

Versatile Applications of Transition Metal Complexes Incorporating Schiff Bases: A Review

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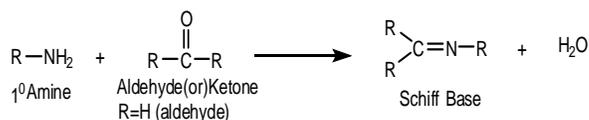
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Abstract - Schiff base metallic complexes have received significant attention in the scientific community for their unique properties and versatile applications across various fields, including industry and biology. These complexes display various biological activities, including antiviral, cytostatic, antibacterial, anticancer, and antifungal properties. The influence of certain metals on the biological activity of these compounds and their intrinsic chemical interest as multidentate ligands has prompted a considerable increase in the study of their coordination behaviour. This review discusses the structural features of metal complexes of the first series of transition metals with Schiff bases as ligands having different type donor sites. Major developments in this field over the past few years and recent research have also been briefly discussed. Further perspectives concerning the synthesis, structural aspects, characterization, and applications are presented.

Keywords- Applications, Schiff Bases, Transition Metal Complexes.

1. INTRODUCTION

The coordination chemistry of transition metal complexes has gained momentum in recent years because of their versatile applications in various fields of chemical and medical sciences and comprises a large body of bio-inorganic chemistry research [1]. The term “Schiff base” is named in recognition of the Italian–German chemist, the noble prize winner Hugo Schiff (1834–1915), who first synthesized this group of compounds. A Schiff base (SB) is comprised of imine group (–RC=N–) and is generally synthesized by condensation between a primary amine (R–NH₂) and an active carbonyl (RCOR') compound (an aldehyde or ketone) [Scheme 1] [2].



Scheme 1: General method of Synthesis of Schiff base [2]

Schiff Bases are used extensively as organic compounds that coordinate with metal ions through imine or azomethine nitrogen (C=N) and support an ample spectrum of biological behaviours of these azomethinic compounds [3]. The interaction study between DNA and transition metal Schiff base complexes has fascinated several benefits because of their importance in molecular biology, chemotherapy and the design of new kinds of pharmacological molecules [4] [5] [6]. Transition metal complexes containing Schiff base ligands have a wide range of biological applications, including antibacterial, fungicidal, anti-inflammatory, agrochemical, and antiviral therapy [7] [8] [9]. They also have various properties as biochemical, clinical, and pharmacological. The presence of the imine group in

these compounds is the main reason they show many biological properties [10] [11] [12]. A wide variety of applications of several SBs is reported in various fields, including the organic and inorganic chemistry, analytical, catalysis, pharmaceutical, biological, food and dye industries, and pharmacological activities [13] Such as anti-inflammatory [14], antitumor [15], anticonvulsant [16], antifungal [17], analgesic [18], antibacterial [19], antimalarial [20], antiviral [21], anthelmintic [22], antioxidant [23] and so forth. SBs effortlessly form stable complexes with main group elements, transition metals, lanthanide, and actinides elements as they easily retain tenability of their stereo-electronic structures, which explains why they are regarded as “privileged ligands” [10].

2. TRANSITION METAL COMPLEXES OF SCHIFF BASE LIGAND

2.1 TITANIUM COMPLEXES

A titanium (IV) Schiff base complex, $[\text{Ti}(\text{L})_2] \cdot \text{H}_2\text{O}$, was synthesized by treating $\text{TiO}(\text{acac})_2$ with an ONO-donor Schiff base ligand (H_2L) derived from the condensation of 4-aminobenzohydrazide and 3-methoxysalicylaldehyde. The synthesized ligand and its respective complex were characterized by various spectroscopic techniques and elemental analysis (CHN). A single-crystal X-ray diffraction (SC-XRD) analysis was also accomplished to ensure the molecular structure of the complex. The geometry around the central metal ion in $[\text{Ti}(\text{L})_2] \cdot \text{H}_2\text{O}$ was distorted octahedral as revealed by the data collected from diffraction studies. Hirshfeld surface analysis showed that H...H interatomic contact is the most significant contributor to the crystal packing of the complex. Moreover, theoretical calculations of the Schiff base complex were carried out by DFT at the B3LYP/Def2-TZVP level of theory, which showed a good correlation with the experimental findings [24]. The titanium (IV) complexes of Schiff bases derived from aroylhydrazine e.g. benzoylhydrazine, salicyloylhydrazine, nicotinic acid hydrazide with aldehyde or ketone are reported and characterized based on spectroscopy, magnetic susceptibility and molar conductance measurements. Complexes are found to possess 1:2 (metal:ligand) stoichiometry. The prepared ligands were act as dibasic tridentate ligands. On the basis of experimental evidences octahedral geometry has been proposed for prepared complexes. Geometry was confirmed by the optimized structure obtained from computational study. The synthesized ligands, in comparison to their titanium (IV) complexes, were also screened for their microbial and antioxidant properties [25].

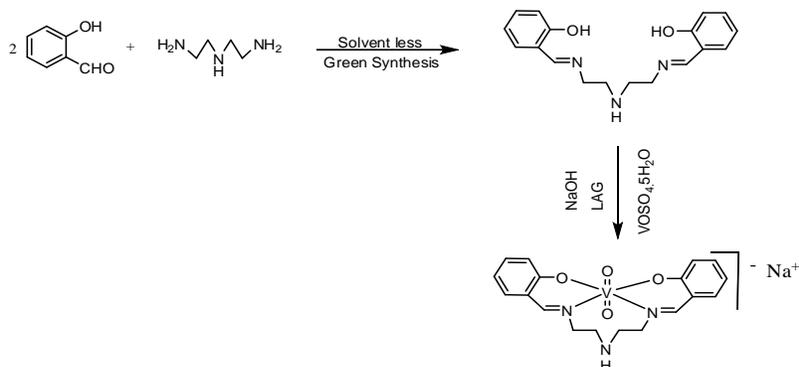
2.2. VANADIUM COMPLEXES

A novel oxovanadium complex, prepared from the reaction of hydrated VOSO_4 with an azo-ligand derived from the synthesis of 2-hydroxy-5-(phenyldiazenyl)benzaldehyde and L-serine, was structurally investigated using powder XRD, Rietveld analysis, infrared, ultraviolet-visible (UV-Vis), circular dichroism (CD), fluorescence measurements, cyclic voltammograms (CV), electron spin resonance (ESR), and a superconducting quantum interference device (SQUID). In addition, the stability of the

complex in the presence of laccase was also explored. The UV-Vis absorption spectra of the studied complex exhibited a maximum degradation of $\sim 60\%$ and minimum degradation of approximately $\sim 10\%$ after two days of exposure to laccase based on the decrease in absorbance induced by azobenzene $\pi-\pi^*$ absorption. However, the rate of degradation is considerably slower than predicted [26].

Four dioxidovanadium (V) complexes with formula $[\text{VO}_2(\text{L})]^-$ (where L = Schiff base ligand, formed by reacting 3-hydroxy-2-naphtic hydrazide with 5-chlorosalicylaldehyde or 5-bromosalicylaldehyde) have been isolated and structurally characterized based on elemental analysis, IR and UV-Vis spectra results. The X-ray crystal structure diffraction analyses of all complexes indicate a distorted square pyramidal geometry for the vanadium (V) atom, being coordinated by the tridentate Schiff base and two oxido groups. The complexes are charge-balanced by triethylammonium or diethylammonium cations, and the hydrogen bond interactions between the ionic species are discussed. Ionic vanadium complexes are characterized by better solubility in water compared to neutral molecules, and this represents an important feature if these compounds have to be used as pharmaceuticals. The stability of the complexes at $\text{pH} = 2$ and 7 was established by UV-Vis spectroscopy and compared to the previously studied potential insulin-mimetic vanadium (III-V) complexes with Schiff base ligands. The effect of the cation on the solubility of the complexes in water and their stability in solution has been described in detailed [27].

The green synthesis of a Schiff base (H_2L) and its vanadium complex $\text{Na}[\text{VO}_2\text{L}]$ have been studied. The compounds were derived from salicylaldehyde, diethylenetriamine and vanadyl sulphate by applying grinding method to overcome environmental issues with solvents (Scheme 2). The compounds were characterized with elemental, EDX, magnetic susceptibility, molar conductance and spectroscopic analysis. The synthesized vanadium (V) complex was an efficient and selective catalyst towards oxidation of organic sulfides and alcohols. A suitable mechanism for catalytic oxidation was proposed which was verified by theoretical calculations using the GAUSSIAN16 suite. $\text{Na}[\text{VO}_2\text{L}]$ exhibited strong antibacterial activity against Gram-positive and Gram-negative bacterial strains [28].



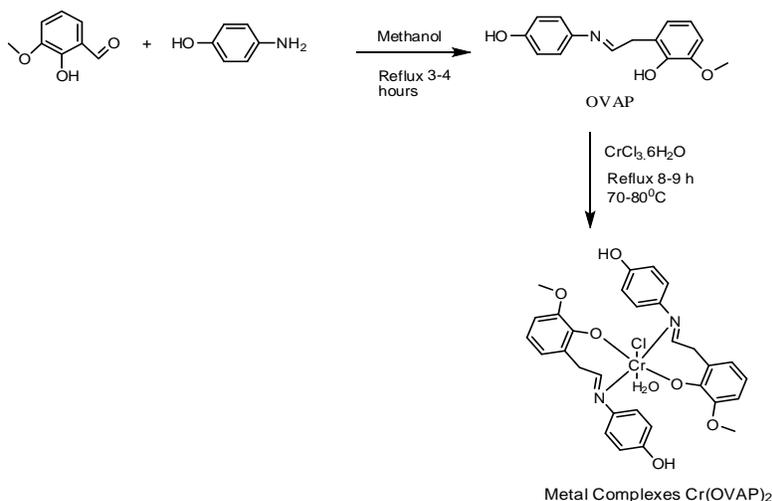
Scheme 2: Green synthesis of H₂L and Na[VO₂L][28]

A new ONO-tridentate Schiff base ligand (H₂L) derived from 3-methoxy-4-hydroxybenzaldehyde and nicotinic hydrazide was synthesized and characterized by elemental analysis, spectral studies and powder XRD studies. Then, oxovanadium (V) Schiff base complex VOL was prepared and characterized by different techniques. Moreover, the catalytic activities of complexes were investigated for the synthesis of benzimidazoles, benzoxazoles, and benzothiazoles under reflux conditions as well as through ultrasonic irradiation. The results revealed several advantages of this procedure, including high product yields, short reaction times, facile work-up procedure, simplicity in operation, eco-friendly reaction conditions, and green aspects by avoiding toxic catalysts and solvents [29].

2.3 CHROMIUM COMPLEXES

2-((4-Hydroxyphenylimino) methyl)-6-methoxyphenol (OVAP) ligand was synthesized by

refluxing 2-hydroxy-3-methoxybenzaldehyde with p-aminophenol and its chromium metal complex [Cr(OVAP)₂] (Scheme 3). The ligand and its metal complexes were characterized by different spectral techniques, elemental analysis and conductivity measurements. The elemental analysis and mass spectral studies suggest 1:2 metal ligand stoichiometry of the type ML₂. All the spectral results suggests octahedral geometry for [Cr(OVAP)₂]. Kinetic parameters of the complex was estimated by Coats–Redfern method, and the complex was found to be thermally stable. DNA binding affinity of this metal complex was explored by means of fluorescence, ultraviolet (UV)–visible and viscosity studies and the studies suggested intercalative mode. The K_b values from the absorption study is 2.98 x10⁵ and K_{sv} values from fluorescence studies are 3.79 x10⁴ for complex [Cr(OVAP)₂] [30].



Scheme 3: Synthesis of ligand (OVAP) and its complex [Cr(OVAP)₂][30]

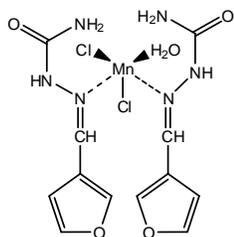
Cr (III) metal complex of Schiff bases was synthesized from the condensation reaction between 4-(dimethylamino)benzaldehyde and 4-amino-3-hydroxy-naphthalene-1-sulfonic acid. Their structure was investigated by different physicochemical techniques. The elemental analysis data suggested a 1:1 [M:L] ratio for the complex. The molar conductance measurements of the complex indicate their electrolytic nature in DMSO as a solvent. The absorption bands in the electronic spectra verified an octahedral environment around the metal ions in the complex [31]. A novel ligand was synthesized from sulfadimidine sodium and 2-hydroxy-1-naphthaldehyde and coordinated with Cr (II) to produce novel micro- and nanocomplexes that was characterized by various physicochemical and spectral analyses. XRD and TEM results revealed that the nano sized Chromium complex was found to be in the sub-nano scale, and temperature variations have a significant impact on the size of the nano complexes. The obtained results from the theoretical study are in good agreement with the experimental results. The antitumor studies on Chromium nanocomplex showed an inhibition of HEPG-2 cell line and the antitumor activity of the nano complex was improved after heating them at 200 °C. Furthermore, a molecular docking study revealed that Chromium nano complex has the highest activity with the receptor of (PDB ID: 5A19) and (PDB ID: 6lu7) in liver cancer and COVID-19, respectively [32]. A new chromium (III) complex was synthesized and characterized by spectral, elemental analysis, TGA, conductivity, XRD, SEM, and magnetic susceptibility measurements. Structural analysis revealed a bi-dentate chelation and octahedral geometry for the synthesized complexes. The optical band gap of the Cr (III)-L complex was found to 3.25 eV, and revealing semiconducting properties. The X-ray diffraction patterns showed nano-crystalline particles for the obtained complexes. In addition, the synthesized metal complexes were examined as corrosion inhibitors for mild steel in acid solution. The electrochemical investigations showed a maximum inhibition efficiency of 95.45%. Frontier Molecular orbital (FMO) and Natural bond orbital (NBO) computations showed good tendency of the ligand to donate electrons to the metal through nitrogen atoms while the resultant complexes tended to donate electrons to mild steel more effectively through oxygen atoms and phenyl groups [33].

2.4 MANGANESE COMPLEXES

Four Mn (II) complexes based on the 2,6-diacetylpyridine bis(isonicotinoylhydrazone) (H_2L^1) and 2,6-diacetylpyridinebis(nicotinoylhydrazone) (H_2L^2), were prepared using different synthetic conditions.

Discrete mononuclear $[Mn(H_2L^1)_2(H_2O)_2](NO_3)_2$ (**1**) and trinuclear $[Mn_3(H_2L^1)_2(NCS)_2Cl_4(H_2O)_2]$ (**2**) complexes and two 2D coordination polymers $\{[Mn_3(L^1)_3(H_2O)_2]1.5C_2H_5OH\}_n$ (**3**) and $\{[MnL^2]dmf\}_n$ (**4**), where $dmf = N,N$ -dimethylformamide have been formed. Single-crystal X-ray diffraction study shows that H_2L^1 and H_2L^2 , which differ only by para or meta position of radicals with respect to the nitrogen atoms in the terminal pyridyl fragments, demonstrate chelate or chelate-bridging coordination mode with N_3O_2 , or N_4O_2 and N_5O_2 donor atoms, respectively. The planar-chelate coordination of these ligands provides the pentagonal-bipyramidal surrounding of Mn (II) and the terminal pyridyl moieties promote bridging function and structure expansion in **2–4** as well as octahedral Cl_2N_4 coordination geometry for one of Mn (II) atoms in the trinuclear complex **2**. All compounds have been investigated in the solid state by IR spectroscopy and thermal analysis in order to understand the influence of the inorganic anion presence/absence on the stability of synthesized compounds [34].

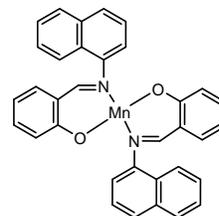
The synthesis, characterization, and examination of anti-corrosion performance of 2-furaldehyde semicarbazone Schiff base (FSC) complex of manganese (II) (scheme 4) on XC38 carbon steel immersed in 1 M HCl solution are performed using experimental investigations and quantum chemical simulation approaches. The theoretical approaches used were DFT calculations and MC simulation. The inhibition effect was also studied by electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PDP). Electrochemical testing results show that these chemical compounds are particularly powerful inhibitors, which FSC-Mn provides a considerable inhibition of 91.48% at 500 ppm [35].



Scheme 4: Structure of 2-furaldehyde semicarbazone Schiff base –MnComplex [35]

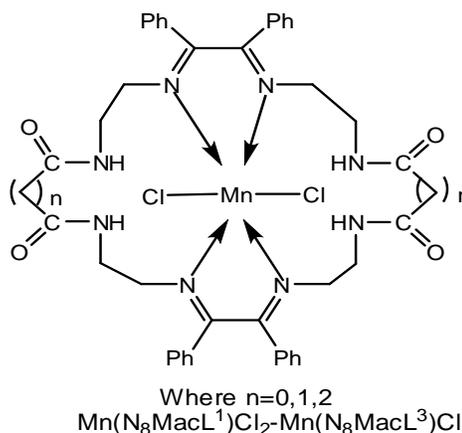
Six catalysts $MnL^1 - MnL^6$, containing two crown ether rings and their analogs supported on the MCM-41 heterogeneous substrate ($MnL^1MCM41 - MnL^5MCM41$) were synthesized and characterized. A mixture of molecular oxygen, as an oxidant, and these catalysts were used for the epoxidation of styrene. As a general result, the supported catalysts showed better performance compared with the unsupported analogs. On the other hand, the supported species, in addition to recyclability, did not require an axial base and reducing agent [36].

The Schiff base ligand 2-hydroxybenzalidene-1-naphthylamine and its Mn (II) complex was synthesized and characterized using, conductivity measurement, magnetic susceptibility, elemental analyses, melting point/decomposition temperature, spectral analysis and solubility test. The molar conductance values range ($6.52 - 23.1 \Omega^{-1}cm^2mol^{-1}$) revealed non-electrolytic nature of the complex. The magnetic susceptibility values; 5.91 BM indicated Mn (II) complex as paramagnetic. The high decomposition temperature range ($201-223^\circ C$) indicated good stability of the complexes. The infrared spectra analysis results suggested that the Schiff base behave as bidentate ligand coordinates to metal ion via azomethine nitrogen and phenolic oxygen (scheme 5). The antimicrobial activity of the Schiff base and its metal complexes were carried out using agar well diffusion method against two bacteria strains; (*Salmonella typhi* and *streptococcus pneumoniae*) and two fungal isolates; (*Aspergillus fumigatus* and *Rhizopus species*). The results revealed that the Schiff base and its metal complexes exhibited moderate antimicrobial activity as compared with the standard drugs; (Gentamycin and Nystatin) [37].



Scheme 5: Structures of Mn (II)- Schiff base complex [37]

A novel Schiff base octaazamacrocyclic ligands ($N_8MacL^1 - N_8MacL^3$) and their Mn (II) complexes [$Mn(N_8MacL^1)Cl_2 - Mn(N_8MacL^3)Cl_2$](Scheme6) were synthesized. The synthesized compounds were characterized by spectral techniques, powder X-ray diffraction studies, together with elemental (CHN) analysis, molar conductance, and magnetic susceptibility measurements. Calculations based on density functional theory (DFT) help in determining the stability of synthesized macrocyclic ligands. Electronic spectra led to the assignment of an octahedral geometry to the synthesized macrocyclic complexes. In vitro cytotoxicity of macrocyclic ligands and their Mn(II) complexes was examined against three distinct cancerous cell lines, including HeLa, A549, and MCF7 cells. Moreover, the antimicrobial activity of the synthesized compounds was also evaluated against bacterial (*E. coli*, *B. subtilis*) and fungal strains (*C. albicans*, *F. oxysporum*). The results indicate that the macrocyclic Mn(II) complexes have more antimicrobial potential than macrocyclic ligands against tested pathogens [38].



Scheme 6: Mn(II) complexes [$Mn(N_8MacL^1)Cl_2 - Mn(N_8MacL^3)Cl_2$] [38]

2.5 IRON COMPLEXES

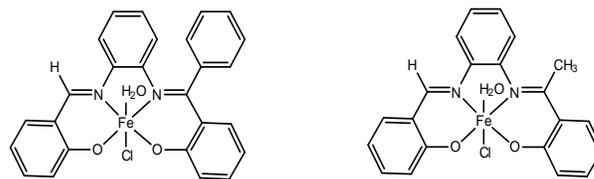
Two new azomethine chelates for Fe (III) were prepared from two dibasic tetradentate chelating imine ligands.

2,2'-((1E,1'E)-((4-nitro-1,2-phenylene)bis(azanylylidene))bis(methanylylidene))bis(4-bromophenol)(NABS) and 2,2'-((1E,1'E)-((4,5-dimethyl-1,2-phenylene)bis(azanylylidene))bis(methanylylidene)) bis(4-bromophenol) (MABS)

Schiff base ligands were used for spectral studies. Alternative spectral and physicochemical tools were applied to inspect the structural composition of the compounds under investigation. The synthesized compounds examined as anticorrosive films of C-steel in acidic chloride medium utilizing theoretical and electrochemical studies such as electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), and potentiodynamic anodic polarization curve (PAP) approaches. The prepared Schiff bases and their iron complexes exhibited protection capacity around 96.8% in the presence of 0.5 mmol/L. A good agreement among experimental techniques and corresponding density functional theory (DFT) results was found, which confirmed the purity of the studied compounds and suggested octahedral geometry around Fe(III) ions in both MABSFe and NABSFe complexes [39].

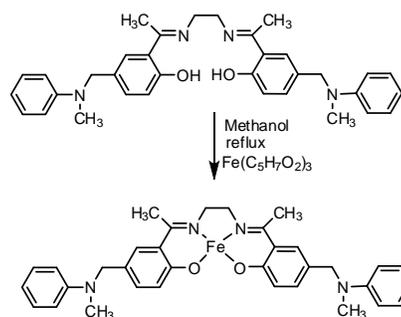
bis-2-((1E)-((Z)-2-(1,2-diphenylethylideneamino)phenylimino)methyl)phenol(L1) and bis-2-((1E)-((E)-2-(1-phenylethylideneamino)phenylimino)methyl)phenol (L2) Schiff base ligand and its Fe (III) complexes synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility and various spectral analysis. Using Gaussian 09 molecular modelling, bond lengths, bond angles and Mulliken charge were also evaluated. In addition to this study of HOMO and LUMO molecular orbital have been performed. The spectral data revealed that the Schiff base acts as a tetradentate ligand coordinating through phenolic oxygen and imino nitrogen and their Fe (III) complexes have octahedral geometry (scheme 7). Oxygen binding study suggested that complex 1 and 2 exhibits significant binding affinity with oxygen. The compounds were screened for antibacterial activity against gram negative bacteria *Escherichia coli* and compared with Amoxicillin. Complexes have exhibited significant antibacterial activity. The corrosion inhibition effect of ligands and complexes

on mild steel in acidic medium was studied for 24, 48 and 72 h using weight loss measurement [40]



Scheme 7: Structure of complex 1 and 2 in octahedral geometry[40].

A new tetradentate Fe (II) Schiff base complexes have been prepared by the interaction of iron (III) acetylacetonate with the ligand obtained from the reaction of ethylenediamine and 50-(N-methyl-N-phenylaminomethyl)-20-hydroxyacetophenone in methanol (Scheme 8). This complex has been characterized by means of different spectroscopic techniques and elemental analysis. In addition thermogravimetric (TG) and differential thermogravimetric analysis (DTG) have been utilized to investigate the thermal stability of these complexes. Cyclic voltammetry has been employed to examine the electrochemical behaviour of the synthesized complex in dimethyl sulfoxide (DMSO) at a glassy carbon electrode. This complex displayed one quasi-reversible single electron transfer peak near 0.255 Vvs. Finally, the antioxidant activity of the newly prepared complexes has been investigated using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging assay [41].



Scheme 8: Synthesis of Schiff base complex of Fe(II) [41]

Developed three reduced amino acid based Schiff base ligands using L-alanine, L-phenylalanine and L-tyrosine as precursors and then these derived ligands were coordinated with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to form the corresponding iron (III) complexes Ala-FeCl, Ph-FeCl and Tyr-FeCl, respectively. The ligands and

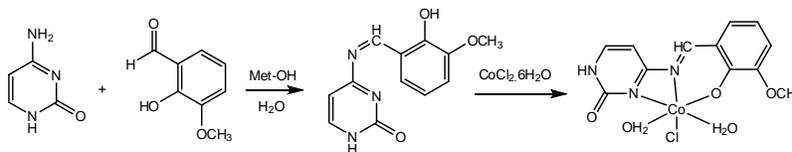
complexes have been characterized using spectral, elemental analysis, ICP-AES analysis. After the structural characterization, these complexes were applied for the oxidation of cyclohexane using hydrogen peroxide as the oxidant under mild conditions. The activity tests showed that the L-phenylalanine-derived reduced Schiff base iron (III) complex (Ph-FeCl) afforded the highest yield of cyclohexanol and cyclohexanone (total yield up to 23.2%) [42].

2.6. COBALT COMPLEXES

Novel dinuclear complex $[\text{Co}_2(\text{HL}^1)_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$ (**1**) obtained from the Schiff base ligands H_3L^1 (formed in situ). The bonding characteristics of the ligands, and distorted octahedral geometry around Co (II) centre, and its characterization data including X-ray studies. The moderate ferromagnetic exchange between the metal centres in molecules has been ascertained by variable temperature magnetic measurements. Theoretical calculations (DFT) also support these magnetic interactions. Complex **1** exhibits potential activity towards the oxidation of the 3,5-DTBC to 3,5-DTBQ and could be employed as model metalloenzyme (catechol oxidase). This activity

has been authenticated by DFT and is attributed to the higher charge contribution on metal in case of complex **1**. Moreover, the present complex **1** screened for HeLa and A549 cells lines have been proven to show better anticancer activity than cis-platin with $\text{IC}_{50} \approx 7.0$ at 48 h [43].

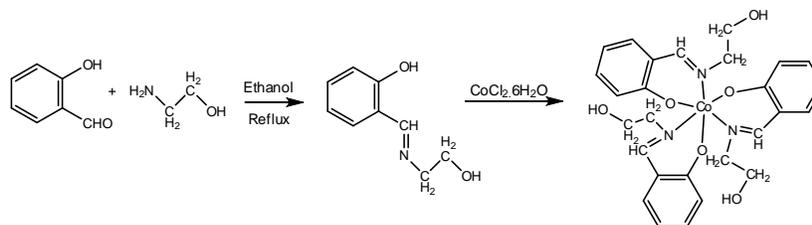
A new Schiff base ligand and its Cobalt (II) complexes $[\text{CoCl} \cdot \text{L}(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ was synthesized (scheme 9). Geometric structures of newly synthesized metal complexes were determined based on the results of spectral, CHN microanalysis, magnetic susceptibility and thermal analysis. All spectroscopic data supports the formation of an octahedral structure to the Co (II) complex. In vitro anticancer activities of the newly synthesized compound were evaluated on the human Caco-2 cancer cell line and biocompatibility characteristics were determined in the L-929 normal cell line by using the MTT assay. These synthesized complexes can be developed as chemotherapeutic agents for colon cancer treatment and can yield promising results in combined applications with EP. Further, studies are needed to expand the application of ECT with different complexes, drugs and vaccines [44].



Scheme 9: The structure of Schiff base complex [44]

Synthesis of four cobalt (II) complexes with the reduced Schiff base N-(2-hydroxybenzyl) phenylalanine (PhAlaSal) in alkaline aqueous solution by pH-metry. UV-Vis and ESI-MS studies confirmed the model of proposed species. Kinetic analysis indicated that the single and bi-ligand cobalt(II) complexes transitioned from octahedral to tetrahedral structures. This PhAlaSal alone appears a more effective antimicrobial than the analogous Schiff base derivative N-(2-hydroxybenzyl)alanine (AlaSal) probably due to the presence of the benzyl group. Due to their cytotoxicity, Schiff base complexes are not suitable for use against fungal and bacterial infections, but may effectively prevent cancer cell growth [45].

Schiff base ligand (HL)=2-(((2-hydroxyethyl)imino) methyl)phenol and its complex of cobalt (III) having the formula $[\text{CoL}_3](\text{CoSal})$ have been synthesized (Scheme 10) and characterized micro-analytically and spectroscopically. The nature of these interactions has been addressed with the aid of Hirshfeld surface analysis. This compound have been used as sensitizer in TiO_2 based dye sensitized solar cells (DSSCs) and the DSSC experiments revealed that Co-Sal offers high photovoltaic performance. The Co-Sal exhibited a J_{sc} of 9.75 mA cm^{-2} with a V_{oc} of -0.648 V , incident photon to current conversion efficiency (IPCE) of 57% and η of 3.84%. The better photovoltaic performance of Co-Sal could be attributed to better light absorption and dye loading [46].



Scheme 10: Synthetic routes for the sensitizer [46]

Two complexes of cobalt (II) were prepared with new Schiff base and amide ligand by using a common condensation reaction between benzidine with 4-hydroxy-3-methoxy benzaldehyde to prepare a first ligand while the other ligand was prepared between 4-chlorobenzoic acid and 1,4-diamino benzene. Both ligands have been added to Cobalt(II) yielded two complexes to identify all of these compounds in addition to measure the molar conductivity of complexes, at end all the evidences proved that formation of complexes with sp^3d^2 hybridization and octahedral geometry. After the incubation period at 37 °C for 24 h, the biological behavior of the binding produced with its antibacterial compounds against (*Staphylococcus aureus* and *Escherichia coli*) at different concentrations (10, 50 and 200) ppm was examined. The results showed that the performance of the prepared compounds was better in resisting and reducing the growth of bacteria tested at high concentrations [47].

2.7 NICKEL AND PALLADIUM COMPLEXES

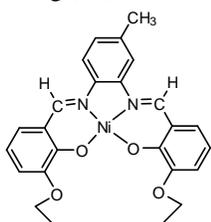
Two Ni(II) complexes $[Ni_2(L^1)_2(SCN)_2(dmf)_2]$ (**1**) and $[Ni(L^2)(SCN)]$ (**2**) [where $HL^1 = 2$ -ethoxy-6-[(2-phenylamino-ethylimino)-methyl]-phenol, $HL^2 = 2$ -[(2-pyrrolidin-1-ylethylimino)-methyl]-phenol, $dmf = N,N$ -dimethylformamide], have been synthesized and characterized by single crystal X-ray diffraction, IR and mass spectroscopic studies. In the centrosymmetric complex **1** two $Ni(L^1)$ fragments are connected via μ_2 -oxo bridges and the metals complete the octahedral coordination with one thiocyanate and one DMF solvent molecule. In complex **2** the Ni(II) ion is coordinated by the tridentate Schiff base and a thiocyanate in a square planar environment. Both the complexes form $1D$ supra-molecular network through C-H... π interactions and complex **2** also via H-bonding. The interaction of complexes with serum albumins was investigated using UV-Vis absorption and fluorescence spectroscopic techniques [48].

Schiff base ligand [3-(2-hydroxyphenylimino)-1,3-dihydroindol-2-one] was synthesized by the condensation reaction of isatin with 2-aminophenol. The Schiff base and its metal complex with Ni (II) was permeated by some physicochemical measurements. Based on analytical data allied with spectroscopic studies spilled that Ni (II) offered square planar geometry. The complex was undergone thermal analysis (TGA and DTG); complexes were found thermally stable up to 200°C. The ligand and the complex were played mild to sturdy antibacterial activity against numerous pathogenic bacteria species, although growth inhibitory activities of complex were enhanced comparatively than their respective ligands. Additionally, molecular docking analysis and quantum computational calculations based on the density functional theory (DFT) approach were used to study the molecular characteristics of the novel complexes and provide in-depth insights into their involvement in their ability to restrict bacterial growth[49].

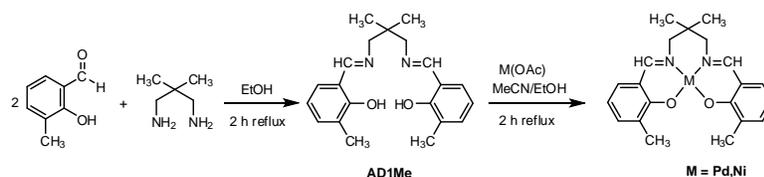
New Schiff base was synthesized from condensation of anthracene-10-carbaldehyde with 4-amino-3-mercapto-1,2,4-triazin-5(4H)-one. Resulted azomethine was characterized via elemental analysis and spectroscopic studies. Thereafter, novel Schiff base complex with Ni (II) metal was prepared and characterized by analytical, conductivity data and various spectroscopic techniques, magnetic moment as well as cyclic voltammetry. Low conductivity data of compound reveal their neutral and non-electrolytic character. Antimicrobial potentials of Schiff base and its metal chelate was evaluated against wide spectrum of bacterial cultures such as *P. aeruginosa*, *S. aureus*, *B. subtilis*, *E. coli* and fungi like *A. niger* and *A. flavus* [50].

A new nickel (II) complex (NiL^{Uns}) is synthesized by the reaction of unsymmetrical tetradentate salophen-based Schiff base (H_2L^{Uns}) with $Ni(CH_3COO)_2 \cdot 4H_2O$. The different techniques were used for structural elucidation of the H_2L^{Uns} and NiL^{Uns} complex. The crystal structure of the nickel complex was studied in

detail with the help of the X-ray diffraction techniques. It was revealed from the diffraction data that the ligand chelates the Ni (II) ion by using its ONNO set of donor sites and forms a square planar geometry (scheme 11). The different types of strong as well as weak intermolecular interactions were explored with the help of Hirshfeld surface investigation. The theoretical parameters of the optimized structures were calculated by the DFT employing the B3LYP/Def2-TZVP level of theory. Furthermore, the synthesized NiL^{Uns} complex was screened against four different bacterial strains to evaluate its biocidal potential, which revealed that metal chelate is slightly more active than the free ligand. The synthesized NiL^{Uns} complex is novel concerning its spectroscopic analysis, diffraction studies, theoretical investigation, and antibacterial screening [51].



Scheme 11: Square planar geometry of Ni(II) complex [51]



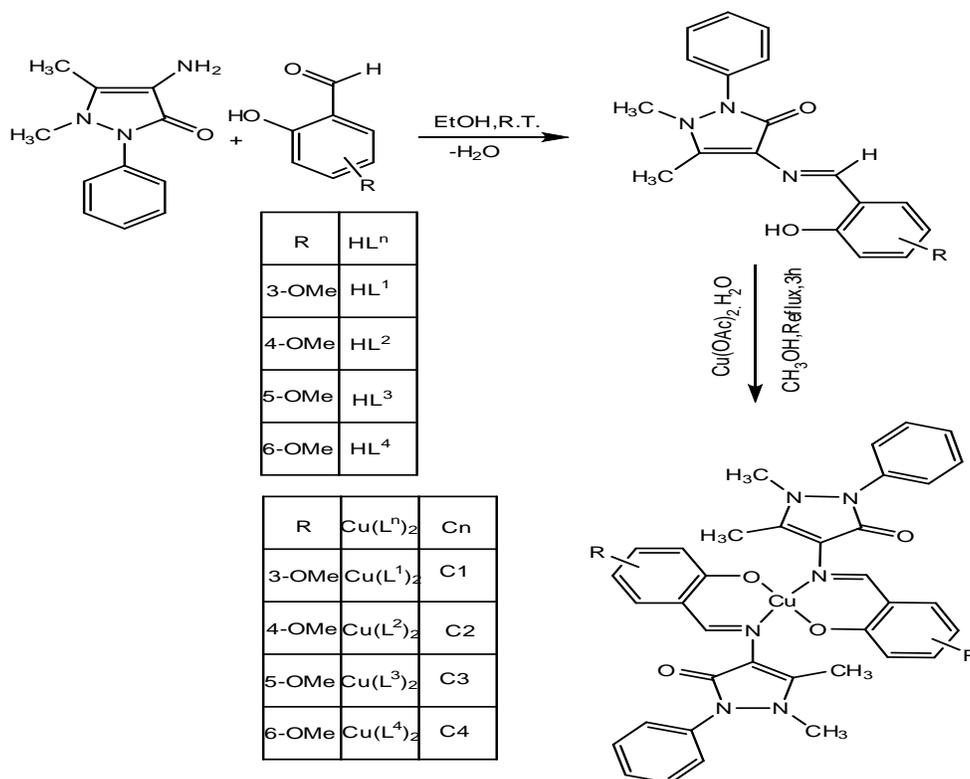
Scheme 12: Synthesis of H₂AD1Me, [Pd(AD1Me)] and [Ni(AD1Me)] [52]

2.8. COPPER COMPLEXES

A novel series of Cu(II) complexes, including [Cu(L¹)₂](1), [Cu(L²)₂] (2), [Cu(L³)₂] (3), [Cu(L⁴)₂] (4), with Schiff base ligands HLⁿ a mixture of 4-aminoantipyrine and the respective salicylaldehyde 3-methoxysalicylaldehyde=HL¹, 4-methoxysalicylaldehyde=HL², 5-methoxysalicylaldehyde=HL³ and 6-methoxysalicylaldehyde =HL⁴) have been synthesized (scheme 13) and characterized by elemental analyses and various spectroscopic techniques. The single crystal X-ray structure of complex 2, illustrates the steric effect imposed by the methyl group has a profound influence on the Cu (II) geometry,

The new tetradentate Schiff base and its Pd (II) and Ni (II) complexes have been prepared via condensation reaction (scheme 12). The formation of the Schiff base and its metal complexes was verified through the physicochemical and spectroscopic analysis. The shifting of significant peaks in spectra indicated that the complexation had taken place through the deprotonation of phenolic proton and shifting of azomethine nitrogen. Based on single-crystal X-ray diffraction, it can be concluded that the ligand coordinated to Pd (II) and Ni (II) ions through ONNO donor atoms and the [Pd (AD1Me)] and [Ni(AD1Me)] adopted distorted square planar geometry. The Hirshfeld surface analysis revealed H...H contacts in the crystal structure of [Pd(AD1Me)] and [Ni(AD1Me)], contributing to their stability. The closest interactions between Pd (II) complex units are H...H (63.4%), C...H (22.7%), and O...H (8.1%). Meanwhile, those for the Ni (II) complex are H...H (63.0%), C...H (23.2%), and O...H (7.4%). Although the [Pd(AD1Me)] showed a positive value of percent growth inhibition against all bacteria strains compared to the ligand and [Ni(AD1Me)], the compound is still considered a negative inhibitor likely owing to the absence of interactions between the molecule and the pathogen-specific protein in the bacteria [52]

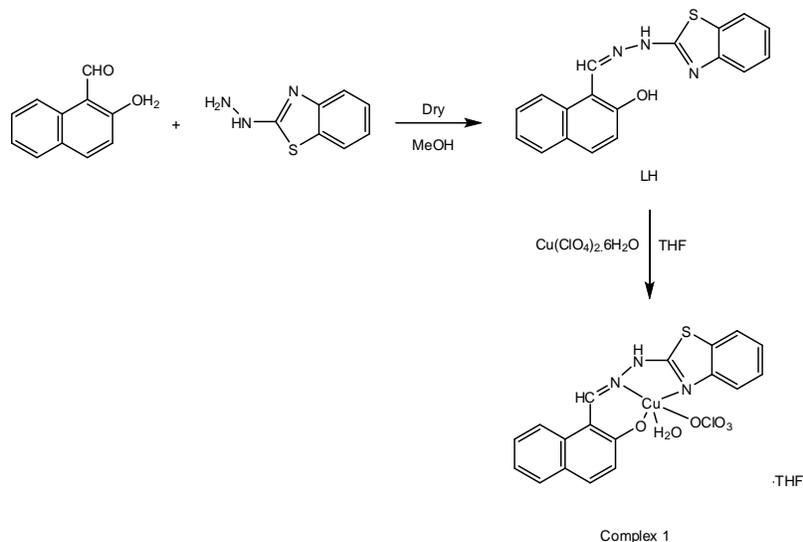
rearranging into a distorted tetrahedral geometry. Theoretical calculation of the synthesized compounds were carried out by DFT using B3LYP method with employing the def2-SVPD (for ligands) and def2-SV(P) (for complexes) basis sets. Calculated data are in good accordance with the experimental investigations. The *in vitro* biological activities of the synthesized ligand and their copper (II) complexes were evaluated against *Staphylococcus aureus* and *Escherichia coli*. The activity data showed that the metal complexes have a promising biological potential comparable with the parent Schiff base ligands against bacterial species [53].



Scheme 13: The synthesis pathways of the HL¹-HL⁴ ligands and Complex 1-Complex 4[53]

The ligand (2-[4-(2,1,3-benzothiadiazol-5-yl)imino]methyl-phenol) HL¹ containing the electron poor benzothiadiazole (BTD) unit, conveniently prepared by condensation of 4-amino-2,1,3-benzothiadiazole and salicylaldehyde has been structurally characterized by single crystal X-ray diffraction. DFT calculations revealed the existence of two close in energy conformers for HL¹ and HL², one corresponding to the experimental X-ray structure and the other to the chelating tridentate form. Reaction of HL¹ and HL² with copper (II) hexafluoroacetylacetonate (hfac), provided the neutral complexes [Cu(L¹)(hfac)] (**1**), [Cu(L²)₂] (**2**) which were structurally characterized with a focus on the coordination sphere of the metal centre and on the intermolecular interactions. Cryomagnetic measurements show for both copper(II) complexes a Curie-Weiss behaviour indicating the occurrence of very weak antiferromagnetic interactions due to the large separation between the metal ions in the crystal structures and the existence of intermolecular π - π stacking interactions [54].

A mononuclear copper(II) complex, [CuL(ClO₄)(H₂O)].THF (**1**) from a naphthaldehyde based Schiff base probing ligand 1-(benzothiazol-2-yl)hydrazonomethyl-naphthalen-2-ol (LH) has been prepared (scheme 14) and characterized by FT-IR, UV-Vis, EPR, CHN analysis, electrical conductivity and magnetic susceptibility measurements. The X-ray crystal structure of complex **1** has also been determined. In vitro enzymatic activity of LH and complex **1** on digestive enzymes like amylase, trypsin and lipase has been investigated. Molecular docking studies have also been performed to corroborate this bioactivity. LH displays quenching of fluorescence intensity only upon addition of a Cu²⁺ ion at 459 nm. Other metal ions under present study, however, offer no influence. The low limit of detection value 0.35 μ M indicates that LH offers high selectivity towards Cu²⁺. Calculations at the level of DFT were also undertaken to have an insight into the electronic environment of both [CuL(ClO₄)(H₂O)].THF (**1**) and LH [55].



Scheme 14: Synthetic route of LH and complex 1 [55]

Cu (II) binary complexes of the type $[Cu(L_n)_2]$, where $n=1-3$, $HL_1=2-((E)-(3,5\text{-dimethylisoxazol-4-ylimino})\text{methyl})-6\text{-tert-butylphenol}$ (C1) $HL_2=2-((E)-(3,5\text{-dimethylisoxazol-4-ylimino})\text{methyl})-4\text{-bromo-6-methoxyphenol}$ (C2) $HL_3=2-((E)-(3,5\text{-dimethylisoxazol-4-ylimino})\text{methyl})-5\text{-methylphenol}$ (C3) have been synthesized and characterized by analytical, structural, and spectral methods. The antioxidant studies of novel Cu(II) complexes revealed, significant activity against DPPH radical. The synthesized compounds were monitored for antimicrobial activities and the results of these studies indicated that the complexes exhibit a good antimicrobial efficiency compared to ligands. Spectral evidence showed the intercalative mode of DNA binding with the complexes. These techniques were found to be an intercalative binding mode of synthesized complexes with CT-DNA. The order of binding affinity is found to be $C1 > C3 > C2$. Agarose gel electrophoresis results revealed that all Cu (II) complexes induced double strand breaks of pBR 322 plasmid DNA in the presence of H_2O_2 and UV light [56].

2.9: ZINC METAL COMPLEXES

Binuclear zinc (II) Schiff base complexes were synthesized through the reaction of ONNO tetradentate Schiff base ligands derived from the condensation of 2,2-dimethyl-1,3-propanediamine and 5-chlorosalicylaldehyde or 5-bromosalicylaldehyde with zinc acetylacetonate salt. The structures of synthesized products were explored spectroscopically

and elemental analysis. Structural analysis of the complexes revealed that the compound is a centrosymmetric dimer in which the five coordinated Zn (II) atoms are linked to the opposite metal centre by making μ -phenoxo bridges through one of the phenolic oxygen atoms of Schiff base ligands. The nature and types of non-covalent interactions present among the sample molecules were also investigated by using the quantum theory of atoms in molecules and non-covalent interactions calculations. The theoretical calculations, performed by density functional theory using the B3LYP/def2-TZVP level of theory, direct that the intended outcomes are in compliance with the actual consequences. Furthermore, from antimicrobial screenings it was revealed that the zinc complexes are more active as compared to the ligands [57].

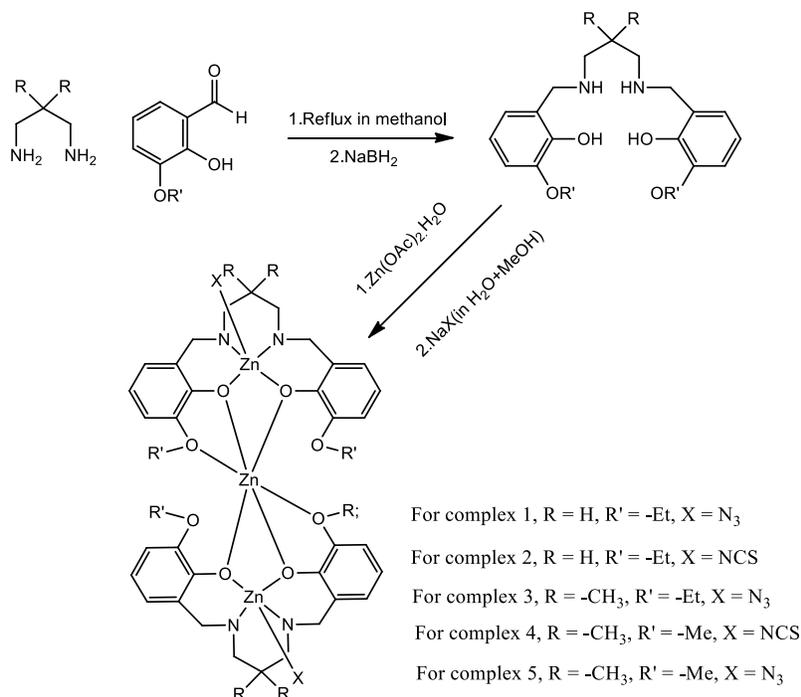
Newly synthesized mononuclear zinc (II) complex containing an azo Schiff base ligand (L), prepared by condensation of 2-hydroxy-5-(2-oxo-2-phenylethyl) benzaldehyde and propylamine, were obtained and then characterized using spectroscopy, and X-ray diffraction. Ligand L behaves as a bidentate chelate by coordinating through deprotonated phenolic oxygen and azomethine nitrogen. The zinc complex crystallizes in orthorhombic systems. In this complex the Zn (II) ion is in a distorted tetrahedral environment. The photochemical behaviors of ligand L, and $[Zn(L)_2]$ were investigated. The azo group in L underwent reversible trans-cis isomerization under UV and visible irradiation. This process was inhibited for the complexes. In addition, ligand L and its zinc

complex was assessed for their in vitro antibacterial activities against four pathogenic strains [58].

A facile method for synthesizing trinuclear zinc (II) complexes

$[\{(N_3)Zn(L^1)\}_2Zn]$ (**1**), $[\{(SCN)Zn(L^1)\}_2Zn]$ (**2**), $[\{(SCN)Zn(L^2)\}_2Zn]$ (**3**), $[\{(N_3)Zn(L^2)\}_2Zn]$ (**4**), and $[\{(N_3)Zn(L^3)\}_2Zn]CH_2Cl_2$ (**5**) with $H_2L^1=2,20-[(1,3-propanediyl)bis(iminomethylene)]bis[6-methoxyphenol]$, $H_2L^2=2,20-[(2,2dimethyl1,3proan$

ediyl)bis(iminomethylene)]-bis[6-methoxyphenol] ligands and $H_2L^3=2,20-[(2,2-dimethyl-1,3-propanediyl)bis(iminomethylene)]bis[6-ethoxyphenol]$, were synthesized (scheme 16) and characterized by elemental and spectral analyses. X-ray crystallographic analyses have confirmed their structures. All complexes may be used as sensors for the detection of nitroaromatics in DMF via turn-off fluorescence response [59].



Scheme 16 : Synthesis of ligand and its Zn(II) complexes[59]

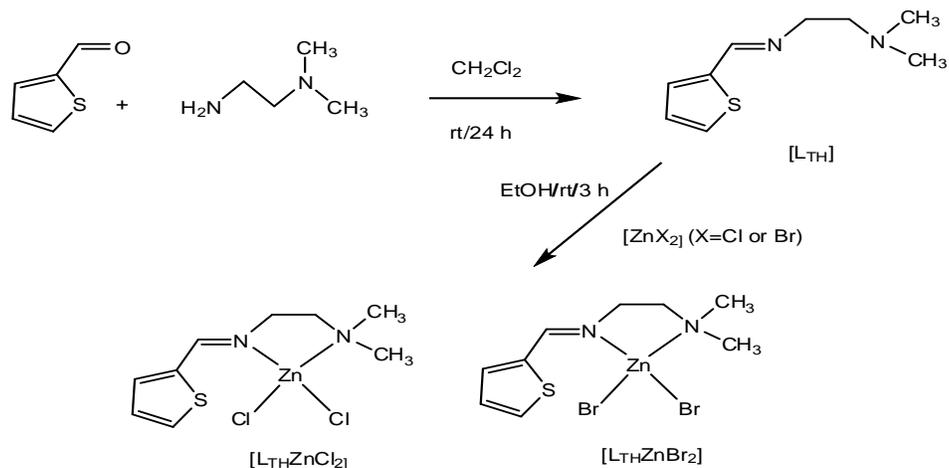
Zn (II) complexes of Schiff bases have potential applications in biomedical sciences as imaging agents, cancer therapeutics and diagnostics. Thus, it is important to understand their interaction with carrier proteins, like serum albumins. It focuses on the binding interactions between Human serum albumin (HSA) and Zn salampy, making use of fluorescence spectroscopic techniques at ensemble as well as at single molecular level. An idea about the binding constant is obtained from the quenching of the single Trp (Tryptophan) residue of HSA by Zn salampy. Fluorescence correlation spectroscopy (FCS) has also been used to monitor the protein-ligand binding. The location of Zn salampy in its complex with HSA is determined by competitive binding experiments and molecular docking calculations. The binding constant obtained from the Zn salampy-HSA

interaction falls in the ideal range for biological applications and the location is found to be in the proximity of Sudlow's site I. The esterase activity of HSA is retained in the presence of the Zn salampy. Hence, it is concluded that this Zn salampy may be a potential probe and biomarker in biomedical applications [60].

Novel Zn (II) complex namely $[L_{TH}ZnX_2]$ (X = Cl, Br) with the iminomethylthiophene-derived ligand (L_{TH}), were synthesized (scheme 15) and characterized. X-ray crystallography revealed diverse coordination geometries of the resultant Zn (II) complex. DFT calculations showed that the rotation of the thiophene moiety of the ligand (L_{TH}) can be observed or Zn (II) center, confirmed by VT-NMR. The preliminary polymerization studies carried out by isopropoxide derivatives of the studied complexes resulted in high

activities with moderate to high hetero tacticities and low molecular weights of PLA. The complexes

geometry might help steer the catalytic performance and stereoselectivity of these complexes [61].



Scheme 15: Synthesis of ligand and complex [L_{TH}ZnX₂][61]

CONCLUSION

In this review article, we have highlighted the synthesis, structural diversities, and coordination modes exhibited by the metal complexes with Schiff bases having different donor sites. Taking into consideration all the aforementioned results, the perspectives concerning future projects relevant to the study of metal Schiff base complexes should comprise the factors that provide the new compounds with structural, spectroscopic, and biological properties attractive to synthetic chemists. More specifically, in this study, the spectrums of metal ions used to synthesize the metal Schiff base complexes have been broadened.

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