ejpmr, 2017,4(10), 193-201

SJIF Impact Factor 4.161

EUROPEAN JOURNAL OF PHARMACEUTICAL AND MEDICAL RESEARCH

www.ejpmr.com

Review Article

ISSN 2394-3211

EJPMR

SCHIFF BASE: MULTIDISCIPLINARY TOOL IN CHEMISTRY

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Article Received on 02/08/2017 **Article Revised on 24/08/2017** **Article Accepted on 15/09/2017**

ABSTRACT

Schiff bases are the compounds which are mainly formed by the condensation of the aldehydes and amines. In this review, an attempt is made to present a current scenario of these compounds which is synthesized by various synthetic methods. Some of those are easily synthesized from the various heterocyclic rings like furan, pyridine, thiophene and most important triazoles especially 1,2,4- triazole. These can also be convert in to metal complexes and reactants that are involved in the formation of this category of Schiff base compounds are called as "chelating agents". Some other compounds which were review here like Chalcones and their heterocyclic analogues, belong to the flavanoid family, which acquire a number of attractive biological properties like antioxidant, cytotoxic, anticancer, antimicrobial, antiprotozoal, antiulcer, antihistaminic and anti-inflammatory.

KEYWORDS: antioxidant, cytotoxic, anticancer, antimicrobial, antiprotozoal, antiulcer, antihistaminic.

INTRODUCTION

Schiff bases are formed typically by the condensation of a primary amine and an aldehyde/ketone. The resultant compound, $R_1R_2C=NR_3$ is called a Schiff base, where R1 is an aryl group, R_2 is a hydrogen atom and R_3 is either an alkyl or aryl group. However, usually compounds where R_3 is an alkyl or aromatic group are also regarded as Schiff bases. Schiff bases that contain aryl substituents are substantially more stable and readily synthesized, while those which contain alkyl substituents are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerisable[1], Schiff bases are generally bidentate[2-3], tridentate[4], tetradentate[5] or polydentate[6] ligands capable of forming very stable complexes with transition metals and form ketimines.[7] They can only act as coordinating ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reacting with a metal ion. Schiff bases are quite valuable chemicals that have the usage properties in the area of electrical conductivity[8], medicine, chemistry, pharmaceutical chemistry, Vilsmeier-Hack reactions[9-12] and industry. Especially in recent years, active research fields have included their use in anticancer.[13] antibacterial,[14-15] antifungal,[16] anti-inflammatuar, analgesic,[17] antiproliferative,[18] anticonvulsant[19] and anti-HIV.[20]

Schiff bases have played a amazing role in the development of coordination chemistry.[21-22] Because of these, complexes of the rare earth ions are a subject of increasing interest in bioinorganic and coordination chemistry.[23] There is good prospectus of study on N and S/O donor systems concerning their biochemical properties that is N and S/O donor ligands possess a range of biological applications like antitumor activity[24], antibacterial[25], antifungal[26], and antifertility[27] activity. Schiff base complexes also exhibit anticoagulation and plant growth regulating activities.[28-30]

Hatice Gamze has studied Schiff base ligand derived from 2-hydroxy-5-methoxybenzaldehyde and 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one and its metal complexes Cu(II), Co(II), Ni(II) and Mn(II)) have been synthesized. Compounds were encouraged us to study on their antioxidant properties and antimicrobial activities against Gram-positive, Gram-negative bacteria and fungi using microdilution procedure.[31]

Synthesis of metal complexes: 0.213 g (0.5 mmol) (HL) of the ligand was solved in 30 ml THF/MeOH (4:1) mixture, and a solution of 0.25 mmol of the metal salt $Cu(AcO)_2 \cdot H_2O$, $Co(AcO)_2 \cdot 4H_2O$, $Ni(AcO)_2 \cdot 4H_2O$ or $Mn(AcO)_2 \cdot 2H_2O$ in 10 ml methanol was added dropwise with continuous stirring. The mixture was stirred further for 30 minutes at 70 °C. The precipitated solid was then filtered off, washed with cold methanol, and dried in a vacuum dessicator (Figure 1). The characterization data for the complexes are given below fig 1.

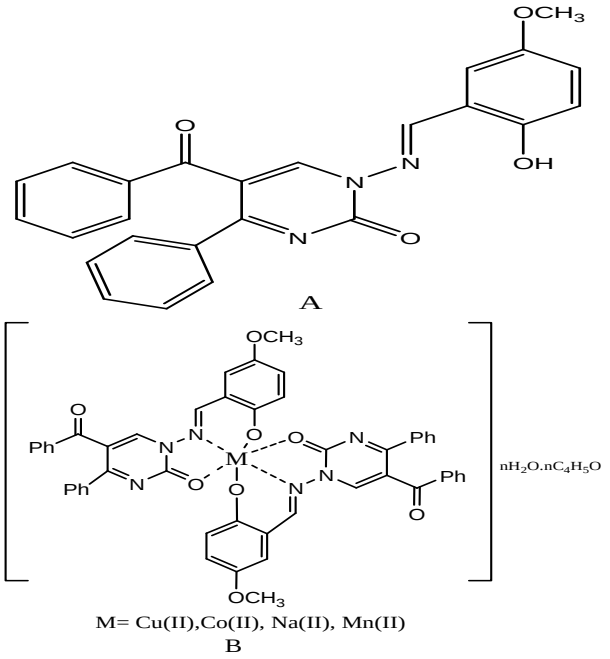


Fig. 1: Structure of the A) schiffs base ligand andB) its metal complex.

M. B. Halli et al gave methods for Metal complexes of some transition metal ions viz Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been synthesized from a Schiff base (L) formed by the condensation of 3-amino-5-bromobenzofuran-2- carboxamide and 2-hydroxy-1-napthaldehyde. Synthesized compounds have been studied by various spectroscopic techniques and evaluated for their DNA cleavage and antimicrobial activities.[32]

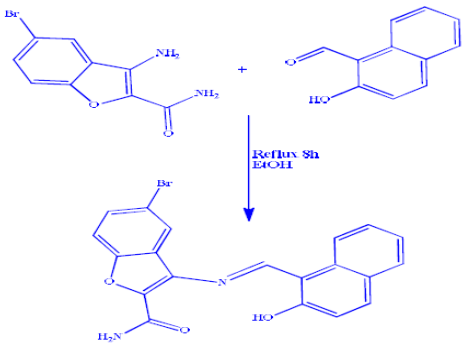
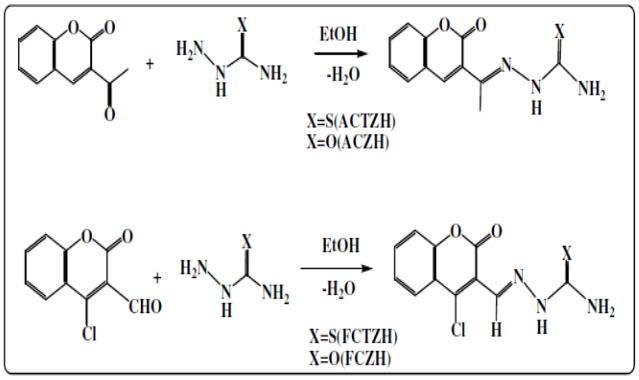


Fig. 2: Synthesis of Schiff base(L).

General procedure for preparation of metal complexes of Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Hg (II) with the Schiff base (L): A Metal chloride (0.01 mol) was mixed with a Schiff base (0.01 mol) in 30 mL ethanolic medium and reaction mixture was refluxed for about 3h on a water bath, then an aqueous solution of sodium acetate was added to the mixture to adjust the pH between 5 to 6 and further refluxed for about an hour.

Coordination complexes of La(III) and Yb(III) with Schiff bases namely 3-acetyl coumarin hydrazinecarbothioamide(ACTSZH), 3-acetylcoumarin hydrazinecarboxamide(ACSZH), 3-formyl-4-chlorocoumarin hydrazinecarbothioamide(FCTSZH) and 3-formyl-4-chlorocoumarin hydrazinecarboxamide (FCSZH) have been synthesized. These complexes were prepared by the interaction of ligands in 1:3 molar ratios and the mixture was heated under reflux for about 13- 16 h in methanol to yield the products shown in Scheme-1.[33]



Scheme -1: Synthetic route of the ligands

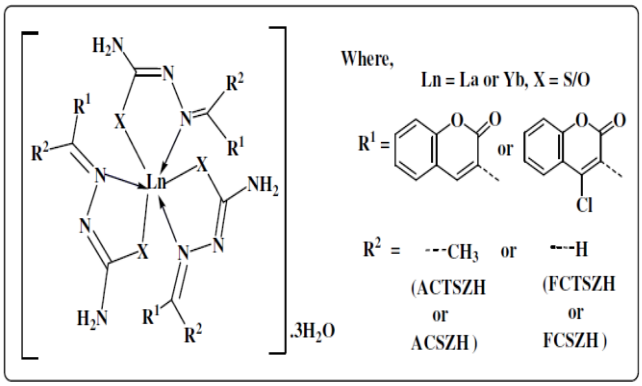
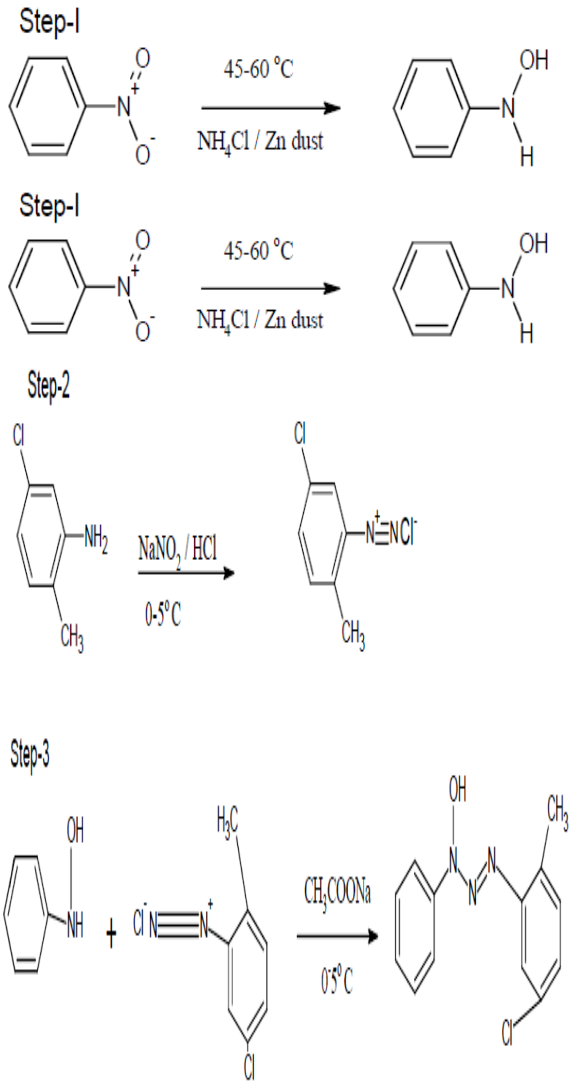


Fig. 3: Proposed Structure of the synthesized metal complexes.

Gowri kumari Vasireddy et al gave Chemical speciation of binary complexes of Co (II), Ni (II), and Cu (II) with L-phenylalanine were investigated pH-metrically in TritonX(100) – water mixtures. The stability constants were calculated using the computer program MINIQUAD75. The best-fit chemical models were selected based on statistical parameters and residual analysis. The models for the binary species contained ML, ML_2 and ML_2H_2 for Co(II), Ni(II) and Cu(II) in TritonX(100) – water mixtures. The trend in variation of stability constants with change in the mole fraction of the medium was explained on the basis of electrostatic and non-electrostatic forces.[34]

Hydroxytriazenes have attracted attention due to their chelating ability as revealed by reviews appearing on them during last few years.[35-37] Hydroxytriazenes and their transition metal complexes have also been found to possess biological activities. Shilpa Jain gave synthesis of3-hydroxy-3-phenyl-1-(5-chloro-2-methyl).

phenyltriazene. The spectrophotometric behaviour of complex of Fe (III) with 3-hydroxy-3-phenyl-1-(5-chloro-2-methyl) phenyltriazene was also studied shown in scheme2. It was observed that 3-hydroxy-3-phenyl-1-(5-chloro-2-methyl) phenyltriazene forms 1:3 complex with Fe (III) between pH 2.8-3.8.[38]



Scheme. 2: Synthesis of Hydroxytriazenes.

Suman Malik et al studied new series of vanadium and copper complexes of tridentate Schiff base derived from the condensation of 1H-Benzimidazol-2-amine with 2-hydroxybenzaldehyde were prepared. On basis of results obtained they conclude that the newly synthesized Schiff base acts as a neutral tridentate ligand coordinating through the oxygen of the phenolic group, nitrogen of the azomethine group and imidazole nitrogen. Based on analytical and spectral investigations octahedral and square planar geometries are proposed to V(III) and Cu(II) complexes respectively.[39]

Structural Interpretation

On the basis of above studies following structures of metal complexes have been proposed.

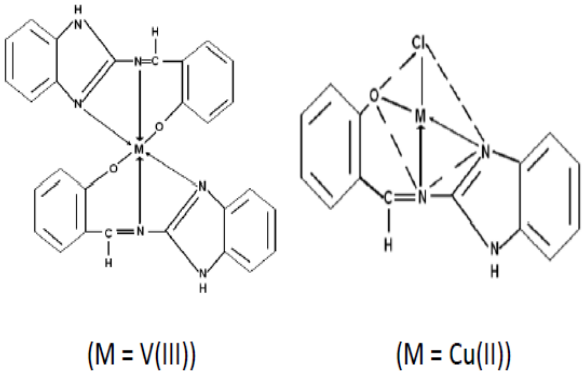
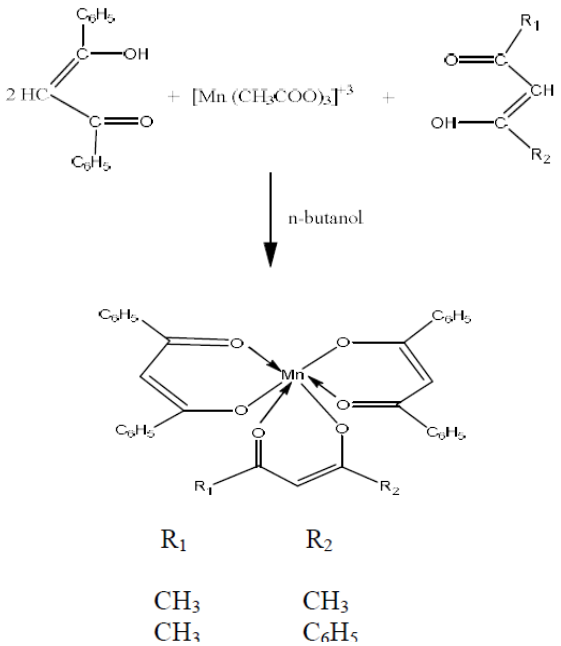


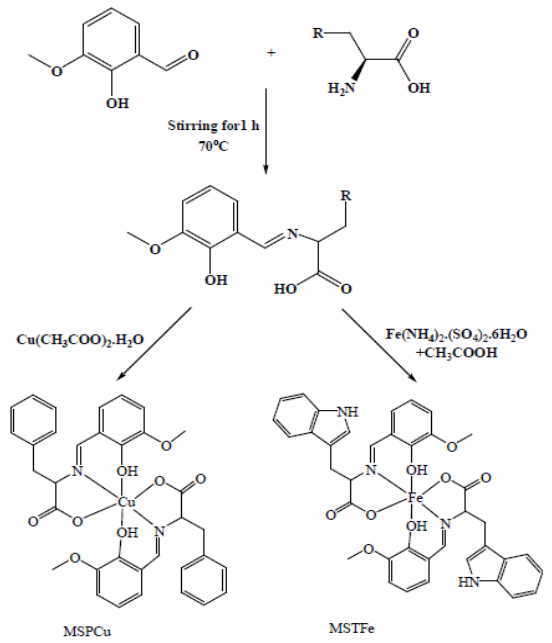
Fig. 4: Structures of metal complexes.

Mithlesh Agrawal et al gave Mixed ligand complexes of the type [Mn (dbzm)2L], (where dbzm = 1,3-diphenylpropane-1,3-dione and HL =pentane-2,4-dione, 1-phenylbutane-1,3-dione, 2-hydroxy- acetophenone, 2-hydroxypropio phenone, 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde) have been synthesized by the reaction of metal salt with the corresponding carbonyl in 1:2:1 molar ratios shown in Scheme 3.[40]



Scheme. 3. Synthesis of mixed ligand complexes of Mn (III) with dbzm and β-diketones.

Laila H. and others gave investigation on Azomethine amino ligands derived from the condensation of 3-methoxysalicylaldehyde (MS) or 4-diethylaminosalicylaldehyde (DS) with α-amino acids (L-phenylalanine (P) and DL-tryptophan (T)) were synthesized. Interaction of the obtained azomethine amino ligands with metal salts produced novel nano sized Fe(II) and Cu(II) complexes. The isolated complexes were characterized by elemental analysis, infrared spectra, ultraviolet-visible and thermal analysis (TGA) in dynamic air atmosphere shown scheme-4.



Scheme. 4: Synthesis of Azomethine amino ligands.

They conclude their study for new dibasic tridentate ONO amino acid Schiff bases ligands and its iron (II) and copper (II) complexes have been synthesized. The structure of these complexes has been confirmed by analytical data, IR, electronic, ^{1}H NMR, magnetic susceptibility, molar conductance and thermal[41] studies. Based on the analytical and spectral studies, octahedral geometry was proposed for the Fe(II) and Cu(II) complexes with general formula $[M(HL)_2].nH_2O$. The prepared complexes have non-electrolytic nature[42]

Omar H. Al-Obaidi gave the synthesis of some Schiff bases as ligands. The ligands are – L_1, 1, 3 - Bis - (2-hydroxy-benzylidene) - thiourea and L_2, 1, 3 – Bis - (2-hydroxy-benzylidene) – urea,). These ligands are complexed with transition metal ions of Mn^{+2}, Co^{+2}, Ni^{+2} shown in fig 5.[43]

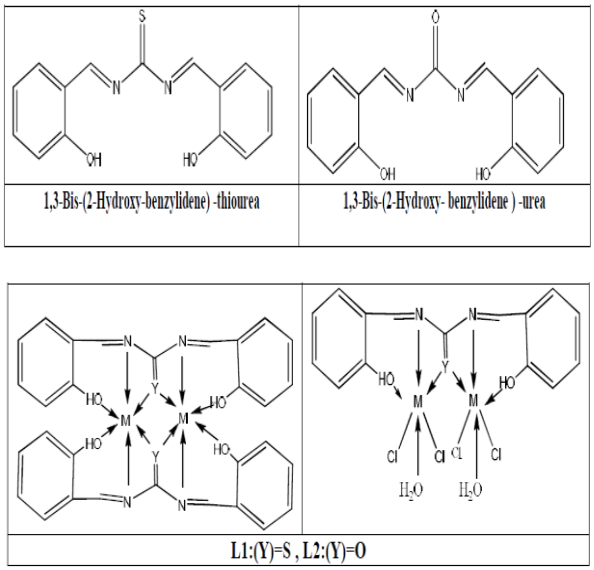
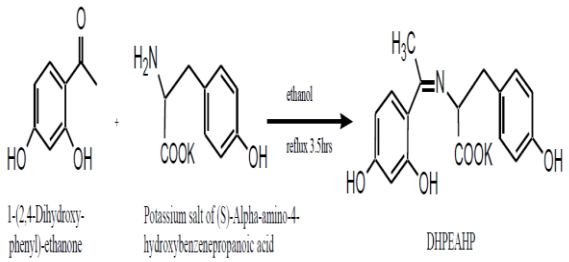


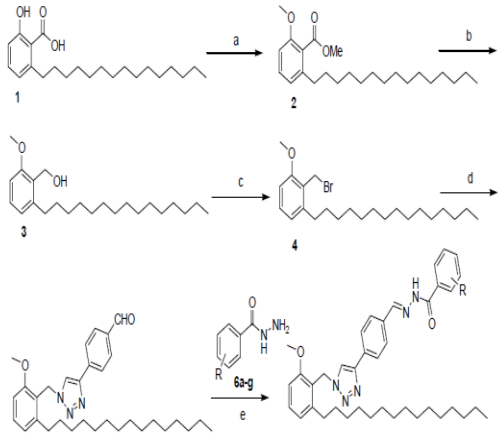
Fig-5: The Proposed Structures of metal complexes.

The amino acid ligand [1-(2,4-dihydroxy-phenyl)-ethanone-(S)-alpha-amino-4-hydroxybenzenepropanoic acid] (DHPEAHP) was prepared by the reaction of 1-(2,4-dihydroxy-phenyl)-ethanone (DHPE) with (S)-alpha-amino-4-hydroxybenzene propanoic acid (AHP). The complexes of this ligand have been prepared using metal acetates of Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) under reflux in methanol Scheme-5.[44]



Scheme-5: Synthesis of [1-(2,4-dihydroxy-phenyl)-ethanone-(S)-alpha-amino-4-hydroxybenzenepropanoic acid] (DHPEAHP).

A.L.V. Kumar Reddy gave the synthesis of novel hydrazone derivatives of anacacrdic acid linked with 1,4-disubstituted triazoles is illustrated in scheme-6. The synthesis of the hydrazone derivatives was accomplished in five synthetic steps from anacacrdic acid utilizing greener solvents/green reagents shown in scheme 6.[45]

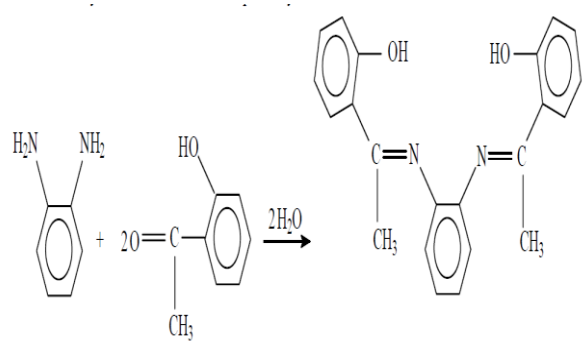


Scheme-6: Synthesis of Novel Anacardic acid Derivatives Bearing 1,4-disubstituted 1,2,3-Ttriazoles.

Experimental conditions

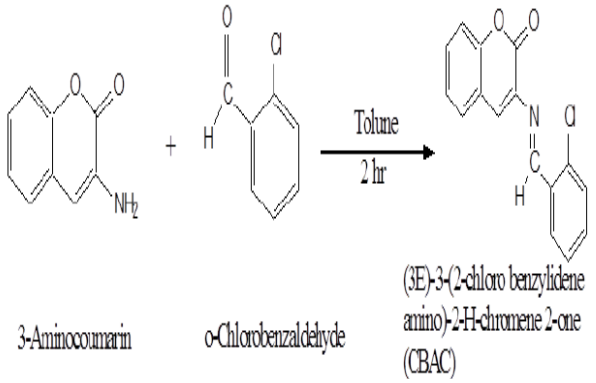
(a) dimethyl carbonate, DBU, 2-Me THF, 140°C, sealed tube; (b) $NaBH_4$, 2- MeTHF, reflux, 1h; (c) 2,4,6-Trichloro-[1,3,5]-triazine, DMF, NaBr, cyclopentyl methyl ether, 25°C, 16h; (d) NaN_3, 4-ethynylbenzaldehyde, CuI, [bmim] $[BF_4]/H_2O$ (1:1), r.t., 6h; (e) Benzohydrazides, ethanol, grinding, 2-3min.

A. M. Hamil et al gave Two complexes of Co(II) and Cu(II) with Schiff base derived from o-phenylenediamine and 2-hydcoxyacetophonone have been synthesized by condensation in acidic medium shown in scheme7.[46]



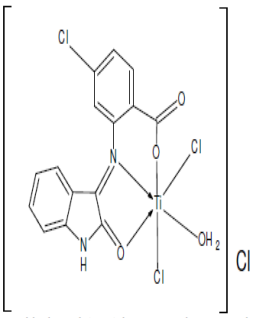
Scheme. 7: Synthesis of ligands o-phenylenediamine and 2-hydcoxyacetophonone.

Shylaja Kotte et al gave a new series of Mn(II), Cu(II) and Pd(II), complexes have been synthesized by the between carbonyl compound i.e. and 3-amino coumarin. The complexes are found to have ML2 based on elemental, conductance and spectral studies; octahedral geometry was assigned for these complexes. The ligand as a bidentate and co- ordinate through nitrogen atom of azomethine group, oxygen atom of keto group of 3-amino coumarin shown in Scheme-8.[47]

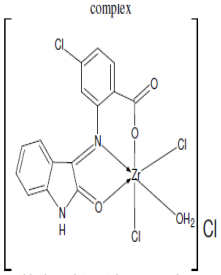


Scheme. 8: Synthesis of Schiff base ligand CBAC.

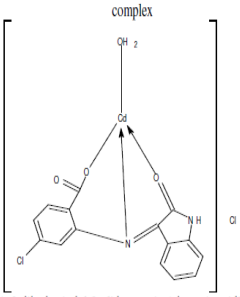
Suraj B. Ade et al has been synthesized schiffs base from 2-amino, 4-chloro benzoic acid and Isatin (ACBAI), Metal complexes of the Schiff base were prepared from chloride salt of Ti(IV), Zr(IV) and Cd(II) in alcoholic medium.[48]



Dichloro-[4-Chloro-2-(2-oxo-1, 2-dihydro-indol-3-ylidene amino)-benzoic acid](ACBAI) aquo Ti(IV) chloride complex



Dichloro-[4-Chloro-2-(2-oxo-1, 2-dihydro-indol-3-ylidene amino)-benzoic acid](ACBAI) aquo Zr(IV) chloride complex



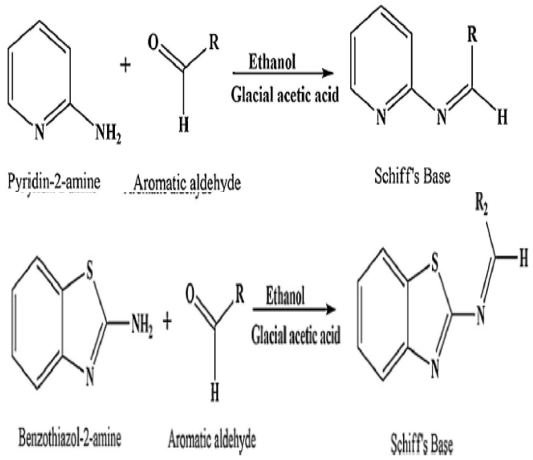
Dichloro-[4-Chloro-2-(2-oxo-1, 2-dihydro-indol-3-ylidene amino)-benzoic acid](ACBAI) aquo Cd(II) chloride complex

Fig.-6.

Synthesis of Schiff base: Schiff base ligand were synthesized by refluxing of 2-amino, 4-chloro benzoic acid (0.01 M) and isatin (0.01 M) in 50ml ethanol on water bath for 2-3 hours in presence of two to three drops of glacial acetic acid. The reaction mixture was poured in crushed ice, where orange colour precipitate was obtained. It was filtered by whatmann paper, washed with distilled water then alcohol, dried in vacuum desiccators'. Pure Schiff base was recrystallized from ethanol.

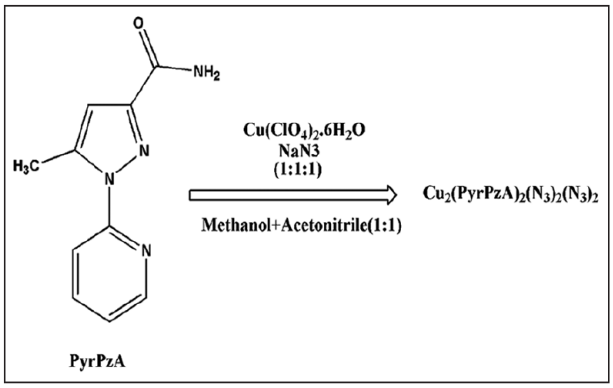
Synthesis of Metal Complexes 0.01 M alcoholic solutions (50ml) of metal salt were mixed with 0.01 M warm alcoholic solution (50ml) of ACBAI in round bottom flask. The PH of reaction mixture is adjusted to 7.2 by adding alcoholic ammonia. Resulting reaction mixture refluxed for 5 to 6 hours on water bath. Pale yellow colour complex was allowed to digest and collected by filtration through whatmann filter paper. Then washed with sufficient quantity of distilled water and little hot ethanol to apparent to dryness and dried in a vacuum desiccators. Obtained product is dried and stored in a sample glass bottle.

Shinu Chacko and Subir Samanta were tried to develop new azomethine based lead compound having multi-receptor action on HCC like sorafenib through molecular modelling, synthesis and pharmacological screening. Twelve different azomethine compounds based on 2-aminopyridine and 2-aminobenzothiazole were designed. Schiff bases of 2-aminopyridine and 2 amino benzothiazole were prepared shown in scheme-9.[49-50]



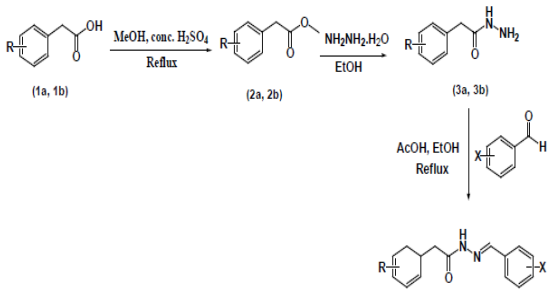
Scheme. 9: Synthesis of Schiff's bases using 2-aminopyridine and 2 amino benzothiazole.

Dhrubajyoti Majumdar and Suman Hazra PyrPzAmide chromophoric N,N bidentate chelating Schiff base ligand (L1) was successfully used to synthesized one binuclear Cu(II) complex Cu_2L with Copper perchlorate as the metal precursor and azide as a versatile bridging co-ligand shown in scheme-10.[51]

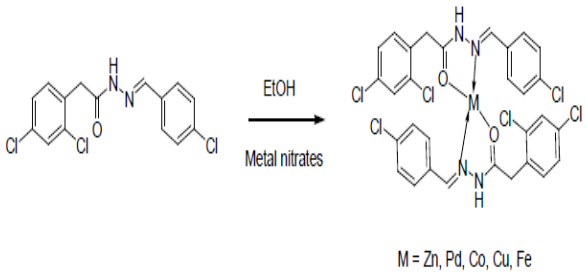


Scheme: 10 Synthesis of complex of Cu_2.L.

Ram U. Ambhure et al gave Schiff bases (E)-N-(4-chlorobenzylidene)-2-(2,4-dichlorophenyl) acetohydrazide and (E)-2-(2,4-dichlorophenyl)-N'-((1-methoxynaphthalen-2-yl)methylene) acetohydrazide were synthesized and further used for the synthesis of metal complexes shown in scheme-11-12.[52]

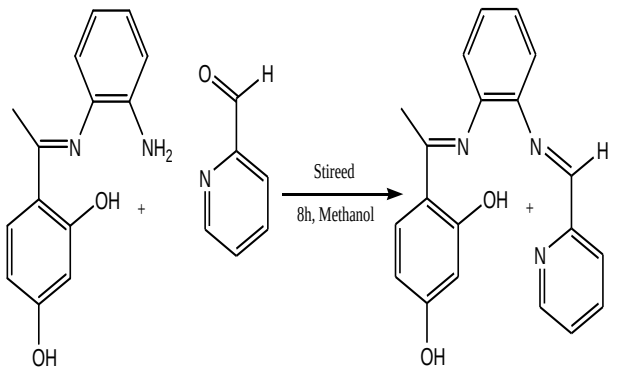


Scheme-11: Synthesis of Schiff bases (E)-N-(4-chlorobenzylidene)-2-(2,4-dichlorophenyl) acetohydrazide.

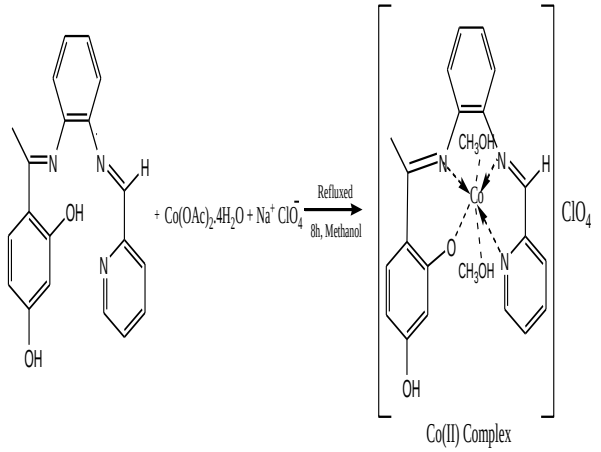


Scheme-11: Synthesis of Schiff bases (E)-2-(2,4-dichlorophenyl)-N'-((1-methoxynaphthalen-2-yl)methylene) acetohydrazide.

Zahra Shokohi-pour has been synthesized a new Schiff base derived from the pyridine-2-carbaldehyde, 1-(2,4-dihydroxyphenyl)ethanone, and benzene-1,2-diamine and Co(II) complex. We have synthesized a novel unsymmetrical Schiff base and Co(II) complex containing ligand. The structure of the ligand and complex was characterized by FT-IR, UV-Vis and other methods. The binding interaction of a biologically relevant Co(II) complex with calf thymus DNA, bioactivity investigation by UV-Vis and fluorescence spectroscopy and other spectroscopic measurements unambiguously suggested the binding of the groove probe with the DNA. The reactivity towards BSA revealed that the quenching of BSA fluorescence was of the static type. The cytotoxic activity of Co(II) complex against all cancer cell lines was significantly high and selective in a dose dependent manner, and in particular the compound appears to be both the most potent and most selective against human leukemia cell line. Based on the present results, Co(II) complexes can be promising agents for cancer treatment without significant side effects on normal cells. However, the observed results need to be confirmed in experimental tumor models in vivo.[53]

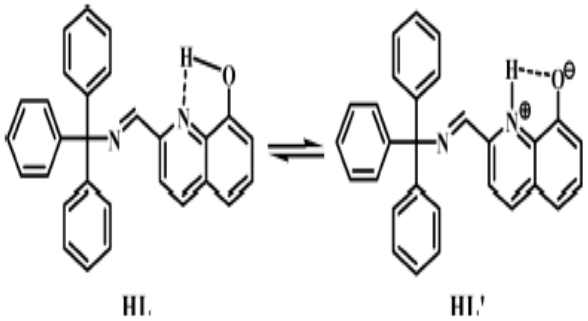


Scheme: 13: Synthesis of novel unsymmetrical Schiff base.



Scheme. 14: Co(II) complex.

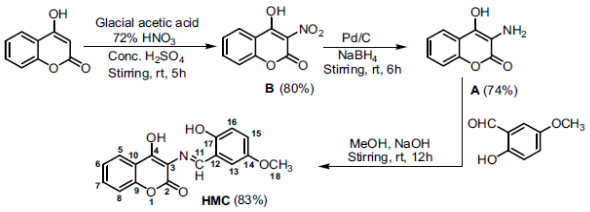
Dan Wang and coworkers gave 2-(Trityliminomethyl)-quinolin-8-ol (HL) and its Zn(II) complex synthesis and characterized by using single-crystal X-ray diffraction. HL is an unsymmetrical molecule and coordinated with Zn(II) ion to form ZnL2 in the antiparallel-mode arrangement via Zn-O (hydroxyl group) and Zn-N (quinoline ring) of HL shown in scheme 15.[54]



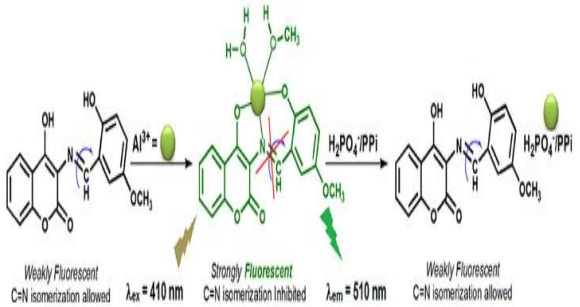
Scheme. 15: Enol Form (HL) and the Zwitterionic Form (HL′).

Now a day's considerable effort has been made to develop highly selective and sensitive fluorescent probes for metal ions detection in environment and in the field of biology.[55-61]

Sanjoy Kumar Sheeta et al were studied a coumarin based simple fluorescent "turn-on" probe, 4-Hydroxy-3-[(2-hydroxy-5-methoxybenzyli- dene)-amino]-chromen-2-one (HMC), to detect metal ion based on the chelation enhanced fluorescence (CHEF), was synthesized by condensing 3-amino-4-hydroxycoumarin and 2-hydroxy-5-methoxyben- zaldehyde. They also found the HMC-Al^{3+} ensemble subsequently detected the biologically important phosphate ions and nucleotides via fluorescence quenching. The live cell imaging study indicated that HMC is highly efficient in the detection of exogenous Al^{3+} in living cell.[62]



Scheme. 16: Synthetic scheme of HMC.



Scheme. 17: Binding mode of Al^{3+} with the probe HMC and the effect of $H_2PO_4^-$/PPi on HMC-Al^{3+}.

CONCLUSION

Schiffs bases are compounds has multidimensional application and also found important tool in chemistry as listed in above review paper. It is our informative attempt made to present a, moieties possessing diverse electron-donating and withdrawing groups. The intension of this review to provide the progress and current scenario of the schiffs base and its derivatives.

ACKNOWLEDGEMENTS

We acknowledge The Principal and Head, Department of Chemistry, S.S.V.P.S's L.K. Dr. P. R. Ghogrey Science College, Dhule for providing the lab facilities and their constant encouragement.

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