7-hydroxy-4-methylcoumarin and o-phenylenediamine/ethylenediamine [136]. The structure of the complexes has been proposed in the light of analytical, spectral (IR, UV-vis, ESR and FAB-mass), magnetic and thermal studies. The complexes are soluble in DMF and DMSO. The measured molar conductance values indicate that, the complexes are non-electrolytes in nature. The redox behavior of the complexes was investigated by electrochemical method using cyclic voltammetry. The Schiff bases and their metal complexes have been screened for their antibacterial (Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa and Salmonella typhi) and antifungal activities (Aspergillus niger, Aspergillus flavus and cladosporium) by Minimum Inhibitory Concentration method. The DNA cleavage activities of La(III) and VO(IV) metal complexes are studied by agarose gel electrophoresis method.

Patil et al., reported a new series of Co(II), Ni(II) and Cu(II) complexes have been synthesized with Schiff bases (H₂L₁ and H₂L₃) derived from 8-formyl-7-hydroxy-4-methylcoumarin or 5-formyl-6-hydroxycoumarin and o-aminophenol [137]. Structures have been proposed in the basis of elemental analyses, spectral (IR, UV-Vis, FAB-mass, and Fluorescence),
magnetic and thermal studies. The measured low molar conductance values in DMF indicate that, the complexes are non-electrolytes in the nature. Elemental analyses indicate ML.3H₂O [M= Co(II), Ni(II) and Cu(II)] stoichiometry. Spectroscopic studies suggest the coordination through azomethine nitrogen, phenolic oxygen of o-aminophenol, and the coumarin moiety via deprotonation. The Schiff bases and their complexes have been screened for their antibacterial and antifungal activities by minimum inhibitory concentration (MIC) method. The redox behavior of the complexes was investigated by using cyclic voltammetry (CV).

Aim and Significance of the Present Research Work

Reactivity of metal complexes is an important area of coordination chemistry [138-141], including reactions on coordinatively-unsaturated donor centers [142-145] or metal complex-formers [142, 146, 147] as well as reactions of self-assembling leading to various supramolecular structures [148-150]. Reactions of coordinated inorganic and organic ligands are of the high interest.

The rational design of coordination architectures based on multitopic organic ligands and metal centres represents one of the most rapidly developing fields in current coordination chemistry owing to their potential as functional materials [151-153]. It is well known from the literature that, much work has been done on the synthesis, characterization and electrochemical studies of first row transition metal complexes of Schiff bases. Metal complexes with Schiff base ligands have played an important role since the early days of Coordination Chemistry. Indeed, a great deal of work has been carried out on the synthesis and characterization of transition metal compounds with Schiff bases as ligands, mainly due to their applications in the field of organic chemistry and in the catalytic processes. Also, the past decade has seen an upsurge of interest in metal ion therapeutics for both diagnosis and treatment of diseases.

It is in this context that, the author undertook a comprehensive research work on the synthesis of some transition and inner transition metal complexes.

Chapter-I
of various bidentate, tridentate and tetradentate Schiff bases. Thus, the aim of present research work is to synthesize some Schiff bases derived from coumarin, triazole and isatin etc. and to stitch these Schiff bases with various transition and inner transition metal ions to form metal complexes.

The Schiff bases and their metal complexes were characterized by extensive spectroscopic and analytical methods. The structural properties of Schiff bases have been studied by FT-IR, UV-vis., FAB-Mass, NMR (\(^1\text{H}\) and \(^{13}\text{C}\)) and elemental analyses. Owing to the fluorescence properties of precursors, some of the Schiff bases have been evaluated for their fluorescence properties.

X-ray crystallographic study is the most definite source of information regarding the structure of a complex. But, due to the difficulty in obtaining the crystals of metal complexes suitable for X-ray crystallographic study, has rendered this method less suitable for these complexes. In such cases, a variety of other techniques can be used with good effect and have been done in this investigation. The structural diversities of metal complexes have been undoubtedly proposed in the light of FT-IR, UV-vis., FAB-Mass, NMR and ESR spectral data wherever possible or applicable, elemental analyses, conductance measurements, magnetic measurements and thermogravimetric analyses studies. Electrochemical behaviour of some metal complexes has been studied by the Cyclic Voltametry. From the study, electron transfer mechanisms were proposed. Thermal decomposition studies of some metal complexes resulted some valuable information regarding the thermal stabilities of the metal complexes. The fluorescence properties of some metal complexes have also been investigated.

With respect to the significant applications of Schiff bases and their metal complexes in medicinal field, appropriately termed as “Medicinal Inorganic Chemistry”; Schiff bases and their metal complexes have been evaluated for their antibacterial and antifungal activities. Also, some of the metal complexes have been tested for their DNA cleavage properties on isolated genomic DNA of various human pathogens.
The main purpose of this research work has been to synthesize some new Schiff bases to utilize as ligands and to study the ligands and their metal complexes from a structural point of view. These ligands with a variety of bonding interactions, tautomeric phenomena, potential variety of bonding modes and hydrogen bonding interactions, were expected to provide stimulating results. This expectation became fruitful. Metal chelates of Schiff bases hold exciting possibilities for the future concerning to their wide applications viz. in designing new catalytic systems, in formulating new synthetic route, in developing new analytical reagents and in metal based antimicrobial agents etc., Hopefully, the results of this investigation would attract increased interest in this field.

Schiff Bases Synthesized in the Present Investigation

The following series of new Schiff bases have been synthesized in the present research investigation.

- Synthesis of Schiff bases derived from 2-Methoxy benzaldehyde and Chloro/Nitro substituted Thiosemicarbazide (Figure-I).
- Synthesis of Schiff base derived from 5-formyl-6-hydroxycoumarin/8-formyl-7-hydroxy-4-methylcoumarin and methyl substituted Thiosemicarbazide. (Figure-II).
- Synthesis of Schiff bases derived from methyl substituted Thiosemicarbazide and Isatin/Chloro substituted Isatin. (Figure-III).
- Synthesis of Schiff bases derived from Phtalaldehyde and isatin /Chloro Isatin monohydrazone. (Figure - IV).
- Synthesis of Schiff bases derived from 2-Hyrazino benzo thiazole and Isatin/Chloro Isatin. (Figure - V).
- Synthesis of Schiff bases derived from 2, 6-diamino pyridine and 8-formyl-7-Hydroxy-4-Methylcoumarin. (Figure - VI).
- Synthesis of Schiff bases derived from 3-substituted-4-amino-5-mercaptop-1,2,4-Triazoles and 5-Formyl-6-Hydroxy coumarin (Figure-VII).
REFERENCES:


Introduction

Introduction


Chapter-I 23
Introduction


Chapter-I
Introduction


Chapter-I 25
Introduction


Chapter-I

26


112. Sulekh Chandra, Smriti Raizada, Monika Tyagi, Archana Gautam Hindawi Publishing Corporation Bioinorganic Chemistry and
Introduction

Applications Volume 2007, Article ID 51483, 7 pages


Chapter-I 28
Introduction


Chapter-I
Introduction


Chapter-I 30