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Schiff Base Metal Complexes of 4-Hydroxyquinolin-2-one: A Short Review

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Abstract:

Schiff base metal complexes derived from 4-hydroxyquinolin-2-one has drawn significant interest owing to its structural broad spectrum, coordination adaptability, and potential biological applications. This review provides a comprehensive overview of the synthesis, characterization, coordination behaviour, and functional properties of Schiff base ligands based on the 4-hydroxyquinolin-2-one scaffold and their corresponding metal complexes. The presence of multiple donor sites, including azomethine nitrogen, phenolic oxygen, and carbonyl functionalities, enables these ligands to form stable complexes with a wide range of transition metal ions such as Cu(II), Ni(II), Co(II), Zn(II), and Fe(III). Various synthetic strategies, including conventional reflux and green chemistry approaches, are discussed in detail, highlighting recent advancements in ligand design and complex formation. Spectroscopic, analytical, and crystallographic techniques employed for structural elucidation, such as FT-IR, NMR, UV–Vis, mass spectrometry, and X-ray diffraction, are critically examined to establish coordination modes and geometrical configurations. The review further explores the electronic, magnetic, and photophysical properties of these complexes, emphasizing their structure–property relationships. Overall, this review aims to consolidate current knowledge and identify emerging trends in the development of 4-hydroxyquinolin-2-one-based Schiff base metal complexes. It underscores their potential as multifunctional agents in medicinal chemistry and materials science, while also outlining future research directions to address existing challenges related to selectivity, toxicity, and mechanistic understanding.

Keywords: 4-hydroxyquinolin-2-one, metal Complexes, Schiff.

Introduction:

Schiff base metal complexes constitute an important class of coordination compounds formed by the condensation of primary amines with carbonyl compounds, generating azomethine (–C=N–) linkages that serve as robust chelating sites for a variety of metal ions.[1] These complexes have been widely investigated due to their synthetic versatility, structural diversity, and broad spectrum of physicochemical and biological properties, which make them significant in fields ranging from catalysis[2] and material science[3] to bioinorganic chemistry[4] and pharmacology[5]. Schiff base ligands are particularly valued for their ability to stabilize metals in different oxidation states and to modulate the reactivity and functionality of the resulting complexes. Their coordination with transition metals often enhances properties such as antimicrobial,[6] antioxidant,[7] anticancer,[8] anticoagulant,[9] and anti-malarial[10] activities, reflecting their potential as therapeutic candidates and advanced functional materials. The 4-hydroxyquinolinone scaffold, characterized by a heterocyclic quinoline core with proximal nitrogen and hydroxyl donor atoms, provides an excellent platform for Schiff base formation and subsequent metal complexation due to its inherent ability to form stable chelate rings.[11]

Moreover, quinolinone-based ligands are known for diverse biological activities, and their integration into Schiff base systems is expected to further expand the functional applications of the resulting metal complexes. In this review, we critically examine the synthesis, structural characterization, and multifaceted applications of Schiff base metal complexes derived from 4-hydroxyquinolinone ligands, highlighting recent advances and identifying future research directions.

The derivatives of 4-hydroxyquinolin-2(1H)-one and its tautomers are also known to be more valuable in natural product chemistry. The structures of 4-hydroxyquinolin-2(1*H*)-one are shown in Fig. 1. [12] The structures of 4-hydroxy-2(1H)-quinolone have been assigned by UV, IR, MS and NMR spectroscopy.[13,14] The two intense bands at 269 and 314 nm are observed in 'UV' in methanol. The band IR spectrum is observed at 3360 cm^{-1}, 1657 and 1508 are assigned to (-O-H) stretching, (>C=O) stretching, and (C=C) aromatic stretching respectively. The PMR spectrum, singlet at 12.90 and at 11.18 are assigned OH and NH signals respectively. A singlet at 5.77 ppm, is a typical chemical shift for >C=C< non-aromatic hydrogen. Two complex multiplets, of the same intensity, due to the C-5, C-6, C-7 and C-8 protons are also seen. Among the isomers (A to E), A, B and C are frequently studied isomers. Although 3C is proved to be more stable,[15] 3A and 3B predominates in solution.

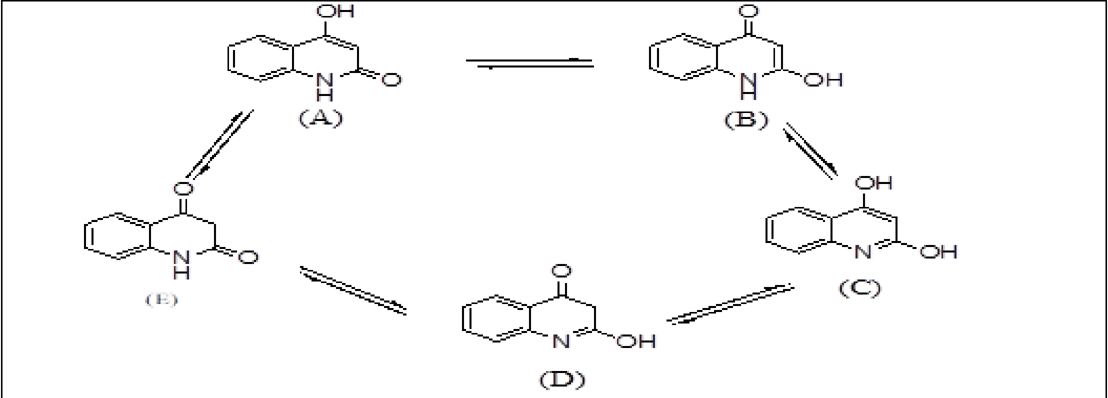

Fig.1: Possible tautomeric structures of 4-hydroxyquinolin-2(1*H*)-one (A-E).

In addition, these 4-Hydroxy-2(1H)-quinolinones along with their derivatives are among the group of valuable heterocyclic compounds associated with many pharmacological,[16-21] various medicinal values such as analgesic, anti-inflammatory,[22-23] diuretic,[24] antiallergenic,[25] anti-platelet,[26] orally active antagonists,[27] cardiovascular agents,[28] anticonvulsant,[29] antimicrobial (antibacterial and antifungal),[30] antitubercular,[31] dye-stuffs,[32] herbicides.[33]

Schiff Base Metal Complexes of 4-Hydroxyquinolinone:

Khalil described the synthesis and structural characterization of new Schiff base complexes.Ni(II), Cu(II), UO_2 and VO.[34] A Schiff base ligands prepared by condensation of 3-formyl-4-hydroxy-6-methylquinolin-2(1H)-one and ethane-1,2-diamine and propane-1,2-diamine. (Figure 1.4.4) These synthesized ligands were separately treated with metal salts such as $CuCl_2.2H_2O$, $Cu(OAc)_2.H_2O$, $NiCl_2.6H_2O$, $Ni(OAc)_2.4H_2O$, $FeCl_3.6H_2O$,$UO_2(OAc)_2.2H_2O$, and $VOSO_4.2H_2O$. Complexes with varied structural motifs were formed when the same metal salt and solvent system were reacted with different ligands. This variation is attributed to the presence of an additional methyl substituent in one of the ligands. Furthermore, treatment of the ligands with different metal salts or changes in the solvent employed during synthesis led to the formation of complexes with distinct structures and compositions. The proposed structures of the complexes were substantiated through electronic and IR spectroscopic analyses, along with magnetic susceptibility measurements (μ_{eff}).[34]

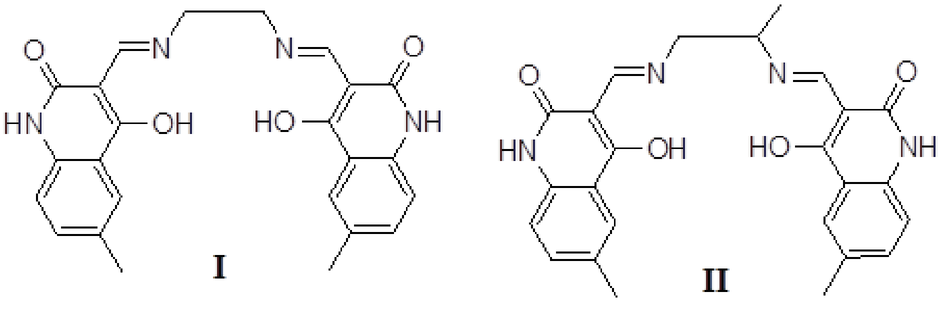

Fig 2 Schiff Base ligand of 4-Hydroxy-2(1H)-quinolinone

The mixed or asymmetric tetradentate Schiff base ligands H_2L_I and H_2L_{II}, (Fig. 1.4.5) were synthesized. This was achieved by reaction of 4-hydroxy-6-methyl-2-oxo-1,2-dihydroquinoline-3-carbaldehyde and benzene-1,4-diamine, and then condensation with pentane-2,4-dione and 2-hydroxybenzaldehyde respectively. The complexes of Ni(II), Cu(II), UO2(II) and VO(II) were prepared with the general formula $[L_2M_2\ nH_2O]$. However, the uranyl complex of the ligand

H_2L_I had the formula $[L_IUO_2)_2(OAc)_2(OH_2)_2]$. The ligands and metal complexes were characterized by elemental analyses, IR, UV-visible, mass and ESR of Cu(II) complexes were recorded spectra and magnetic moment measurements (μ_{eff}). The complexes were assigned distorted tetrahedral geometry, octahedral, square pyramidal pentagonal bipyramidal for Cu(II), Ni(II), VO(II) and UO_2(II) respectively.[35]

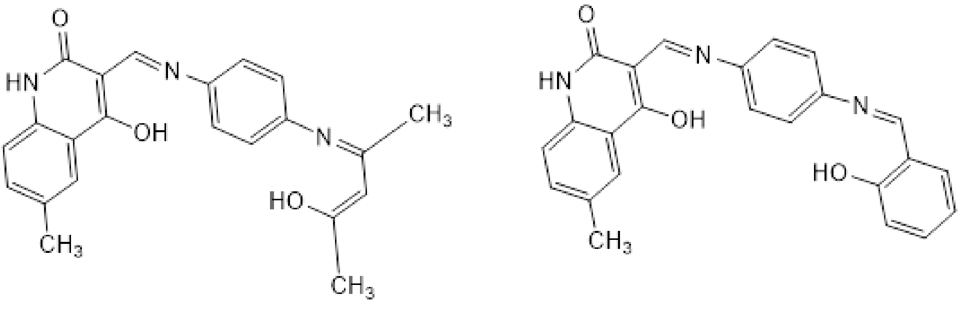

Fig.3 Asymmetric TetradentateSchiff base Ligand H_2L_I and H_2L_{II}

Emara[36] reported the synthesis of asymmetric tetradentate Schiff base ligands H_2L_1 and H_2L_2 and their Cu(II), Ni(II), UO_2 (VI) and Fe(III) complexes. The synthesis of ligand was achieved by reaction of 4-hydroxy-6-methyl-2-oxo-1,2-dihydroquinoline-3-carbaldehyde and benzene-1,2-diamine, and then condensation with pentane-2,4-dione (H_2L_1) and 2-hydroxybenzaldehyde (H_2L_2) respectively. The synthesized Schiff base ligands H_2L_1 and H_2L_2, were used to prepare Cu(II), Ni(II), UO_2 (VI) and Fe(III) complexes using respective salts. The structures of the compounds were established by standard elemental analyses, IR-spectra, UV-visible spectra, mass spectra and magnetic moment measurements (μ_{eff}). Both Cu(II) and Ni(II) cations are coordinated to the N_2O_2 coordinating sites of the ligands. Various geometries were assigned for different metal complexes which were attributed based on their complexing behaviour with a different type of ligand, salts as well as solvent used.

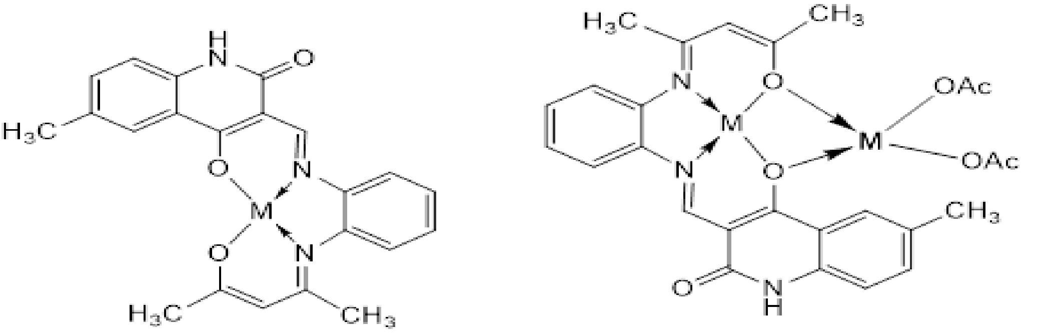

Fig. 4 Monomeric Cu(II) and Ni(II) of asymmetric Ligand H_2L_1

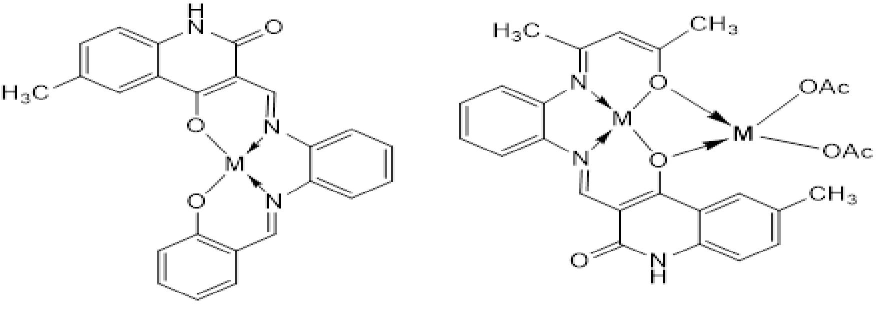

Fig.5 Monomeric Cu(II) and Ni(II)of asymmetric Ligand H_2L_2

Giorgos37 and co-workers reported synthesis and characterization of Mg(II), Zn(II) and Ba(II) complexes with 3-acetyl-4-hydroxyquinolin-2(1H)-one and 3-acetyl-4-hydroxy-1-methylquinolin-2(1H)-one ligands using MgCl2, ZnCl2 and BaCl2 salt respectively. The structure of the synthesized complexes has been justified by elemental analyses, FT-IR spectroscopy and 1H/13C NMR Spectroscopy and Mass Spectrometry. The data confirms the magnesium complexes having general formula Mg2(OH)L3(H2O)z and those of Zn(II) and Ba(II) as ML2(H2O)Z where z=2.

Saied38 and co-workers prepared Schiff base ligand H2L1 and H2L2 by reacting separately benzene-1,2-diamine and benzene-1,4-diamine with 4-hydroxy-6-methyl-2-oxo-1,2-dihydroquinoline-3-carbaldehyde respectively. With different ligands, metal salt and solvent, four Cu(II) complexes, four Ni(II) complexes, two VO2+ complexes two Fe(III) complexes and two UO22+ complexes. The characterization of the ligand was done by elemental analysis and comparison of physical constant with earlier reported work. The complexes were characterized by UV-vis, IR, magnetic moment studies. Fig. 1.4.7 illustrates the geometry, composition and structural prediction of all the synthesized Schiff base metal complexes.

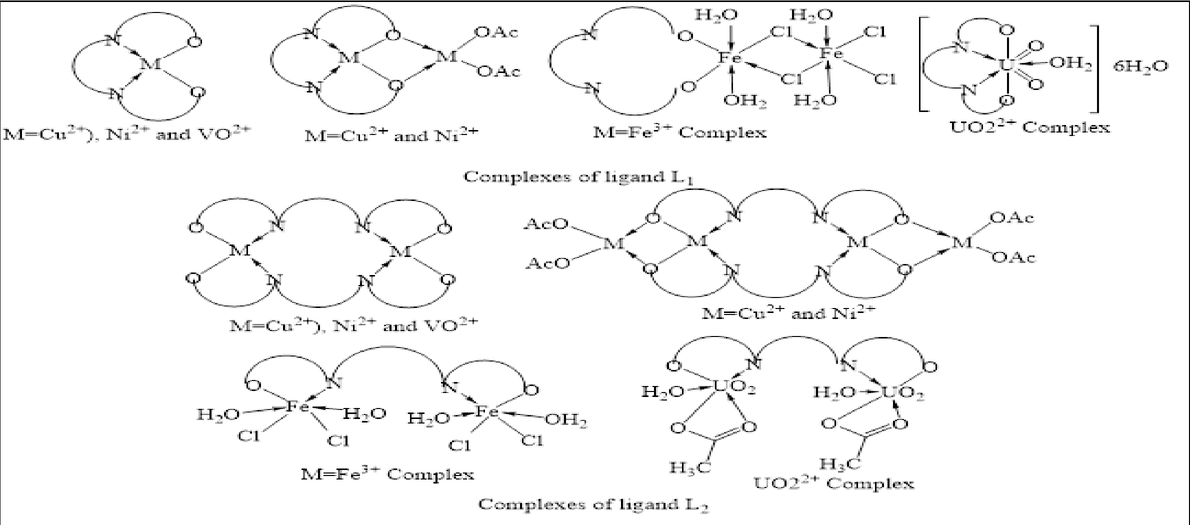

Fig. 6 Complexes of M= Cu(II, Ni(II), Fe(III), V(IV) and U(VI)

A monobasic tetradentate Schiff base ligand 3-(((2-aminophenyl)imino)methyl)-4-hydroxy-6-methylquinolin-2(1H)-one derived from 6-methyl-3-formyl-4-hydroxy-2-(1H)-quinolone and benzene-1,2-diamine was prepared. The ligand was reacted with both metal chlorides and metal acetates. When series of complexes having general formula $[MLX]_2$, where M = Cu^{2+}, Ni^{2+} , Fe^{3+}; X = chloride and acetate ion were obtained. Here the ligand behaves as a tetradentate ligand. However, the reaction of $M(ClO_4)_2.6H_2O$ with the ligand, complexes of the type $[ML_2]$ were obtained. In such cases, the ligand behaved as bidentate. The metal complexes were characterized by elemental analyses, UV-visible, IR and mass spectra. Magnetic susceptibilities measurement (μ_{eff}) was determined to ascertain the structure of complexes.[39]

A dibasic tetradentate (N_2O_2 donor) and dibasic pentadentate (N_3O_2 donor) Schiff base ligands were synthesized. A dibasic tetradentate ligand was prepared from 3-formyl-4-hydroxy-6methyl-quinolin-2-one and 1, 3-diaminopropane. A dibasic pentadentate ligand was prepared from the action of 3-formyl-4-hydroxy-6methyl-quinolin-2-one with N-(2-aminoethyl)-l, 3-propanediamine. These ligands were employed for the synthesis of Cu(II), Ni(II), Zn(II), Cd(II) Co(II), Mn(II), Fe(III), VO(IV), UO_2(VI) and Th(IV), complexes. The synthesized complexes were characterized by elemental analyses, IR, electronic, mass and ESR spectra. Magnetic susceptibility measurements (μ_{eff}) were calculated. The metal complexes formed were having mono and di-nuclear composition. The structural geometries were also justified from thermal analyses. [40]

Issac and co-workers,[41] synthesized a novel series of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with a Schiff base ligand. The ligands 4-(((4-hydroxyquinolin-2-yl)methylene)amino)-N-(pyridin-2-yl)benzenesulphon amide was prepared by condensation of 4-amino-N-(pyridin-2-yl)benzene sulfonamide and 2-formyl-4-hydroxyquinoline.
Characterization of the complexes has been carried out by elemental analysis, IR, UV-vis, PMR Spectroscopy, TGA-DTA analysis, Conductivity measurement and magnetic moment measurements (μ_{eff}). All the metal complexes were attributed with octahedral geometry. The complexes show higher anti-microbial activity than ligand. The nuclease activity of the complexes was examined by gel electrophoresis and the results prove that metal complexes ease the process of DNA cleavage more than the ligand.

Lakshmi[42] reported synthesis and characterisation of a new ligand 3-(2-(1-(2,4-DihydroxyPhenyl)ethylidene)hydrazinyl)-2H-benzo[b][1,4]oxazin-2-one. The ligand was the product of the condensation reaction of 2,4-dihydroxyacetphenone and 3-hydrazineyl-2H-benzo[*b*][1,4]oxazin-2-one. The latter was earlier prepared from 1,4-benzoxazine-2,3-dione by treating it with hydrazine hydrate in methanol. This ligand was employed for the synthesis of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} metal complexes. (Fig. 1.4.8) The prepared complexes were characterized by elemental analysis, electronic spectra, IR spectra, conductivity measurements, magnetic moment measurements (μ_{eff}) and thermal analysis. ESR studies of Cu(II) was carried out. The physio-chemical analysis suggests octahedral Cu(II) and Zn(II) complexes. However, Co(II) and Ni(II) complexes exhibit octahedral as well as square planar within the same complex.

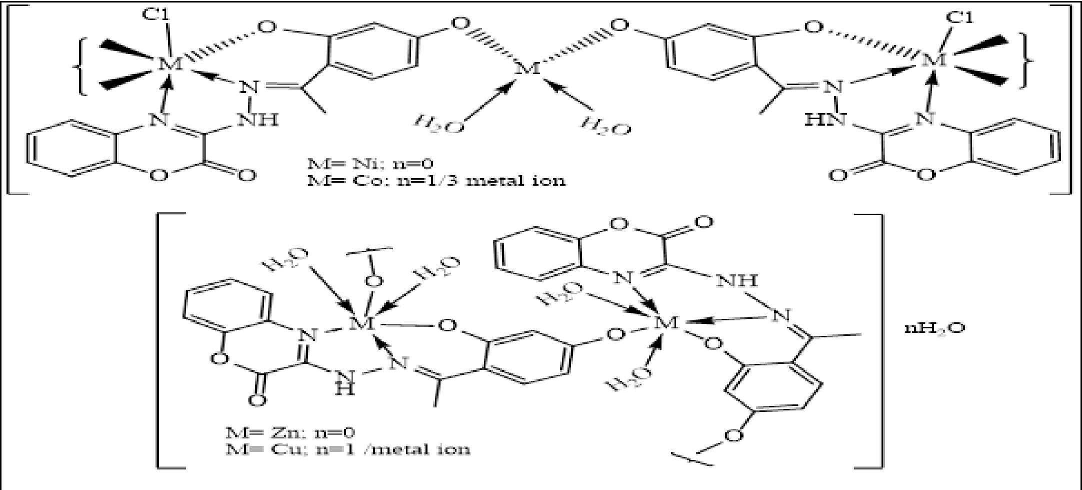

Fig. 6: **Complexes of Co(II), Ni(II), Cu(II) and Zn(II)**

Creaven [43] and co-workers reported the preparation of different Schiff bases by reaction of substituted 2-hydroxybenzaldehydes with 7-amino-4-methyl-quinolin-2(1*H*)-one. Schiff base ligands synthesized were characterised by elemental analysis, spectral methods such as UV-vis, IR, ^{1}H and ^{13}C NMR. The copper(II) complexes of Schiff base ligand were prepared and characterised by elemental analyses, spectral methods such as UV-vis, IR, ^{1}H and ^{13}CNMR and atomic absorption spectroscopy , magnetic and conductance measurements. The X-ray crystal structure studies further justify the coordination of Cu(II) metal ion with a ligand at azomethine nitrogen and phenolic oxygen. (Fig. 1.4.9)

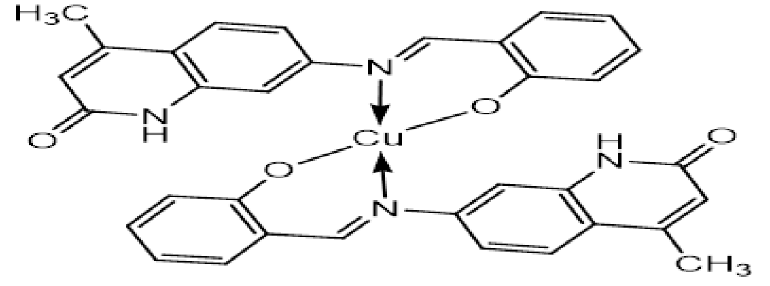

Fig.7: Schiff bases Copper(II) complexes of derived from 7-amino-4-methyl-quinolin-2(1*H*)-on

The ligand and all of the Cu(II) complexes were investigated for their antifungal activities against *Candida albicans*. The complexes were found to have excellent anti-Candida activity. Selected compounds were also screened for their in vitro anticancer potential using the human hepatic carcinoma cell line, Hep-G2. Many derivatives have shown better activity in comparison with cisplatin.

Rehab and co-workers[44] reported new mix-ligand complexes synthesized by reaction of metal ions such as V(III), Cr(III), Fe(III), Rh(III) and Al(III) with Schiff base N'1,N'3-bis((E)-2-hydroxybenzylidene) malonohydrazide as a primary and 8-hydroxy quinoline as secondary ligand respectively. Schiff base was prepared by reacting with 2-hydroxy benzaldehyde and malonohydrazide. The structures of the ligands and the complexes were explained by elemental analyses, atomic absorption spectroscopy, FT-IR-spectra, UV-visible spectra, mass spectra, conductivity measurements and magnetic moment measurements (μ_{eff}). The bonding pattern is shown in Fig. 1.4.10. The ligands and complexes were screened for their antibacterial activity against *E. coil* and *S. aureus*. The ligands and complexes were also screened antifungal activity against *penicillum* and *A. niger* well diffusion method.

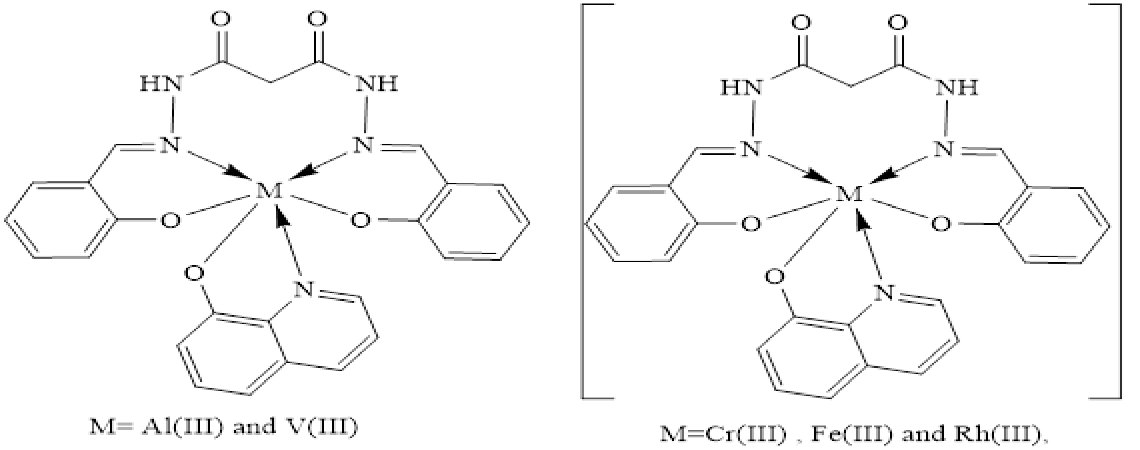

Fig. 8: Complexes of M=Cr(III) , Fe(III) Rh(III), Al(III) and V(III)

Siddappa and Co-workers[45] prepared and characterized new complexes of the type ML_2, and M´LCl [where M = Cu(II), Co(II), Ni(II) and Mn(II); M' = Zn(II), Cd(II) and Hg(II)] with the Schiff base ligand. The Schiff base was prepared by condensation of 2-hydroxyquinoline-3-carbaldehyde and 3-amino-2-methylquinazolin-4(3H)-one. The synthesized ligand (E)-3-(((2-hydroxy quinolin-3-yl)methylene)amino)-2-methylquinazolin-4(3H)-one has been characterized by elemental analysis and also, IR, ^{1}HNMR and ^{13}CNMR spectral studies. The complexes were evaluated by elemental, IR-spectral, electronic spectral, ESR spectral and 'H NMR spectral characterization along with Conductance and magnetic susceptibility (μ_{eff}) measurements. Based on spectral analysis as well as magnetic susceptibility (μ_{eff}) measurements, complexes of Co(II), Ni(II) and Mn(II) have assigned octahedral geometry. Zn(II), Cd(II) and Hg(II) complexes were assigned tetrahedral geometry. The complex of Cu(II) has assigned distorted octahedral geometry- The ligand and its complexes were assessed for their antibacterial activity and antifungal activity.

The condensation reaction of 4*H*-1,2,4-triazol-4-amine with 4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carbaldehyde,4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinoline-3carbaldehyde and 1-ethyl-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carbaldehyde was carried out to obtain three new Schiff bases as L_1, L_2 and L_3.

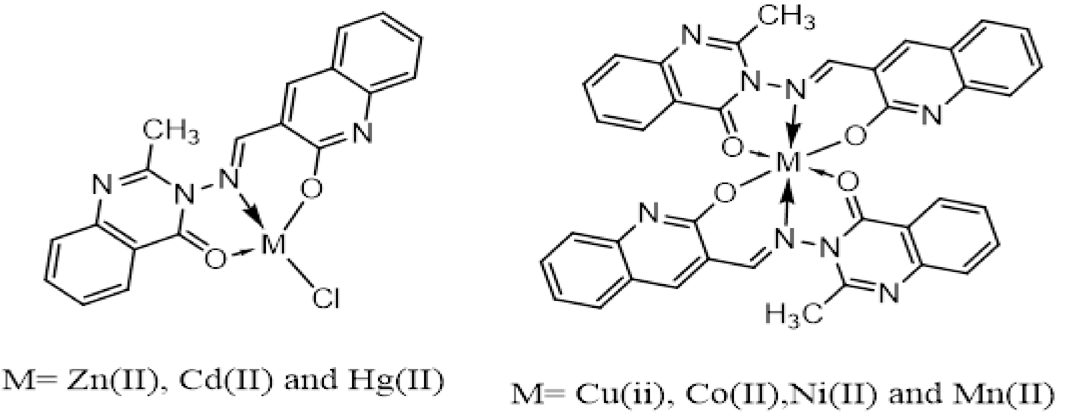

Fig. 9: Schiff base complexes

Schiff base ligands synthesized and characterized by UV-Vis, IR, ^{1}HNMR and ^{13}CNMR spectral analysis. In this Schiff base, both the moieties that are amine as well as aldehyde are heterocyclic. Cu(II) and Zn(II) complexes of these ligands were prepared and were evaluated for structural determination by performing standard techniques. The bonding of bidentate Schiff base ligands was established with metal ion through –OH and azomethine nitrogen and reported to possess octahedral geometry. This was further ascertained by X-ray crystallography studies of complexes. All complexes and ligands were investigated for their antimicrobial activities against *Candida albicans*, The compounds were found to be active against *C. albicans*.[46]

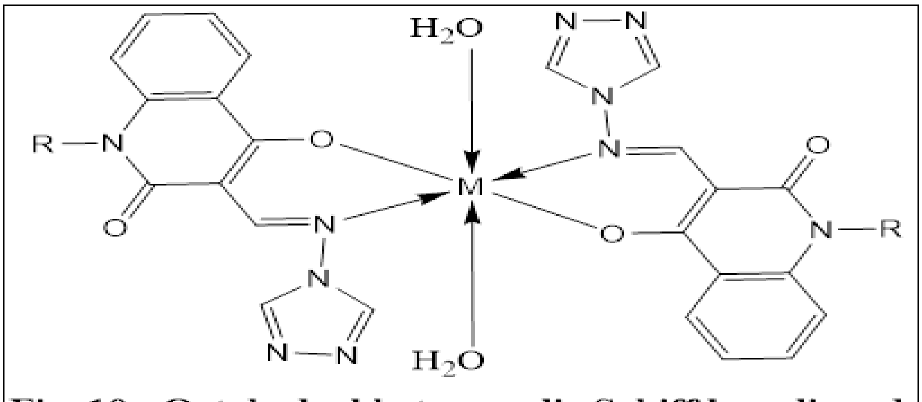

Fig. 10 : Octahedral heterocyclic Schiff base ligand

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