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BIOLOGICAL APPLICATIONS OF TRANSITION METAL COMPLEXES OF NOVEL SCHIFF BASE LIGANDS

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ABSTRACT

The universal importance or significance of Schiff Base ligand/metal chemistry shows diverse type of biological activities like, antifungal, antibacterial, antiviral, antidiabetics, anticancer, antiprolifertive, antidepressant, antitumor, antioxidant activities and also shows DNA binding ability. This book chapter relate with the review of these activities and focuses on the scope of these derivatives of Schiff base ligand along with its derivatives.

KEYWORDS: Novel Schiff Base Ligand, Metal Complexes, Azomethane, DNA, Biological activities.

INTRODUCTION

The reaction of Schiff base ligand was discovered by noble prize winner, who was a German chemist Hugo Schiff on 155 years ago, and research work on Schiff base is constantly carried by the scientists and research students due of its broad range of important applications in numerous fields**.** Schiff bases are synthesized by condensation reaction of an aldehyde or ketone with primary amine under virtual conditions. Structurally a Schiff base outlined as a nitrogen (N) correlative of an carbonyl group of aldehyde/ketone in which the carbonyl group (CO) has being replaced by an azomethine group(-CH=N-)or imine group(>C=N-).[1]

Novel Schiff base ligands are able to cast very steady complexes with various transition metal atoms stabilize in different oxidation states.[2] Synthesis of transition metal complexes and signalisation of transition metal complexes from the novel Schiff base ligands is interesting topic of the research field because of their importance in the industrial field, medicinal chemistry, pharmaceuticals field, analytical use, nanotechnology; it also shows pharmacological as well as biological activities.[3] They have shown anti-inflammatory, anticancer and antioxidant activities,[4] Antifertility, analgesic, herbicidal application and antimicrobial activities.[5,6]

The applications of Schiff bases are determination, identification and detection of aldehyde or ketone, purification of amino compounds, purification of carbonyl compounds, protection of amino and carbonyl groups during the reactions. Schiff bases are usually bidentate or tridentate ligands able to form very stable complexes with different transition metals atom.[7] Novel Schiff base ligands contain nitrogen or oxygen as donor atoms are organic compounds able to binding with various metal atom are interested in medical and non-medical properties.[8,9] The extensive importance in broad range of numerous areas the transition metal complexes of Schiff base ligands in biochemistry, inorganic chemistry and matallo-organic chemistry.[10,11] They exhibit different magnetic properties, optical and chemical properties by reorganizing with various Schiff base ligands.[12,13] Chelated Schiff base ligand with nitrogen and oxygen is essential in the main group i. e. s and p block elements (non-transition elements) and transition metal because of them stability in diverse oxidative and reductive conditions.[14] Schiff base is popular, attractive and interesting ligands in coordination chemistry reason is the nitrogen atom of azomethine group present lone pair of electrons in the sp2 hybridized orbital so Nitrogen atom of azomethine group show strong chelating ability on Schiff bases when specially incorporating with one or more donor atom (generally N, O, S or more etc).[15] Transition metal complexes of Schiff base ligands with donor atom Nitrogen, Oxygen and Sulphur is highly active against pathogens and the activity of pathogens causes diseases this activity reduced by nitrogen atom. The presence of nitrogen atom in azomethine group (-CH=N-) or imine group (>C=N-) are active against microorganisms. Nitrogen atom is the

one of the most important element in biological and chemical processes.[16]

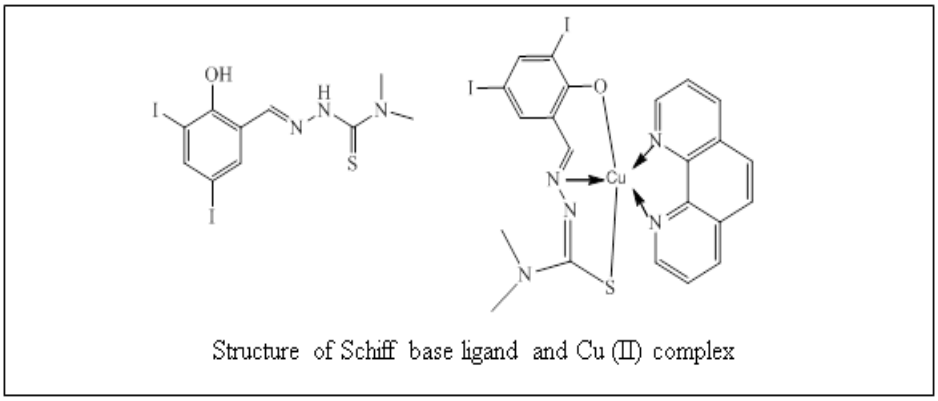
Number of application of transition metal complexes of Schiff base ligands is applied in agrochemical, analytical chemistry, dye and food industry, polymers, catalysis, antiradical activities, cytotoxic activities, antibacterial activities, antifungal activities, antitumor activities and also enzymatic agents.[17,18] The biochemist attracted towards research work on Schiff bases ligands because design medicinal compounds and their medicinally importance. The important application of transition metal complexes of novel Schiff base is in medicinal chemistry is formation of non toxic drugs molecules. Now the metal based drugs molecule has become active research area for scientist and research students.[19]

The transition metals complexes of platinum (Pt), silver (Ag) and gold (Au) have approaches to antitumor effects as well as antiprolifertive activities.

Considering the above facts in view, need to focus more and more for the diverse application of transition metal complexes of Schiff base ligands and their biological activities.

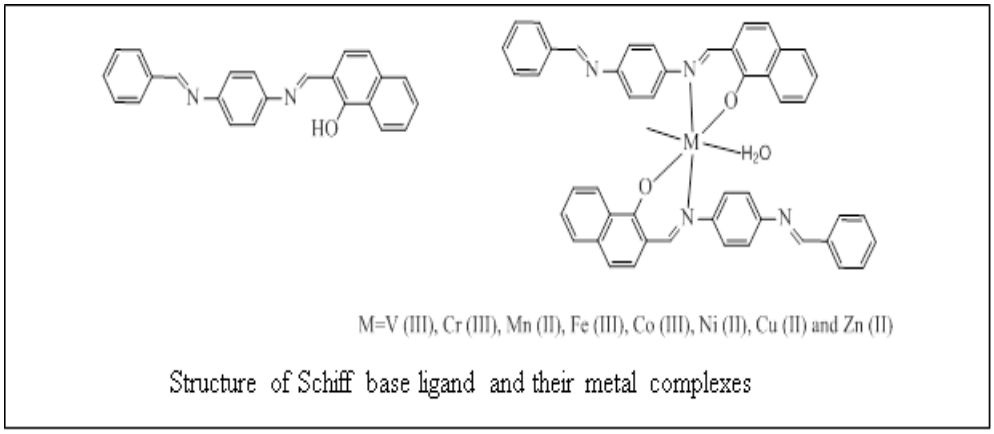
Biological significance of transition metal complexes of Schiff base ligand

The metal complex of Cu (II) with Schiff base ligand (*Z*)- *N* '-((*E*)-2-hydroxy-3, 5-diiodobenzylidene) - *N*, *N*-dimethylcarbamohydrazonothioic acid acquired from the liquefaction reaction of 3, 5- diiodosalicylaldehyde and 4, 4-dimethyl-3- thiosemicarbazide[20]. The Cu (II) metal complex show square pyramidal geometry by XRD analysis. The ligand and Cu (II) complex reveal productive response to brain blood barrier and human intestinal absorption for drug discovery by swissadme analysis. They attract with main protease of COVID-19 spike protein fight against novel corona virus.



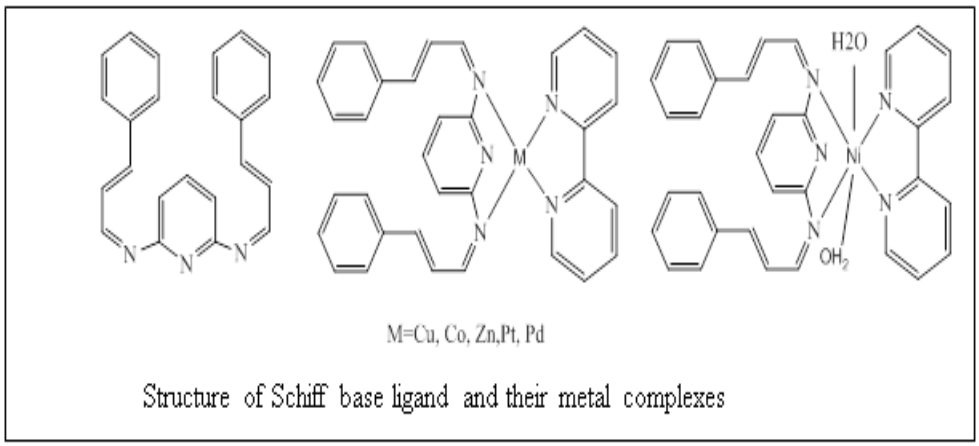
Structure of Schiff base ligand and Cu (II) complex

The metal complexes of V (III), Cr (III), Mn (II), Fe (III), Co (III), Ni (II), Cu (II) and Zn (II) with Schiff base ligand 2-((E)-((4-(((E)-benzylidene)amino)phenyl) imino) methyl)-naphthalene-1-ol derived from liquefaction reaction of p-phenylenediamine with 2-hydroxy-1-naphthaldehyde and benzaldehyde.[21] The Schiff base ligand and metal complexes analyzed by elemental analysis, ^{1}H NMR, FT- IR, and UV spectroscopy, TGA, DTA, XRD and TEM.The Co (II) and Zn (II) complexes shows antibacterial activity against Salmonella enterica serovar typhi, V (III) complex show highest antifungal activity against C. albicans fungi. The metal complexes exhibit higher antitumor activity against PC-3, SKOV3, and HeLa tumour cell lines than well known anti cancer agent's cis platin, etoposide and estramustine.



Structure of Schiff base ligand and their metal complexes

The heteroleptic(the complexes in which metal ion is surrounded by more than one ligand) metal complexes of Co (II), Cu (II), Ni (II), Pd (II), Pt (II) and Zn (II) with Schiff base ligand [(N2E, N6E)–N2, N6-bis((E)-3-phenylallylidene)pyridine-2,6-diamine] (L1)derived from Pyridine-2,6-diamino and trans-cinnamaldehyde under solvent free condition.[22] Another Schiff base ligand 2, 2-bipyridine (L2). The metal complexes characterized by elemental analysis, magnetic susceptibility, molar conductivity, FTIR, ^{1}H NMR, UV spectroscopy, mass spectrometry, and TGA. The metal complexes of Co (II), Cu (II), Pt (II), Pd (II) and Ni (II), Zn (II) adopted square planar and tetrahedral, octahedral geometry respectively. The Zn (II) and Pd (II) metal complexes show antimicrobial activity against Gram-positive bacteria S. Aureus and Gram-negative bacteria E. coli.



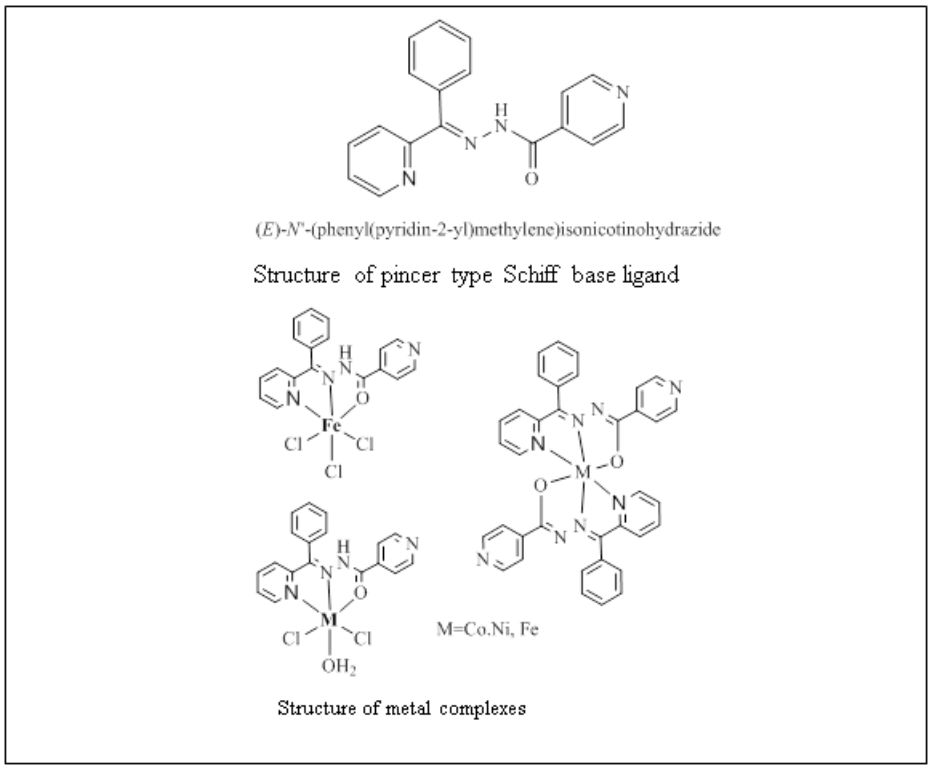
Structure of Schiff base ligand and their metal complexes

The metal complexes of Co (II), Ni (II), Cu (II) and Zn (II) with four heterocyclic Schiff base ligand synthesized.[23] such as,

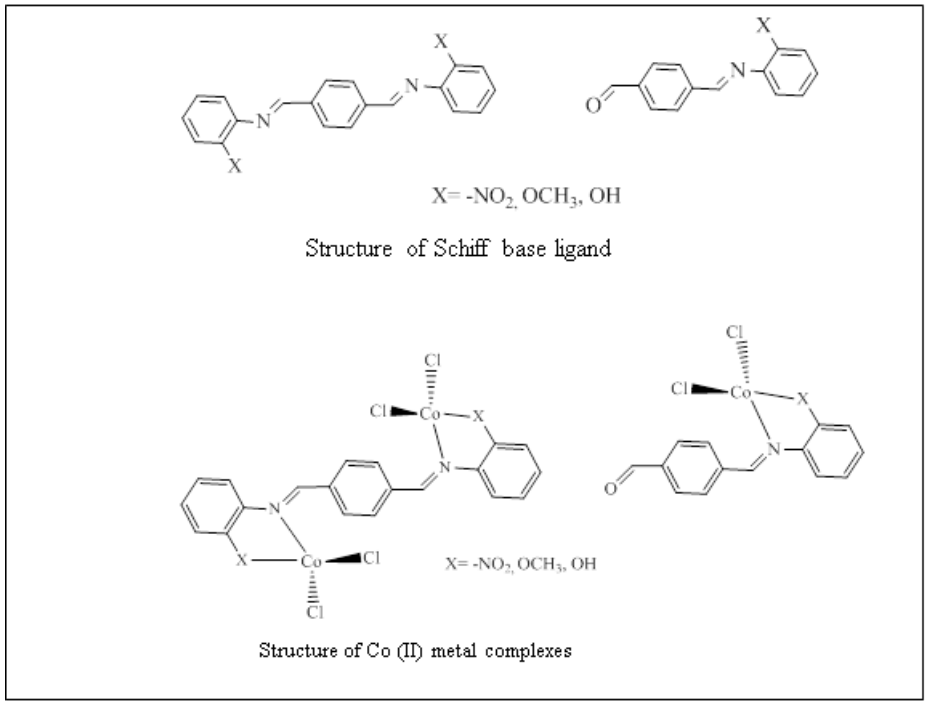
- The heterocyclic Schiff base ligand 2-ethoxy-6-(((3-(4-hydroxyphenyl)-5-mercapto-4H-1, 2, 4-triazol-4-yl) imino) methyl) phenol(L1) derived from the condensation reaction of4-(4-amino-5-mercapto-4*H*-1, 2, 4-triazol-3-yl) phenol and 3-ethoxysalicylaldehyde.
- The heterocyclic Schiff base ligand 4-bromo-2-(((3-(4-hydroxyphenyl)-5-mercapto-4H-1, 2, 4-triazol-4-yl) imino) methyl) phenol (L2) derived from the condensation reaction of4-(4-amino-5-mercapto-4*H*-1, 2, 4-triazol-3-yl) phenol and 5-bromosalicylaldehyde.
- The heterocyclic Schiff base ligand 2-(((3-(4-hydroxyphenyl)-5-mercapto-4H-1, 2, 4-triazol-4-yl) imino) methyl)-4-nitrophenol (L3) derived from the condensation reaction of 4-(4-amino-5-mercapto-4*H*-1, 2, 4-triazol-3-yl) phenol and 5-nitrosalicylaldehyde.
- The heterocyclic Schiff base ligand 2, 4-dibromo-6-(((3-(4-Hydroxyphenyl)-5-mercapto-4H-1, 2, 4-triazol-4-yl) imino) methyl) phenol (L4) derived from the condensation reaction of 4-(4-amino-5-mercapto-4*H*-1, 2, 4-triazol-3-yl) phenol and 3, 5-dibromosalicylaldehyde.

The heterocyclic Schiff base ligand along with their metal complexes characterized elemental analysis and spectral analysis such as FT-IR, ESR,^{1}H NMR, ^{13}C NMR, HRMS, XRD, TGA and SEM. The Schiff base ligand (L3) and its Co (II), Ni (II), Cu (II) and Zn (II) exhibit antifungal and antibacterial activity against Aspergillus Niger, Candida albicans and two Gram-positive bacteria B subtilis, S aureus, two Gram-negative bacteria P aeruginosa, E coli respectively. Metal complexes Zn(L2)(H2O)(CH3COO), Cu(L4)(H2O)(CH3COO) and Zn(L4)(H2O)(CH3COO)show anticancer activity against human colon cancer (HCT-116), prostatecancer (DU145), lung cancer (A549) cell line by MTT assay.

The metal complexes of Co (II), Fe (III) and Ni (II) with novel NNO pincer type Schiff base ligand (E)-N'-(phenyl(pyridin-2-yl)methylene)isonicotinohydrazide derived from the liquefaction reaction of 2-benzoyl pyridine and isonicotinylhydrazide.(Pincer ligand is chelating agent that binds tightly to three adjacent coplanar sites in a meridonial configuration)[24] The metal complexes signalised by elemental analysis and spectral data such as FT-IR, UV spectroscopy, ^{1}H NMR ^{13}C NMR and magnetic suscebility, molar conductance. The metal complex [Ni (PPMINH) $_{2}$] exhibit high anticorrosion activity by weight loss measurement. The metal complex [Fe (PPMINH) 2] shows highest antibacterial activity against gram-positive bacteria B. subtilis and gram-negative bacteria E. coli.

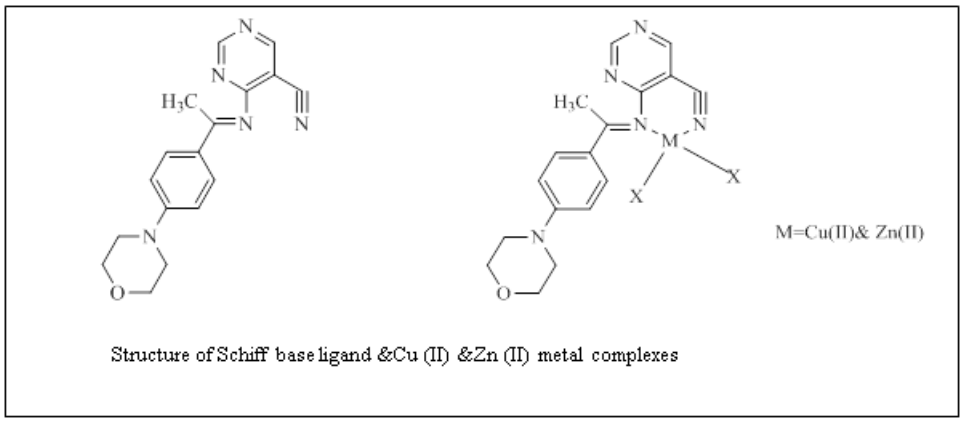


The metal complex of Co (II) with Schiff base ligand acquired from liquefaction reaction of terephthalaldehyde and ortho-aniline derivatives by using N-propyl-benzoguanamine-SO3H magnetic nanoparticles as a catalyst[25]. The biological active ligands and cobalt (II) complexes were analysed by spectroscopic techniques i. e. ^{1}H-NMR, FT-IR, UV-Visible, mass spectroscopy and molar conductance. The Schiff base ligands and metal complexes were screened for antibacterial activity using disc diffusion and broth dilution methods against E.*coli*, S. *marcescens*, P. *aeruginosa* (gram negative bacteria), B.*Subtilis* and S.*aureus* (gram positive bacteria). The report shows that the metal complexes have much higher antibacterial activity compare to the ligands.



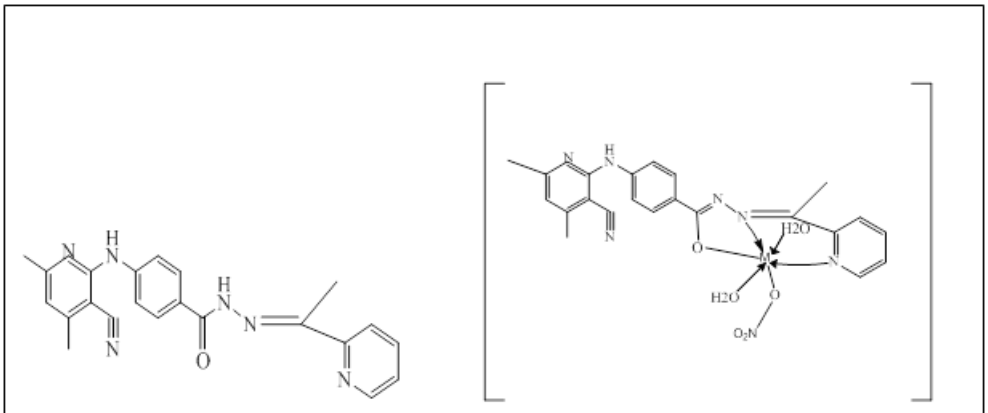
The metal complexes of Zn (II) & Cu (II) with Schiff base ligand 4-(1-(4-morpholinophenyl) ethylideneamino) pyrimidine-5-carbonitrile derived from 4-morpholinoacetophenone and 4-amino-5

pyrimidinecarbonitrile[26].The synthesized Schiff base ligand and metal complexes characterized by multiple analytical and spectroscopic techniques. The structure of Cu (II) and Zn (II) complexes may be follow square planar geometry according to spectral data. The LMCT mechanism between Schiff base ligand and metal complex was theoretically confirmed by DFT calculation. The Schiff base ligands and metal complexes were screened for antimicrobial activities against E. *coli* bacteria and C. *albicans* fungi. The binding of ligand and metal complexes with CT-DNA were confirmed by electronic absorption, competitive binding, viscometric and cyclic voltammetric studies. The anticancer activities reveals that complexes have commonplace cytotoxicity opposed to cancer cell lines and low toxicity on normal cellline than Schiff baseligands.



Structure of Schiff base ligand &Cu (II) &Zn (II) metal complexes

The metal complexes of Ni (II), Co (II) and Cu (II) with novel Schiff base ligands (E)-4-((3-cyano-4,6-dimethylpyridin-2-yl)amino)-N'-(1-(pyridin-2-yl) ethylidene) benzohydrazide acquired by the liquefation of Acetyl pyridine and 4-(3-cyano-4, 6-dimethylpyridin-2-ylamino) benzohydrazide.[27] The novel Schiff base ligand and metal complexes characterized by ^{1}H NMR, ^{13}C NMR, XRD analysis, UV spectroscopy, magnetic measures and elemental analysis. All synthesized metal complexes adopted octahedral geometry by magnetic and electronic spectra. The calf thymus DNA binding activity of the ligand and Metal complexes of Co (II), Ni (II), and Cu (II) studied by viscosity and absorption spectra. The Cu (II) complex exhibit cytotoxic activity against MCF-7 and HePG-2 cell lines. The DFT approach shows the molecular modeling such as the bond lengths, the bond angles, and quantum Chemical factor. The compounds useful in medicinal application. Molecular docking used to show the activity of synthesized Schiff base ligand against COVID-19 and anticancer activity. All the synthesized metal complexes show antioxidant activity by using DPPH free radical scavenging assay. And also shows antibacterial activity against gram+ve bacteria and gram-ve bacteria.

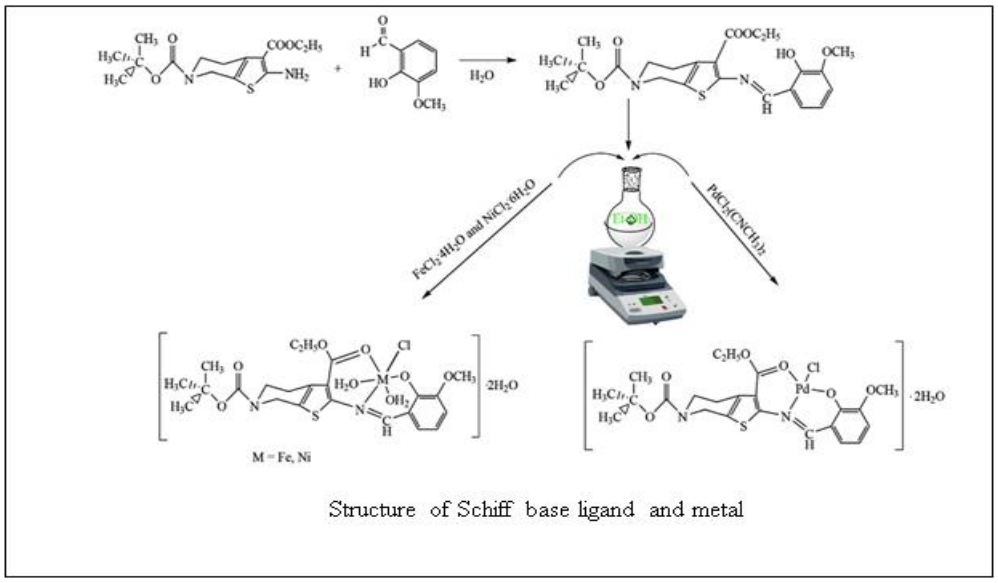


Structure of novel schiff base ligand & metal complexes

[M=Co (II), Ni (II), and Cu (II)]

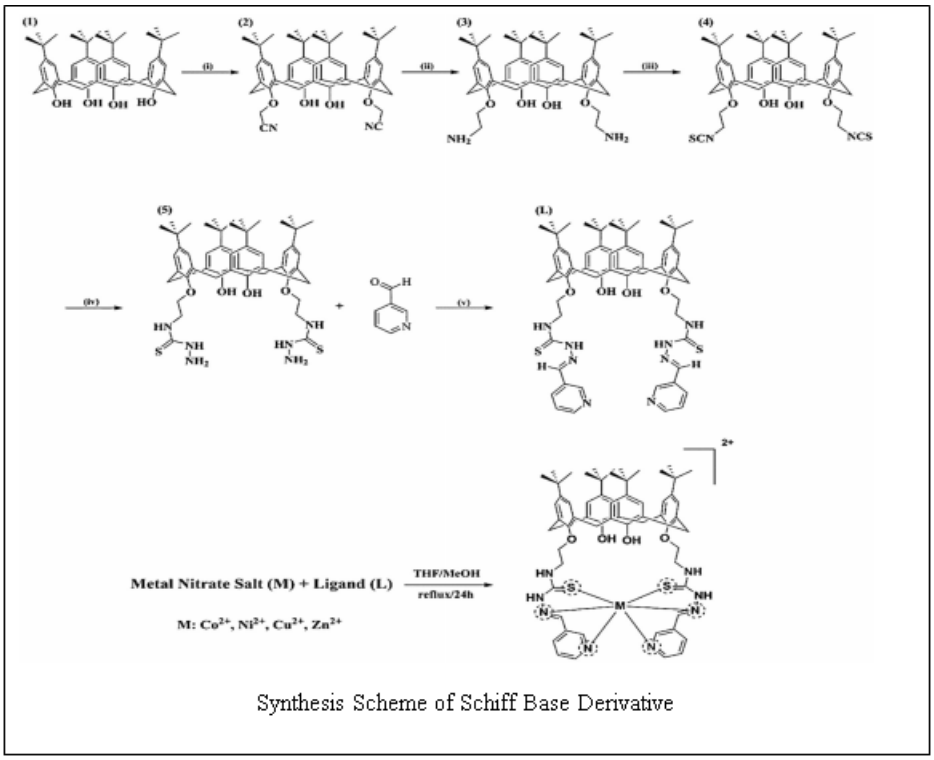
The metal complexes of Fe (II), Ni (II), and Pd (II) with novel Schiff base ligand ((E)-6-tert-butyl 3-ethyl 2-(2-hydroxy-3-methoxybenzylideneamino)-4,5-dihydrothieno[2,3-c]pyridine-3,6(7H)-dicarboxylate)[28]

The novel Schiff base ligands and metal complexes were characterized by elemental analysis and spectroscopic techniques i.e. magnetic moment, TGA, IR, ^{1}H NMR, ^{13}C NMR, mass spectroscopy, UV spectra. The metal complex of Fe (II), Ni (II) and Pd (II) shows octahedral geometry and a square planar geometry subsequently. The Schiff base ligands and metal complexes of Fe (II)/Pd (II) were screened for antioxidant activities against a-tocopherol, ascorbic acid, BHT and BHA by using FRAP and DPPH antioxidant method. Enzyme inhibitions of the metal complexes of Ni (II) and Pd (II) were reported against glutathione S-transferase enzymes (GST), butyrylcholinesterase enzymes (BChE) and acetylcholinesterase enzymes (AChE) shows best inhibition value is (2.63 ± 0.04 lM) and (10.17 ± 1.88 lM) respectively.



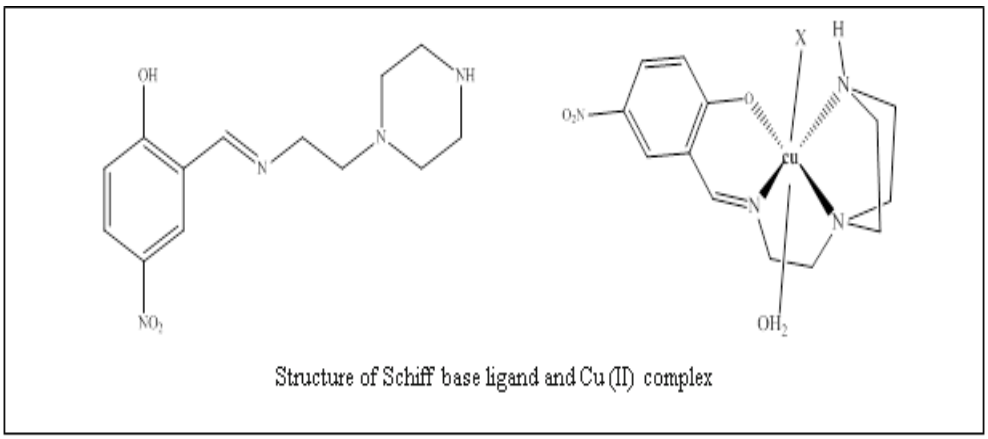
Structure of Schiff base ligand and metal

The metal complexes of Co (II), Ni (II), Cu (II), and Zn (II) with multidentate Schiff-base ligand calix [4]arene-based thiosemicarbazone[29] The ligand and metal complexes characterized by FT-IR,^{1}H-NMR, ESI-Mass spectroscopy, SEM, EDI, elemental analysis. The ligand and metal complex shows antibacterial activity against gram +ve and gram –ve bacteria.All metal complexesshowed antiproliferativeactivity against MG-63 and Saos-2 cells and anticancer activity against MG-63 cell line by MTT assay. Zn (II) and Ni (II) complexes have high blood compatibility by hemolysis assay.



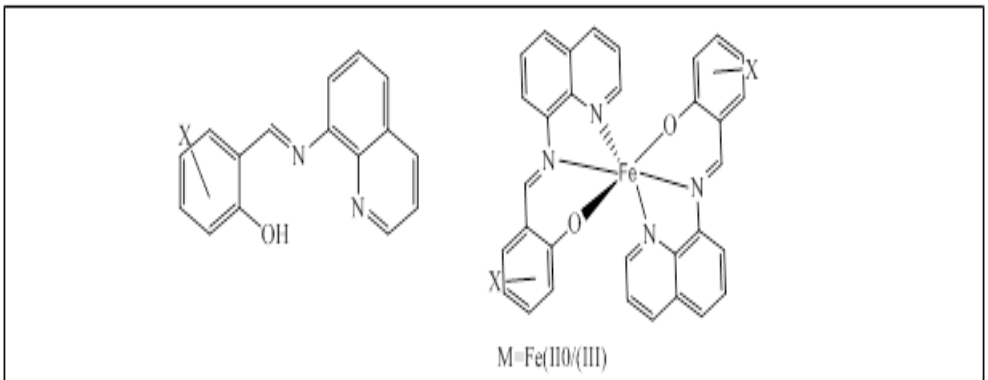
Synthesis Scheme of Schiff Base Derivative

The metal complex of Cu (II) with tetra dentate Schiff base ligand (E)-4-nitro-2-(((2-(piperazin-1-yl) ethyl) imino) methyl) phenol derived from the condensation reaction with 2-hydroxy-5-Nitrobenzaldehyde and 2-(1-piperazinyl) ethylamine[30] The tetra dentate Schiff base ligand and their metal complex signalised by spectroscopic techniques FT-IR. UV spectroscopy as well as thermal and florescence analysis. By using green oxidant as hydrogen peroxide (H_2O_2) under mild oxidation catalytic environment. The oxidation of benzyl alcohol to benzaldehyde usinga diverse catalytic conditions including supported metal catalyst such as new Cu (II) complex used as a catalyst in this reaction.



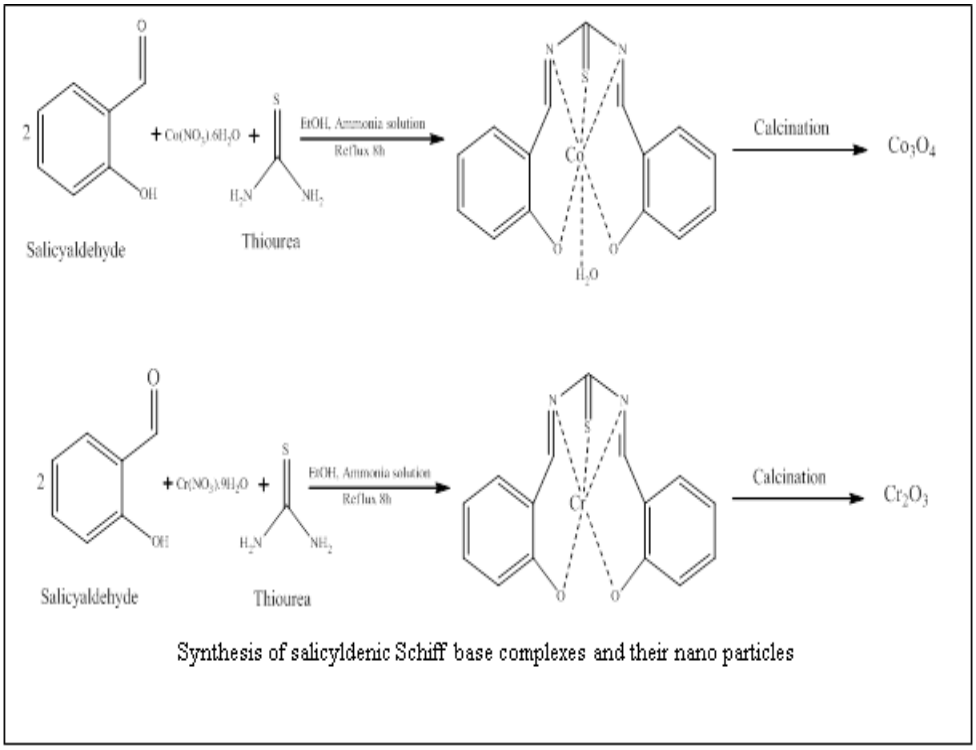
Structure of Schiff base ligand and Cu (II) complex

The metal complexes of Fe (II) and Fe (III) with Schiff base ligand halogenated *N*-(8-quinolyl) salicylaldimine.[31] The complexes characterized by spectroscopic technique FT-IR, UVspectroscopy, mass spectroscopy, TGA, fluorescence spectroscopy. By intercalative mode the metal complexes show good DNA binding activity.The metal complex [Fe (qsal-Cl2)2] Cl exhibithighly antiproliferative activity (better than two popular anticancer agents such as Cisplatin and Etoposide) againstA549 human lung adenocarcinoma cell line.



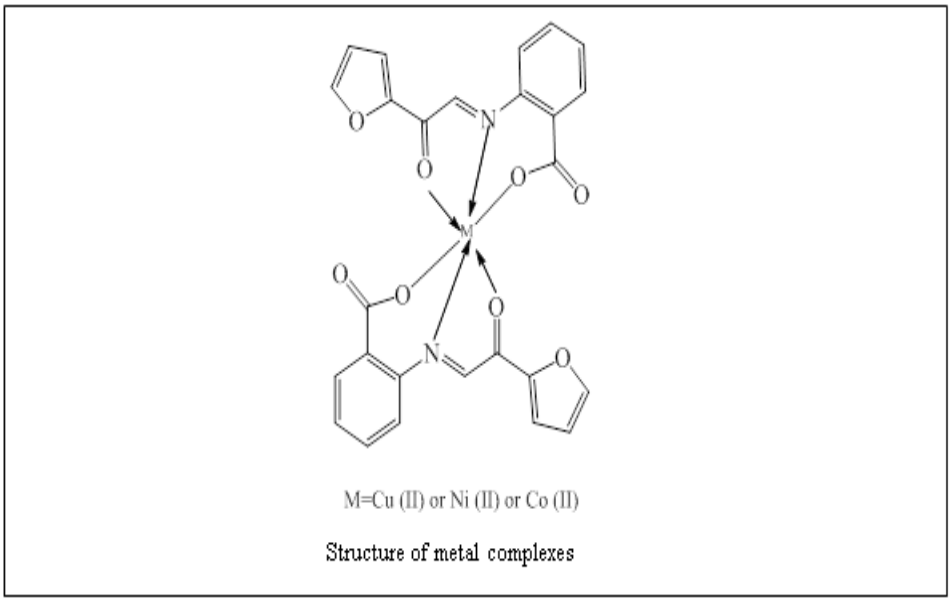
Structure of Schiff base ligand and Fe (II)/(III) metal complexes

The metal complexes of Co (II) and Cr (III) with Schiff base ligand derived from the condensation reaction of salicylaldehyde and thiourea.[32] The metal complexes characterized by elemental analysis, FT-IR, UV spectroscopy, XRD, conductivity measurement and magnetic moment. The metal complexes of Co (II) and Cr (III) adopted octahedral and square-pyramidal geometry respectively. These Schiff base metal complexes were used for synthesis of nanoparticles such as Co_3O_4 and Cr_2O_3 by using solid thermal decomposition method. This method is environment friendly, simple and useful. These metal oxide characterized by XRD, FT-IR and SEM. They show antibacterial activity against E. coli, S. aureusand Bacillus subtilis. The Co (II) complex show catalytic activity for oxidation of toluene by using hydrogen peroxide as a oxidant but Cr (II) complex did not show any activity.



Synthesis of salicylderic Schiff base complexes and their nano particles

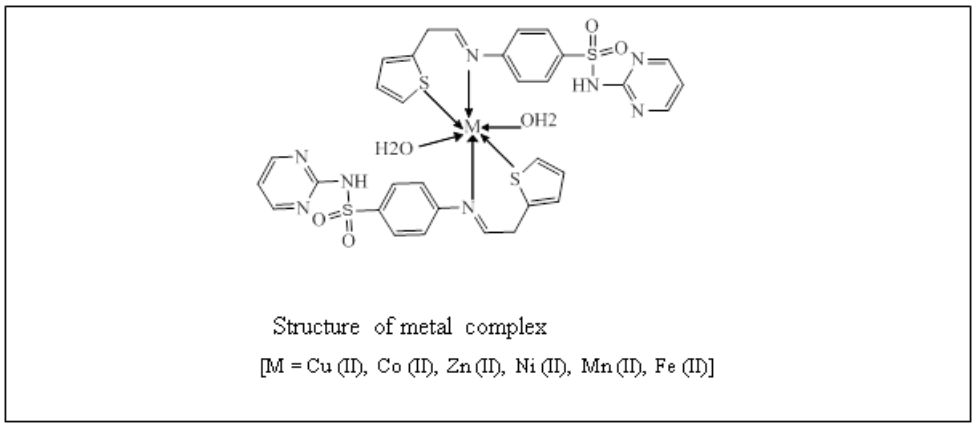
The metal complexes of Co (II), Ni (II) and Zn (II) with novel Schiff base ligand 2-furylglyoxal–anthranilic acid (FGAA)[33] The metal complexes signalised by elemental analysis and spectral data such as FT-IR, ^{1}H NMR, ^{13}C NMR and UV spectroscopy. The metal complexes show octahedral geometry by spectral data. All metal complexes exhibit anticancer activity against HOP62 and BT474cancercells. They also exhibit antibacterial as well as antifungal activity against bacteria and fungi respectively.



M=Cu (II) or Ni (II) or Co (II)

Structure of metal complexes

The metal complexes of Cu(II), Co(II), Zn(II), Ni(II), Mn(II) and Fe(II) with novel Schiff base ligand *N*-4-(thiophene-2-yl methyleneaminopyrimidin-2-yl-benzene sulfonamide derived from the condensation of sulphadizine and thiophene-2-carbaldehyde[34] The novel Schiff base ligands and metal complexes were characterized by elemental analyzer FT-IR, H1 NMR, mass spectroscopy, microanalysis, TGA. The Schiff base ligands and metal complexes were transmited for antibacterial activity against selected microbes.



Structure of metal complex

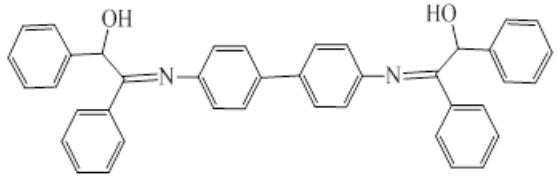
[M = Cu (II), Co (II), Zn (II), Ni (II), Mn (II), Fe (II)]

The metal complexes of Cu (II) and Hg (II) with Schiff base ligand have been synthesized in recent days[35] such as,

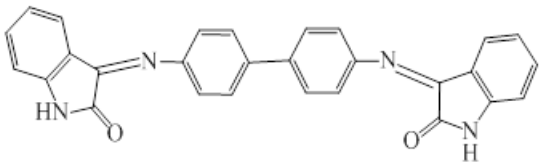
- The Schiff base ligand 2,2-(biphenyl-4,4diylbis (azan-1-yl-1-ylidene))bis(1,2-diphenylethanol)] (L1)derived from the liquefaction of benzidine and benzoine
- Another Schiff base ligand [3, 3-(biphenyl-4, 4-diylbis (azan-1yl-1-ylidene)) diindolin-2-one] (L2) derived from the liquefaction of the benzidine and isatin.

The Schiff base ligands and metal complexes were signalised by molar conductance, vibration electronic, ^{1H} NMR and FT- IR spectroscopy, UVspectroscopy and other analytical techniques.The metal complexes of [Cu_2 (L1) (L2)] $Cl_2$and [Hg_2 (L1) (L2) (H_2O) $_4$] Cl_2 shows tetrahedral and octahedral geometry respectively by analytical and spectral data.

Theyelectrolytic in nature.The metal complexes of Hg (II) & Cu (II) show antimicrobial activity as antifungal and antibacterial activities against Candida tropicalis, Canidia albicans andE. Coli, S. aureus respectively.

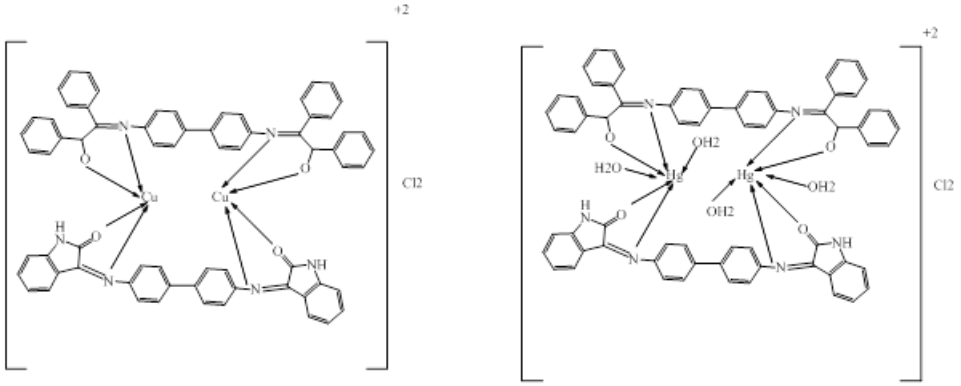


2,2-(biphenyl-4,4diylbis(azan-1-yl-1-ylidene))bis(1,2-diphenylethanol)](**L1**)



3,3-(biphenyl-4,4diylbis(azan-1-yl-1-ylidene)diindolin-2-one)](**L2**)

Structure of Schiff base ligand (L1) and (L2)



Structure of Cu (II) & Hg (II) complexes

CONCLUSION

This Book Chapter broadly suggest that the chemistry of novel Schiff base ligand is an versatile importance of human being. It shows broad peaks of biological activities against antiviral, antifungal, anticancer, antidiabetics etc. Not only Schiff base ligand but its derivatives(Metal Complexes) also exhibit strong biological activities like DNA binding. Now a day drug synthesis is carried out along with metal complexes novel Schiff base. Further there is more scope in the chemistry of Coordination compounds.

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