



A Comprehensive Review on Anthranilic acid-derived Schiff bases and their Metal chelates: Structures and Applications

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ABSTRACT

The worthwhile contributions made to the literature by researchers on the ligation behaviour of Schiff bases derived from anthranilic acid and their applications is hitherto not togetherized. This review covers a comprehensive bibliographic perusal of anthranilic acid-derived Schiff bases and their chelates reported circa over the last three decades (1990 – 2022) with a view to furnishing information that will help researchers in the design and development of new Schiff bases as potential candidates in different applications. A scrupulous survey of the literature suggests that anthranilic acid-derived Schiff bases preferentially ligate metal ions through azomethine nitrogen ($-N=CH-$) and the hydroxyl oxygen (OH) of the carboxyl group after deprotonation rather than chelating via the carbonyl oxygen ($C=O$). However, a pocket of the literature reported the coordination sites as the iminic nitrogen ($-N=CH-$) and carbonyl oxygen ($C=O$) of the carboxylic group. While most first row transition metals complexes of diverse geometries with the Schiff bases' denticity ranging from N,O-bidentate, O,N,O-tridentate and N_2O_2 -tetradentate amongst others have been documented, only few heavier transition metals are reported. Furthermore, these Schiff bases find promising applications in medicinal, pharmaceutical, catalytic, and analytical chemistry, especially in the separation, identification, and detection of several metal ions and anions. In addition to these, they are used as corrosion inhibitors, as odorants, etc. Notably, the chelates most often exhibited more potency as antibacterial, antifungal, anticancer, antidiabetic, antioxidant, antiulcer and molluscicidal agents than the free Schiff base ligands. This review exhaustively did synthesized most significant works on the subject.

1. Introduction

A Schiff base is a nitrogen analogue of aldehyde or ketone in which the $C=O$ group is replaced by $C=N$ with the nitrogen atom connected to an aryl or alkyl group, but not hydrogen [1]. Hugo Schiff first discovered Schiff base in 1864 through the condensation process of primary amine with a carbonyl compound, resulting in the formation of secondary aldimine moieties, $RHC=N-R'$, where R and R' are alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted [2]. Organic compounds containing substituted imine are called azomethines, anils [3], aldimines, benzanils,

ketimines or Schiff's bases [4]. A generic representation of this class of compounds is furnished in figure 1.

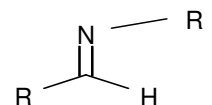


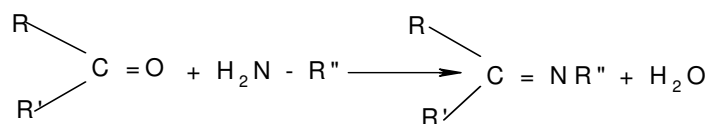
Figure 1. General structure of Schiff base

The schematic illustration of the formation of Schiff base and other related compounds is depicted in scheme 1.

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where R'' = Alkyl or aryl, the product is a Schiff base; R'' = NH₂ (hydrazine), the product is a hydrazone; R'' = NHCONH₂ (semicarbazone), the product is semicarbazide and R' = OH (hydroxylamine), the product is an oxime.

Scheme 1. General synthetic pathway for Schiff bases and related compounds [5]

The term Schiff base is normally applied to these compounds when they are used as ligands to form coordination complexes with metal ions. Such

compounds do occur naturally, for instance corrin, but the majority of Schiff bases are artificial (Figure 2).

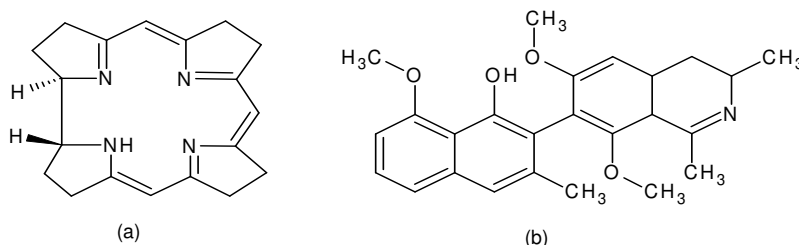
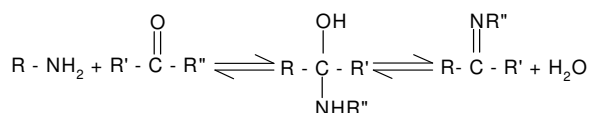


Figure 2. Naturally occurring Schiff base ligands: (a) corrin (b) anostrocladidine [6]

Schiff bases with aryl substituent are substantially more stable and more readily synthesized, while those which contain alkyl substituent are relatively unstable [7,8]. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable, while those of aromatic aldehydes having effective conjugation are more stable. In general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centres of

aldehyde are sterically less hindered than that of ketone [9].

The formation of Schiff base from aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis or upon heating. The formation of the Schiff base is generally driven to completion by separation of the product or removal of water, or both [10].



1° amine Aldehyde or Ketone Carbinoalamine N-substituted imine

Scheme 2. Formation of Schiff base through carbinoalamine

Schiff bases can only act as coordinating ligands if they bear a functional group, usually the hydroxyl or carboxyl, 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 [8,11].

2. Description of Anthranilic Acid

Anthranilic acid, synonymous to *o* - aminobenzoic acid or 2-aminobenzoic acid is an aromatic acid with the formula C₆H₄(NH₂)(COOH), molar mass of 137.14 g mol⁻¹, density of 1.412 g cm⁻³, melting point of 146-148 °C and a boiling point of 200 °C [12,13]. The molecule consists of a substituted benzene ring, hence is classed as aromatic, with two adjacent, or 'ortho' functional groups, a carboxylic acid and an amine (Figure 3). Consequently, the compound is amphoteric [14]. Sometimes referred to as vitamin L₁, anthranilic acid is the biochemical precursor to the amino acid

tryptophan, as well as a catabolic product of tryptophan in animals. It is one of the best compound used by degrading ancient dye indigo [15,16].

Anthranilic acid is a vital moiety present in more than 70 pharmaceuticals, 50 clinical drugs, 20 agrochemicals, and diverse fine chemicals. Over 400,000 tons are produced annually for drug synthesis (e.g., alprazolam, furosemide, clonazepam, etc.) and agrochemical production (e.g., bentazone) [17]. Besides, the anthranilic acid and its analogues serve as a starting material for the synthesis of marketed drugs such as Methaqualone, sold under the brand name Mandrax; in addition to forming an active pharmacophore in "Glafenine," "Floctafenine," and in "Fenamates" class of anti-inflammatory drugs [18]. Anthranilic acid is a versatile ligand that can bind metal ions in a variety of ways. The amine can bind metals neutrally or

deprotonated, alone or as a bidentate chelate with the carboxylate. The carboxylic acid is usually deliberately deprotonated to promote ligation, but under some conditions it can also coordinate metals while it remains protonated. One or both oxygen atoms of the carboxylate can bind directly to a metal [19].

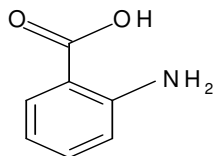
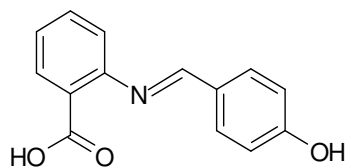
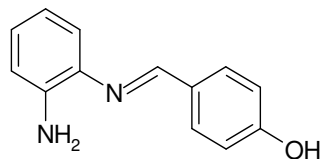


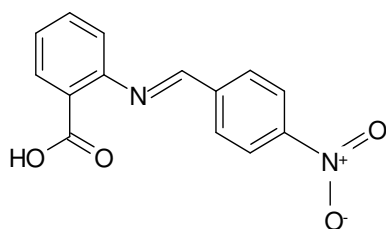
Figure 3. Structure of anthranilic acid



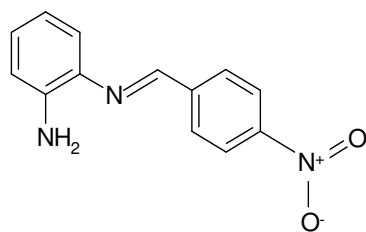
2-Hydroxybenzylidene-2-carboxyaniline



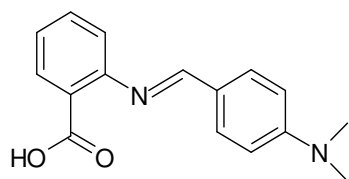
N-(4-Hydroxybenzylidene)-benzene-1,2-diamine



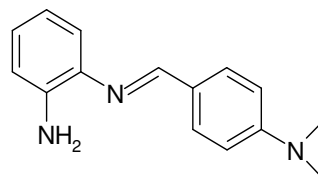
p-Nitrobenzylidene-2-carboxyaniline



N-(4-Nitrobenzylidene)-benzene-1,2-diamine



2-(N,N-Dimethyl)aminobenzylidene-2-carboxyaniline



N-(4-Dimethylaminobenzylidene)-benzene-1,2-diamine

Figure 4. Structures of Schiff bases

In 2013, Ejia et al. [21] investigated the effect of substituent position on antimicrobial activity of Schiff bases derived from salicylaldehyde and isomeric aminobenzoic acids in three solvents of different polarities with the aid of electronic absorption spectra. The absorption maxima in all the solvents used exhibited dependence on the position of substituent with the absorption maxima undergoing red shift as the solvent polarity increases. The bio-efficacy study of the compounds (figure 5) against some clinical bacteria determined in DMF and 1,4-dioxane revealed that the ortho and meta substituted (2-aminobenzoic acid and 3-aminobenzoic acid) Schiff bases exhibited better antibacterial activity in the solvents used.

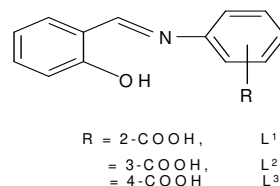


Figure 5. structure of Schiff bae from salicylaldehyde and isomeric aminobenzoic acid

In the same year, Raj et al. [22] synthesized Schiff base, 2-[[[(3Z)-2-oxo-2,3dihydro-1H-indol-3-ylidene]amino] benzoic acid by condensation reaction between isatin and 2-aminobenzoic acid. The structure was elucidated from FT-IR and ^1H NMR spectroscopy. The biological activities of the synthesized compound were predicted

by using PASS (online software for bioactivity prediction). 2-[[[(3Z)-2-oxo-2,3-dihydro-1H-indol-3-ylidene]amino]benzoic acid (figure 6) has biological activities such as acute neurological disorder, gastrointestinal hemorrhage, superoxide dismutase inhibitor and, hypothermia of 79.7 %, 73.7 %, 72.1 % and, 71.0 % respectively.

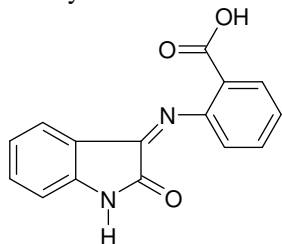
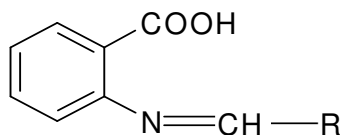


Figure 6. Structure of 2-[[[(3Z)-2-oxo-2,3-dihydro-1H-indol-3-ylidene]amino]benzoic acid

Schiff bases of anthranilic acid have been screened for their *in vitro* growth inhibition activity against different strains of bacteria and fungi as reported in 2015 by Elagab [23]. Notably, their activities were comparable to that of standard drugs such as Gentamycin and Fluconazole. Compound (b) exhibited the highest antibacterial activity while compound (a) showed the best antifungal activity. The Schiff bases are shown in figure 7.



R= o-hydroxyphenyl (a), p-hydroxyphenyl (b), furfuryl (c), p-nitrophenyl (d)

Figure 7. Structures of Schiff bases

Also in 2015, Mohammed [24] compared a classical Schiff base prepared from ortho-amino benzoic acid (anthranilic acid) and 4-hydroxy-3-methoxy benzaldehyde using lemon juice as a green acid catalyst, by conventional/non-ultrasonic (NUS) and ultrasonic methods (figure 8). Synthesized Schiff base was characterized by FT-IR and ^1H -NMR. X-RD, PSM, and SEM analysis were performed to understand the particle physical characteristics i.e. particle size, crystallinity and morphology of the two methods. Experimental data indicated that ultrasound assisted method was better in terms of high yield, economical, mild reaction condition, eco-friendly, and easy work-up procedures. It was also found that ultrasonically synthesized Schiff base have more crystallinity compared to conventional one. Most importantly, ultrasonically (US) synthesized Schiff base was more energy efficient than conventional/non-ultrasonic (NUS) method. Thus a total green approach was achieved.

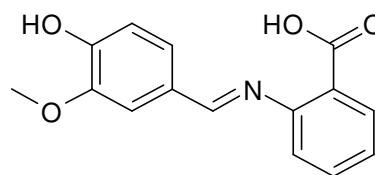


Figure 8. structure of the Schiff base

In 2016, Schiff base of pyridine-4-carbaldehyde with 2-aminobenzoic acid has been synthesized by Shamim and coworkers [25]. The compound was characterized by FT-IR, NMR and mass spectrometry; evaluated for its antioxidant and DNA binding interactions. The compound showed good inhibition of free radicals generated by DPPH. The DNA binding interaction was determined using UV-visible absorption titration method. Noteworthy, the synthesized Schiff base has high positive binding constants (k) value, indicative of the efficient binding of the Schiff base with DNA. Molecular docking studies also suggested the minor groove binding of the DNA. The structure of the compound is depicted in figure 9.

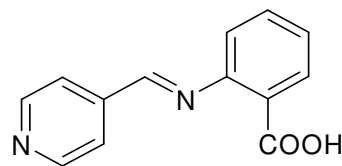


Figure 9. Schiff base of pyridine-4-carbaldehyde with 2-aminobenzoic acid

Also in 2016, Kaushik et al. [26] reported nine odorant Schiff bases, namely 2-(4-methoxybenzylideneamino)benzoic acid, 2-(benzylideneamino)benzoic acid, 2-(3-phenylallylideneamino)benzoic acid, 2-(3,7-dimethyloct-2,6-enylideneamino)benzoic acid, 2-(3,7-dimethyloct-6-enylideneamino)benzoic acid, 2-(4-isopropylbenzylideneamino)benzoic acid, 2-(3,4-dimethoxybenzylideneamino)benzoic acid, 2-(1-phenylethylideneamino)benzoic acid, and 2-[(4-(2,6,6-trimethylcyclohex-2-enyl)-but-2-enylideneamino)benzoic acid (figure 10), which were prepared by condensation of anthranilic acid with corresponding naturally occurring carbonyl compounds (anisaldehyde, benzaldehyde, cinnamaldehyde, citral, citronellal, cuminaldehyde, veratraldehyde, acetophenone, and α -ionone) employing conventional and microwave irradiation methods. These compounds were characterized with the aid of elemental and spectral (FT-IR, ^1H NMR, and ^{13}C NMR) analysis. Microwave irradiation method was efficient in terms of reduced reaction time, solvent use, and increased yields of these compounds without affecting their olfactory

characteristics. These Schiff bases also exhibited olfactory characteristics for various fragrance compositions and varied antimicrobial activity against

Aspergillus niger, *Penicillium chrysogenum*, *Staphylococcus aureus* and *Escherichia coli*.

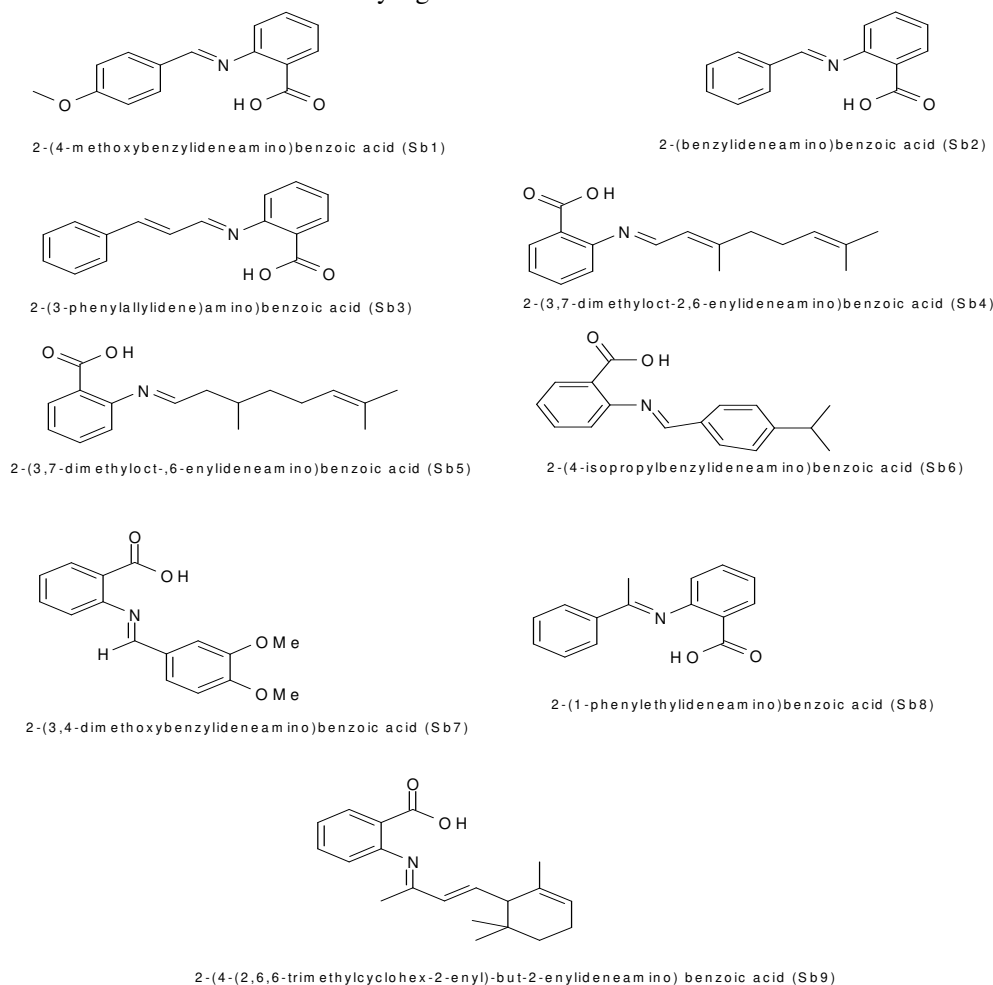


Figure 10. Structures of the synthesized odorant Schiff bases

A new azo-Schiff base receptors containing azo and azomethine groups with a conjugated group (benzyl ring of anthranilic acid) (figure 11) was synthesized in 2019 by Özdemir [27]. Azo-hydrazone/phenol-keto tautomerism and solvatochromism were investigated. Studying its sensing ability towards cations (Co^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , Mn^{2+} , Fe^{3+} , Cr^{3+} , and Al^{3+}), high sensitivity and selectivity were recorded for Fe^{3+} by naked eye and UV-Visible spectra in DMF-aqueous HEPES buffer (v:v, 1:1, pH 6.8). The colour of Schiff base solution instantly changed from yellow to deep orange. The interactions of receptors with F^- , Cl^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, H_2PO_4^- , and OH^- anions were also investigated in DMF-HEPES 1:1 and 4:1 solvent mixtures. The Schiff base sensitively responded to anions according to the order of $\text{OH}^- > \text{C}_2\text{O}_4^{2-} > \text{F}^-$ in the 1:1 mixture and $\text{OH}^- > \text{F}^- > \text{CH}_3\text{COO}^- > \text{C}_2\text{O}_4^{2-}$ in the 4:1 mixture in UV-Vis spectra with color changing from pale yellow to dark

yellow.

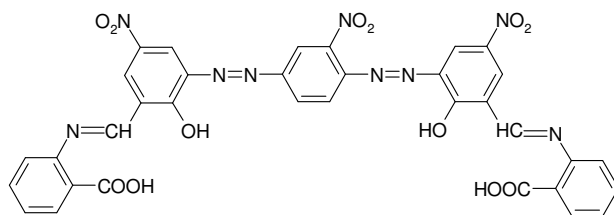


Figure 11. The structure of azo-linkage Schiff base

In the beginning of the decade, Ibrahim et al. [28] studied the corrosion inhibition of zinc sheet in 2 M H_2SO_4 by 2-[(4-Hydroxy-benzylidene)amino]benzoic acid Schiff base (figure 12) derived from condensation reaction of 4-hydroxybenzaldehyde and 2-aminobenzoic acid at room temperature using weight loss measurements. Determination of corrosion rate at 1 h immersion time with varying concentrations of the

inhibitor at room temperature was also studied. The weight loss obtained for sample A (blank sample) with initial and final weight of 3.1900 and 2.061 g respectively was 1.1294 g while for samples B, C, D and E were in the range of 0.504 – 0.076 g. The results obtained from the calculated data showed that inhibition efficiency increased when the inhibition concentration increased. Remarkably, the synthesized Schiff base showed maximum inhibition efficiency of 96.3 % at 0.1 M concentration of the inhibitor and as such the Schiff base can be used as a corrosion inhibitor.

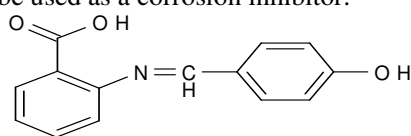


Figure 12. Structure of 2-[(4-Hydroxy-benzylidene)amino]benzoic acid

In 2021, Kaur and co-workers described the exploration of a Schiff base (figure 13) derived by condensation of 2,6-diformyl-4-methylphenol and anthranilic acid as a “Turn-ON” probe for the detection of highly toxic selenite (Se^{IV}) and arsenite (As^{III}) species in aqueous medium. The selectivity of the Schiff base towards Se^{IV} and As^{III} in the presence of other ions has been investigated using some spectrofluorimetric and ^1H NMR spectroscopic techniques [29]. The studies revealed the interaction between the Schiff base and As^{III} via deprotonation of phenolic – OH which enhanced the conjugation in phenolate ion and in turn enhanced the emission response. Noteworthy, the Schiff base has analytical prospect of quantifying As^{III} and Se^{IV} with good sensitivity (LODs: 5.15 ppb for Se^{IV} and 3.12 ppb for As^{III} calculated by $\text{S/N}=30\delta/\text{K}$. in addition, it can be used to evaluate real and synthetic Some applications of anthranilic acid-derived Schiff bases are presented in Figure 15.

samples for the presence of As^{III} and Se^{IV} species as well as fabrication of on-spot recognition devices.

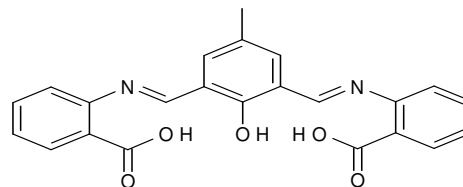


Figure 13. Schiff base obtained from 2,6-diformyl-4-methylphenol and anthranilic acid

Halz et al. (2022) reported the formation of the Schiff bases, namely, 3-[(2-carboxyphenylamino)methylidene]pentane-2,4-dione, 1, 3-[(3-carboxyphenylamino)methylidene]pentane-2,4-dione, 2, and 3-[(4-carboxyphenylamino)methylidene]pentane-2,4-dione, 3, by treating 3-formylacetylacetone with corresponding isomeric *o*-, *m*- and *p*-aminobenzoic acids (figure 14). These compounds contain a planar amino-methylene-pentane-2,4-dione core with a strong intramolecular N—H - -O hydrogen bridge. The carboxyphenyl groups attached to the nitrogen atom are almost coplanar to the central molecular fragment. Depending on the position of the carboxyl unit, different supramolecular structures with hydrogen bonding networks are formed in the three title structures [30].

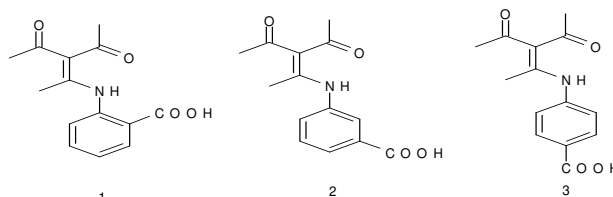


Figure 14. Schiff base of 3-formylacetylacetone with isomeric *o*-, *m*- and *p*-aminobenzoic acids

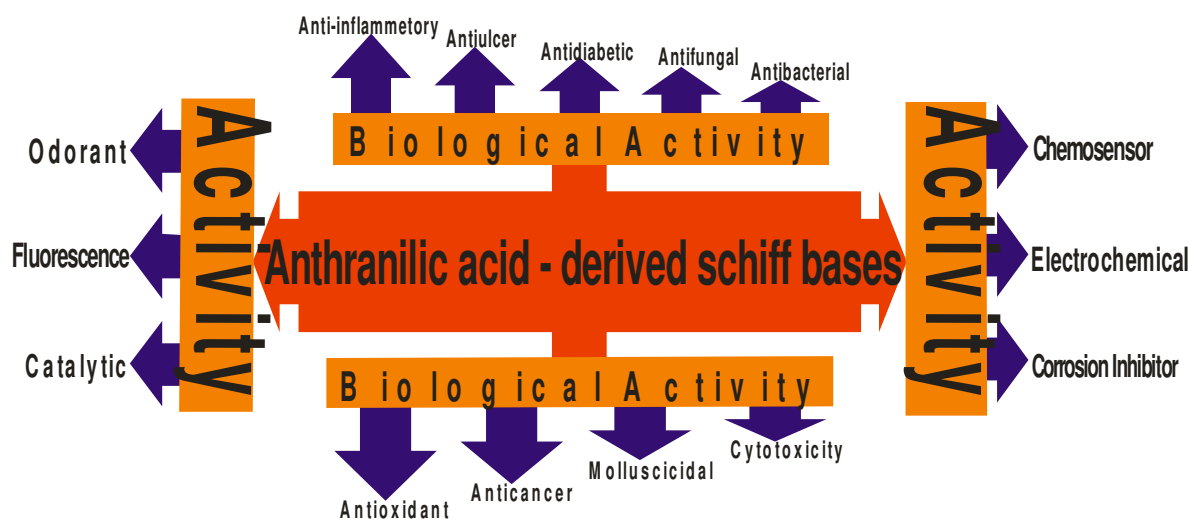


Figure 15. Schematic representation of some applications of anthranilic acid-derived Schiff bases

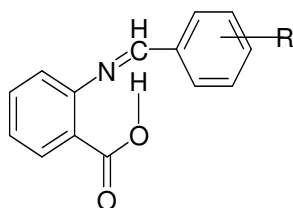
4. Schiff base complexes of anthranilic acid

Schiff bases have been used extensively in coordination chemistry because of their extraordinary synthetic and structural properties, fine tunability, and chemical selectivity of the central metal atom and coordination behavior.

They are considered the most promising ligands, due to their exceptional chelating properties with diverse geometries, ranging from N,N'-bidentate to N,N',X-tridentate and N,N',N,X'-tetradentate amongst others, to produce variety of advantageous metal complexes [31,32]. Both Schiff bases and coordination compounds have broad range of multidisciplinary applications like catalysts, pharmaceuticals, the food industry, and the dye industry, biological activities, including antifungal, antibacterial, larvicidal, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic activities [33].

4.1 Bidentate Schiff bases and their Complexes

Homo- and hetero-binuclear complexes of arylideneanthranilic acids with Cu(II), Ni(II) and Co(II) were prepared and characterized by chemical analysis, spectral and X-ray diffraction techniques as well as conductivity measurements [34]. Two types of homo-binuclear complexes were formed (figure 16). The first was formulated as $M_2L_2Cl_2(H_2O)_n$ where $M = Cu(II)$, $Ni(II)$ and $Co(II)$, $L = p$ -hydroxybenzylideneanthranilic acid (bba) and p -dimethylaminobenzylideneanthranilic acid (daba) and p -nitrobenzylideneanthranilic acid (nba); and $n=0-3$. The second type has the formula $M_2LCl_3(H_2O)_n$ in which M is the same as in first type, $L =$ benzylideneanthranilic acid (ba), (daba) (in case of Cu(II) and Ni(II)) and $n = 1 - 5$. Heteronuclear complexes having the formula $(MLCl_2H_2O)MCl_2(H_2O)_n$ were also obtained from reaction of Cu(II) binary chelates with Ni(II) and/or Co(II) chlorides.



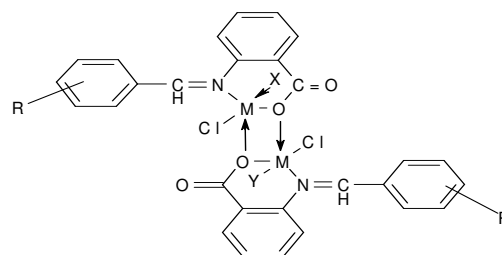
$R = p\text{-OH}$, p -hydroxybenzylideneanthranilic acid H(hba);

$R = H$, Benzylideneanthranilic acid H(ba);

$R = p\text{-N(CH}_3)_2$, p -dimethylaminobenzylideneanthranilic acid H(daba);

$R = p\text{-NO}_2$, p -nitrobenzylideneanthranilic acid H(nba).

(a)

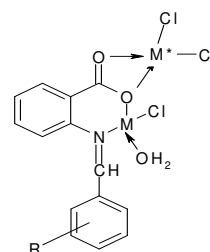


$R = p\text{-OH}$; $M = Cu(II)$, $Co(II)$, or $Ni(II)$; $X = H_2O$, $Y = H_2O$

$R = p\text{-NO}_2$; $M = Cu(II)$, $Co(II)$, or $Ni(II)$; $X = O$; $Y = O$

$R = p\text{-N(CH}_3)_2$; $M = Co(II)$; $X = H_2O$; $Y = O$

(b)



$R = H$; $M = M' = Cu(II)$, $Co(II)$, $Ni(II)$

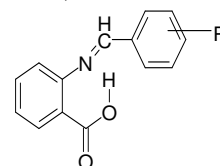
$R = p\text{-N(CH}_3)_2$; $M = M' = Cu(II)$, $Ni(II)$

$R = p\text{-OH}$, H , $p\text{-N(CH}_3)_2$ or $p\text{-NO}_2$; $M = Cu(II)$, $M' = Co(II)$ or $Ni(II)$

(c)

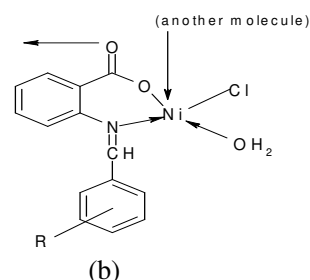
Figure 16. Structure of (a) arylideneanthranilic acid Schiff base (b) heterobinuclear complex (c) homobinuclear complex

Some binary and ternary complexes of Ni(II) with arylideneanthranilic acids and Lewis bases have been prepared and fully characterized [35]. The IR indicated that the Schiff bases act as monobasic bidentate ligands except for the ortho-hydroxy derivative which acted as a dibasic tridentate ligand. The X-ray data revealed the both binary and ternary Ni(II) chelates were isostructural (figure 17).



$R = o\text{-OH}$, L1; $R = p\text{-OH}$, L2; $R = H$, L3; $R = p\text{-N(CH}_3)_2$, L4; $R = p\text{-NO}_2$, L5

(a)



(b)

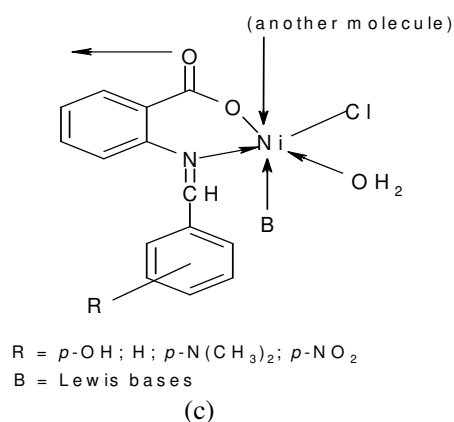


Figure 17. Structure of (a) arylideneanthranilic acid Schiff base (b) binary Ni(II) complex (c) ternary Ni(II) complex

In 1990, Parashar et al. synthesized and screened for anti-inflammatory and antiulcer activity Schiff bases derived from salicylaldehyde and 2-substituted aniline and their metal chelates with Cu(II), Ni(II), and Co(II) ions. The compound salicylidene anthranilic acid (SAA) was found to possess the anti-inflammatory and antiulcer activity. The copper complexes showed an increased antiulcer activity. The SAA is perhaps acting by influencing prostaglandin biosynthesis [36].

Similarly, Maurya et al. (1993) synthesized Schiff base derived from salicylaldehyde and anthranilic acid which was used to obtain mixed ligand complexes of copper(II) of the general formula M(SB)(L-L)(H₂O) where L-L=2'PYBZ, HOEPS or 2'APBX and SB=hbzaa 2' with respective heterocyclic organic donors in ethanol. The resulting complexes have been characterized to possess octahedral geometry [37].

In 1993, a six-coordinate vanadium(V) complex, LVO(OEt)(EtOH), where H₂L = N-(2-hydroxyphenyl)salicylideneamine was reported by Clegue et al. [38] to be a catalyst precursor in the oxidation of bromide by hydrogen peroxide in DMF solution. The oxidized bromine species is trapped by organic substrates and, by product analysis, is shown to be a two-electron-oxidized species, rather than a bromine radical. The bromination reaction is quantitative with respect to hydrogen peroxide. The acid dependence of the stoichiometry of the bromination reaction was established. Interestingly, the active catalyst was LVO(OH), which upon binding peroxide and releasing H₃O⁺, oxidized bromide and binds another equivalent of peroxide, generating the observed LVO(O₂)⁻. More so, L^{*}VO(OEt)(EtOH), where H₂L^{*} is N-(2-carboxyphenyl)salicylideneamine supported catalytic bromination reactions with dissociation of L^{*} upon the complexation of peroxide. The structures of LVO(OEt)(EtOH) and

L^{*}VO(OEt)(EtOH) have been determined by X-ray crystallography (Figure 18).

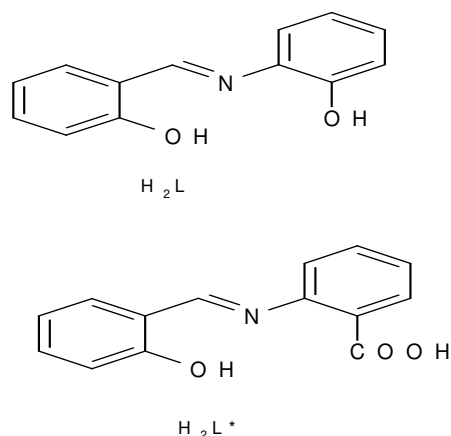


Figure 18. structure of N-(2-hydroxyphenyl)salicylideneamine (H₂L) and N-(2-carboxyphenyl)salicylideneamine (H₂L^{*})

In 1995, Thomas and Parameswaran prepared and characterized copper(II), zinc(II) and cadmium(II) complexes of the Schiff base, fluorenone anthranilic acid. The thermal decomposition kinetics and mechanism of these chelates was studied from TG data [39].

Rehina and Parameswaran (1999) synthesized Co(II), Ni(II), Cu(II) and Zn(II) complexes of two Schiff bases citronellal anthranilic acid and citronellal-5-bromoanthranilic acid (figure 19). Based on spectral, magnetic and thermal data, octahedral geometry has been assigned to the complexes [40].

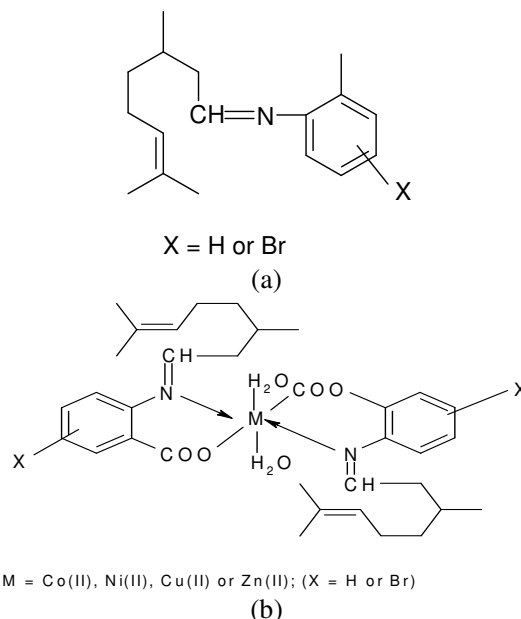
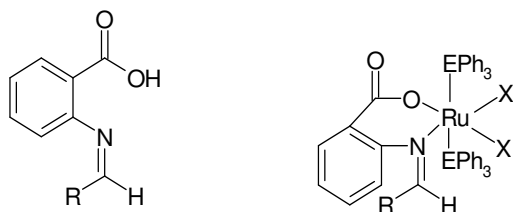


Figure 19. Structure of (a) Schiff base (b) metal complexes

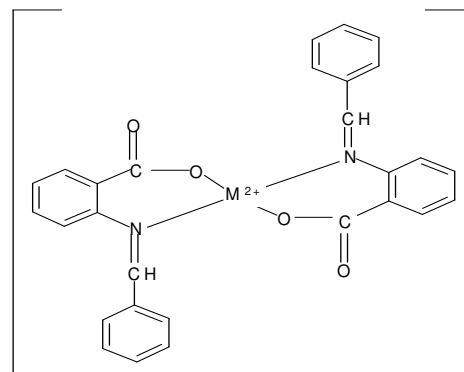
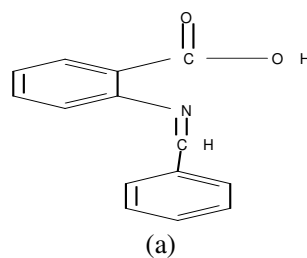
In 2002, Thangadurai and coworkers [40] reported hexa-coordinated ruthenium(III) complexes of the type $[\text{RuX}_2(\text{L})(\text{EPh}_3)_2]$ ($\text{X} = \text{Cl}$ or Br ; L = monobasic bidentate Schiff base ligand; $\text{E} = \text{P}$ or As) which have been synthesized by the reactions of $[\text{RuCl}_3(\text{PPh}_3)_3]$, $[\text{RuCl}_3(\text{AsPh}_3)_3]$, $[\text{RuBr}_3(\text{AsPh}_3)_3]$ or $[\text{RuBr}_3(\text{PPh}_3)_2(\text{MeOH})]$ with the appropriate ligands such as anthranilic acid-cinnamaldehyde (Hanthcin), anthranilic acid-*p*-tolualdehyde (Hanth-*p*-tol) and anthranilic acid-*p*-anisaldehyde (Hanth-*p*-ans) (figure 20). All of these new complexes were characterized using various physicochemical methods such as elemental analyses, spectral (IR, electronic and EPR), magnetic moment and cyclic voltammetric data. An octahedral structure has been tentatively assigned to all the complexes. The antibacterial activities of ligands and their complexes have also been determined. Among the complexes and ligands tested, the ligand Hanth-*p*-ans and the appropriate complexes have been found to be more toxic against both species of bacteria (*Enterobacteria feacalis* and *Aeromonas hydrophilla*) than the other ligands and complexes. It has also been observed that the ruthenium chelates have a higher activity than the respective free ligands against the same microorganism under identical experimental conditions.



$\text{R} = \text{CH}=\text{CH}-\text{C}_6\text{H}_5$ (Hanthcin)
 $\text{R} = \text{C}_6\text{H}_4\text{CH}_3$ (Hanth-*p*-tol)
 $\text{R} = \text{C}_6\text{H}_4\text{OCH}_3$ (Hanth-*p*-anz)

Figure 20. Structure of the ligand (left) and Ru complex (right)

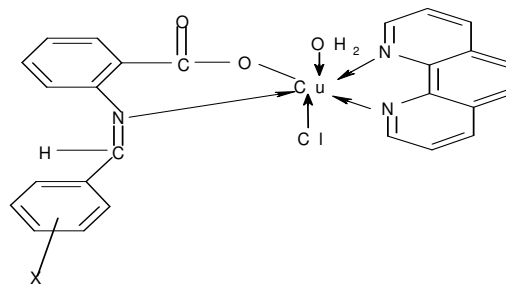
A Schiff base ligand, 2-[phenylmethylamino] benzoic acid derived from benzaldehyde and 2-aminobenzoic acid has been reported by Iqbal *et al* [42]. The synthesized ligand was further used to prepare Co(II) , Ni(II) , Cu(II) , and Zn(II) complexes, which were all characterized by IR, UV-visible, molar conductance, and magnetic moment. The IR spectra of the ligand and its complexes indicated the monoanionic bidentate nature of the ligand coordinating *via* the azomethine nitrogen and carboxylic oxygen after deprotonation. The analytical data showed the metal to ligand ratio to be 1:2 corresponding to the general formula $[\text{ML}_2(\text{H}_2\text{O})]$. The electronic spectra and magnetic moment data suggested an octahedral geometry for the complexes (Figure 20).



$\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)} \text{ and } \text{Zn(II)}$
 (b)

Figure 21. Structure of (a) Schiff base derived from benzaldehyde and 2-aminobenzoic and (b) its metal (II) complexes

Raman and Raja [43] reported the synthesis of a series of copper(II) complexes of mixed ligands with Schiff base derived from 2-aminophenol/2-aminobenzoic acid with substituted benzaldehydes and 1,10-phenanthroline. The structures were elucidated by microanalysis, magnetic susceptibility, FT-IR, UV-visible, cyclic voltammetry, ESR and mass spectroscopic analyses. The complexes were non-electrolytes. The monomeric nature of the complexes was evidenced from their magnetic moments. UV-visible and EPR spectra of the complexes suggested distorted octahedral geometry (Figure 22). The prepared compounds were tested against *Escherichia coli*, *Bacillus subtilis*, *Micrococcus luteus* and *Proteus vulgaris*. The complexes exhibit higher activity than the free ligand and control.

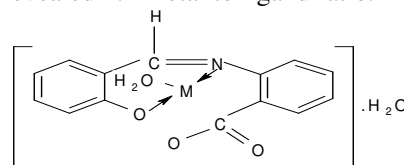


$\text{L}_4 = \text{X}=\text{H}=\text{benzylidene-2-aminobenzoic acid}$
 $\text{L}_5 = \text{X}=\text{NO}_2=3\text{-nitrobenzylidene-2-aminobenzoic acid}$
 $\text{L}_6 = \text{X}=\text{OCH}_3=4\text{-methoxybenzylidene-2-aminobenzoic acid}$

Figure 22. Structure of Cu mixed ligands Schiff base complex

In 2009, Hadi [44] synthesized Cu(II), Zn(II) and Cd(II) metal complexes of Schiff base derived from 2-amino benzoic acid and 4-(N,N-dimethylamino)benzaldehyde. The Schiff base ligand and its complexes were characterized by elemental analysis, IR and electronic spectra, molar conductance and magnetic moment measurements. It was found that the Schiff base behaves as monobasic bidentate (N,O) ligand forming chelates with 1:2 metal to ligand stoichiometry. The conductivity data were consistent with those expected for non-electrolytes. The magnetic moment and electronic spectra data suggested a square planar geometry for Cu(II) complex and tetrahedral structure for Zn(II) and Cd(II) complexes. Raman and coworkers in 2009 reported five copper(II) complexes synthesized using Schiff base ligands, obtained by the condensation reaction of anthranilic acid and Knoevenagel β -ketoanilide condensates (obtained by the condensation of acetoacetanilide and substituted benzaldehydes) [45]. The ligands and copper(II) complexes have been characterized on the basis of microanalytical, Mass, UV-Vis., IR, ^1H NMR, ESR, XRD and CV spectral studies, as well as magnetic susceptibility and conductivity data. On the basis of spectral studies, a square planar geometry has been proposed for the copper(II) complexes. From the XRD data, the CuL_1 complex has the crystallite size of 50 nm respectively. The *in vitro* antimicrobial activity of the compounds was tested against the bacteria *Escherichia coli*, *Salmonella typhi*, *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Pseudomonas aeruginosa* and fungi *Aspergillus niger*, *Rhizopus stolonifer*, *Aspergillus flavus*, *Rhizoctonia bataicola* and *Candida albicans* by well diffusion method. The complexes showed stronger antimicrobial activity than the free ligands. They represented a novel class of metal-based antimicrobial agents which provide opportunities for a large number of synthetic variations for modulation of the activities. In 2011, Aliyu and Ado [46] prepared the complexes of Mn(II) and Ni(II) with Schiff base derived from salicylaldehyde and 2-aminobenzoic acid (Figure 23). The ligand and the complexes were characterized by gravimetry, potentiometry, molar conductance and infrared analyses. The solubility test on the Schiff base and its Ni(II) complex revealed their solubility in most organic solvents except ether, acetonitrile and

tetrachloromethane. However, Mn(II) complex was insoluble in most organic solvents but soluble in dimethyl sulphoxide. The molar conductance of the complexes revealed their non-electrolytic nature. The potentiometric and spectrophotometric studies of the complexes revealed 1:1 metal to ligand ratio.



M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)

Figure 23. Proposed structure of Mn(II) and Ni(II) complexes

Aliyu and Danlami in 2012 [47] reported spectral and potentiometric studies on Mn(II) and Co(II) complexes with Schiff base derived from 2-thiophenecarboxylaldehyde and 2-aminobenzoic acid. The melting point of the Schiff base and the decomposition temperature of the complexes determined were high. The Schiff base ligand and its metal(II) complexes were soluble in common organic solvents but insoluble in water. The molar conductance of the complexes determined suggested that the complexes were non-electrolytes. The empirical formula determination of the complexes indicated the formulation of $[\text{ML}]\cdot\text{H}_2\text{O}$. The dissociation constant of the Schiff base was 6.8, indicating a weak acid. The stability constants of the complexes were high. As reported in 2012 by Iqbal et al., Mn(II), Fe(II), Co(II), Ni(II), and Zn(II) Schiff base complexes containing anthranilic acid and aldoses as part of the base were prepared and characterized by microanalytical, thermogravimetric, and spectroscopic data [48]. The complexes were found to be four-coordinate, anhydrous, and ML_2 -type. The spectral and magnetic data indicated a tetrahedral geometry for Mn(II) and Fe(II) complexes, and a planar geometry for Co(II), Ni(II), and Zn(II) complexes (figure 24). Mn(II) and Zn(II) complexes showed a significant anti-inflammatory activity against kaolin-paw edema. All the complexes exhibited selective inhibition of COX-2 in two different cell models. Earlier in 1993, the author has reported complex of Cu(II) with same Schiff bases [49].

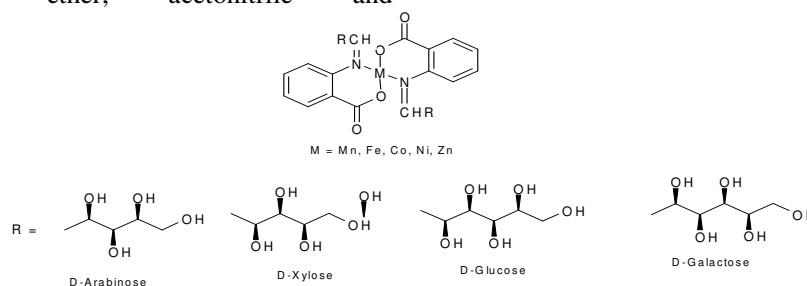


Figure 24. chemical structure of metal complexes containing Schiff base ligands derived from anthranilic acid and different aldoses

Khan et al. in 2015 [50] Organotin(IV) complexes with the general formulae R_3SnL (R = alkyl and L = Schiff base) were prepared using a novel ligand (**1**) derived from 2-aminobenzoic acid and indoline-2,3-dione; and their antibacterial activity was investigated by using the agar well diffusion methods. The synthesized compounds were capable of showing biocidal activity against *Staphylococcus aureus*. The order of increasing activities was ligand < Me_3SnL < Bz_3SnL < Ph_3SnL . The results provided evidence that the studied complexes might indeed be potential sources of antimicrobial agents. On the basis of IR, NMR (1H , ^{13}C and ^{119}Sn) spectral studies and elemental analysis, a trigonal bipyramidal geometry around the tin atom has been proposed through the oxygen atom of the ligand moiety (Figure 25).

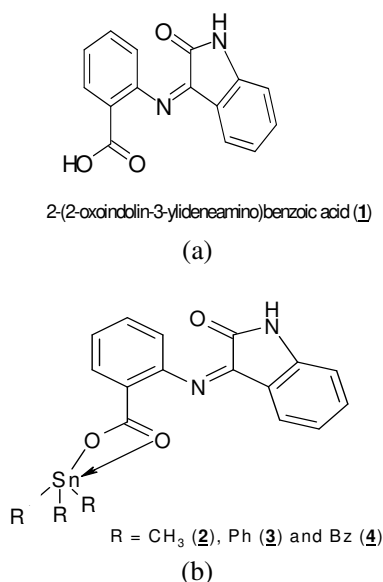


Figure 25. Schiff base from 2-aminobenzoic acid and indoline-2,3-dione (a) and its Sn(IV) complex (b)

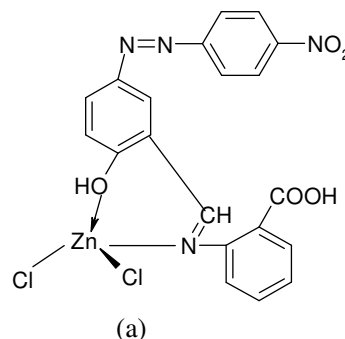
Abass et al. [51] reported the Schiff base ligands derived from Salicylaldehyde and carboxy-aniline, formaldehyde chelating resin and their Co(II) complexes. The compounds were screened for their urease, α - chymotrypsin, acetylcholinesterase and butyrylcholinesterase inhibition activities. The ligands were found active against two bacterial species: *Staphylococcus aureus* and *Escherichia coli*. All the ligands and complexes were evaluated for their thermal degradation studies using TG-DTA analytical methods in static air.

Copper(II) complex of a Schiff base ligand, (2-carboxyphenyl)-pyridine-2-yl ethylene amine, derived from refluxing ethanolic solution of 2-acetyl-pyridine and 2-aminobenzoic acid with 1, 10-Phenanthroline have been synthesized and investigated on the bases of

elemental analysis, IR, electronic spectra, magnetic susceptibility and molar conductance measurements as reported in 2016 by Rathod *et al* [52]. The Schiff base ligand coordinated to the metal ion through the carboxylate oxygen and nitrogen atom of the pyridine as well as the two nitrogen heteroatoms of 1,10-phenanthroline. The complex assumed octahedral geometry. Anticancer activity study showed that *in vitro* of cytotoxic effects on breast cancer MCF-7 cell lines of metal complex was higher than that of ligands.

Co(II), Mn(II), Cu(II) and Zn(II) Schiff base complexes of salicylaldehyde with 2-aminobenzoic acid have been synthesized from metal chlorides in alcoholic medium and characterized as reported in 2016 by Al-Nuzal and Al-Amery [53]. The structures of the Schiff base and the complexes were confirmed by various spectroscopic and physical techniques such as UV-visible FT-IR, 1H -NMR, ^{13}C -NMR, ESI-mass spectra, elemental analysis, flame atomic absorption spectroscopy, molar conductance and magnetic susceptibility measurements.

Four different azo Schiff-bases (L_1 – L_4) ligands were synthesized *via* two steps by Hasan and Murad in 2017 [54]. Firstly, Schiff bases were prepared by condensation of salicylaldehyde with anthranilic acid and 3-aminobenzoic acid. Then, diazotization of aromatic amines and their subsequent coupling reaction with Schiff bases. Treatment of the new ligands with metal salts MCl_2 , where $M = Zn(II)$, $Pb(II)$ and $Cd(II)$ gave metallic complexes of the types: octahedral $[M(L_1)_2Cl_2]$, $[M(L_2)_2Cl_2]$ and tetrahedral $[M(L_2)Cl_2]$, $[M(L_3)Cl_2]$. The ligands behaved as a monodentate and bidentate and coordinated to the central metal ions through either nitrogen atom of the hydrazine group and azo group or through oxygen atom of carboxylic group or through oxygen atoms of hydroxyl group or through azo group (figure 26). All the synthesized ligands and metal complexes were characterized by micro-elemental analysis, infrared spectroscopy, conductivity and magnetic susceptibility measurements.



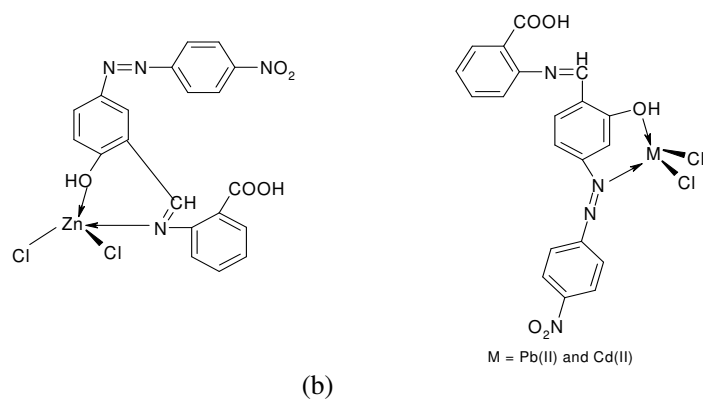


Figure 26. structure of (a) ligand (b) proposed chemical structure of complexes

In 2018, Al-Yusufy et al. [55] reported two chelating resins (Rciaa91 and Rciaa73) with different compositional chelating groups and degree of cross linking were prepared by free radical copolymerization of Schiff bases obtained from condensation reaction of cinnamaldehyde (ci) with anthranilic acid (aa) (figure 27) and 1,4-phenylenediamine (pn) monomers. The synthesized materials were characterized using CHN analyses, FTIR, $^1\text{H-NMR}$, and thermal analyses (TGA, DTA). Batch technique was applied, and the contact time, pH and initial concentration of the metal ions were investigated as factors affecting the uptake behavior. The results obtained indicated that the chelating resin with larger compositional ratio of chelating moieties and lower degree of cross-linking showed lower optimum reaction time and higher uptake affinity towards the metal ions Cu(II) , Cd(II) , Co(II) , Zn(II) , Hg(II) , and Pb(II) , under the same conditions. Both the chelating resins showed uptake behavior of the metal ions in the following order $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+}$ each metal at its optimum pH and at the same reaction time and ion concentration. The thermal degradation behavior and stability of the resins were investigated by using non-isothermal thermogravimetric analysis (TGA/DTG/DTA), at $10\text{ }^\circ\text{C min}^{-1}$ heating rate and under nitrogen. The Coats-Redfern method was used to evaluate the kinetic and thermodynamic parameters (ΔG^* , ΔH^* and ΔS^*) for the prominent degradation steps in the TGA curves at $450\text{--}660\text{ }^\circ\text{C}$ range.

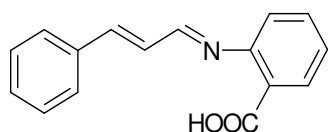


Figure 27. Structure of Schiff base ligand

Schiff base derived from o-vanillin (2-hydroxy-3-methoxybenzaldehyde) and anthranilic acid (2-aminobenzoic acid) have been synthesized and used for complexation with Mn(II) , Fe(II) and Co(II) as reported in 2018 by Pradhan et al [56]. The complexes have been

formulated as $[\text{ML}_2\text{X}_2]$, where $\text{X} = \text{pyridine}$ or $\alpha\text{-picoline}$. Infrared spectral study has been made to confirm the coordination sites of the Schiff base. The magnetic susceptibility and electronic spectral study led to tetragonally distorted octahedral symmetry (T_{4h}) of complexes (figure 28). Their biological evaluation with different strains of bacteria suggested that the complexes were more active than the ligand against both Gram-positive and Gram-negative bacteria.

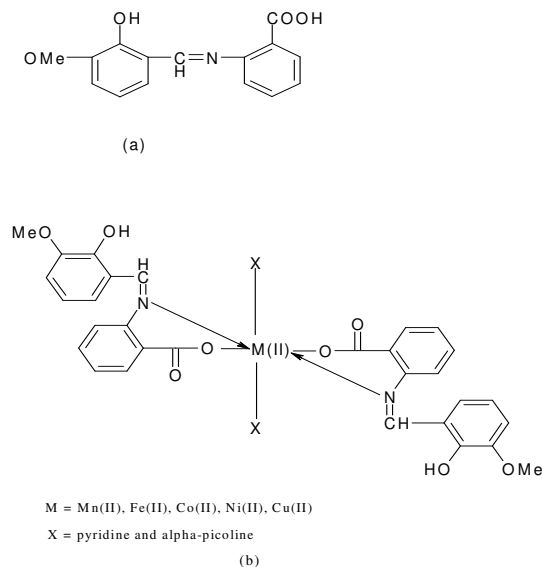


Figure 28. Proposed structure of (a) Schiff base (b) metal complexes

Bidentate azomethine ligands derived from condensation of anthranilic acid with vaniline (SL_1), furfural (SL_2), *p*-hydroxybenzaldehyde (SL_3) and *p*-nitrobenzaldehyde (SL_4) were synthesized by Alzahrani et al in 2019 [57]. These ligands were used to prepare mononuclear metal complexes using Cu(II) , Ni(II) and Zn(II) metal ions and formed square planar metal complexes with ligand to metal ratio of 2:1 (figure 29). Compounds were screened *in vitro* for antimicrobial activity using disc diffusion technique and were tested *in vivo* for molluscicidal activity against *E. vermiculata*

and snails. The ligands SL_1 and SL_3 were inactive (< 10 mm) against both bacterial types. SL_2 and SL_4 showed moderate activity (12.2 - 12.8 mm) against *S. aureus* and (14.8 - 15.6 mm) against *S. pneumoniae* Gram-positive bacterial strains and were resistant against Gram negative bacterial strains. SL_2 and SL_4 ligands showed moderate activity (11.6 - 16.4 mm) against *C. albicans* fungal strains too. While the synthesized coordination compounds showed noticeable improvement in the activity against the *C. albicans* fungal strains, and the Gram-positive bacterial species *S. pneumoniae* and *S. aureus* strains under the same conditions. $[Zn(SL_2)_2]$ and $[Zn(SL_4)_2]$ were highly active against *S. pneumoniae* bacterial species with zones of inhibition 20.4 mm and 30.2 mm respectively. Similarly, $[Zn(SL_2)_2]$ and $[Zn(SL_4)_2]$ were highly active against *C. albicans* with inhibition zones of 22.7 mm and 22.8 mm respectively. The minimum inhibition concentration (MIC)

investigation was carried out and notable susceptibility was indicated for *S. pneumoniae* bacterial strains with MIC values of 25 μ g/disc for the complex $[Zn(SL_4)_2]$. The molluscicidal activity tests showed highest activity at concentration of 0.45 mg/L for the complex $[Zn(SL_2)_2]$.

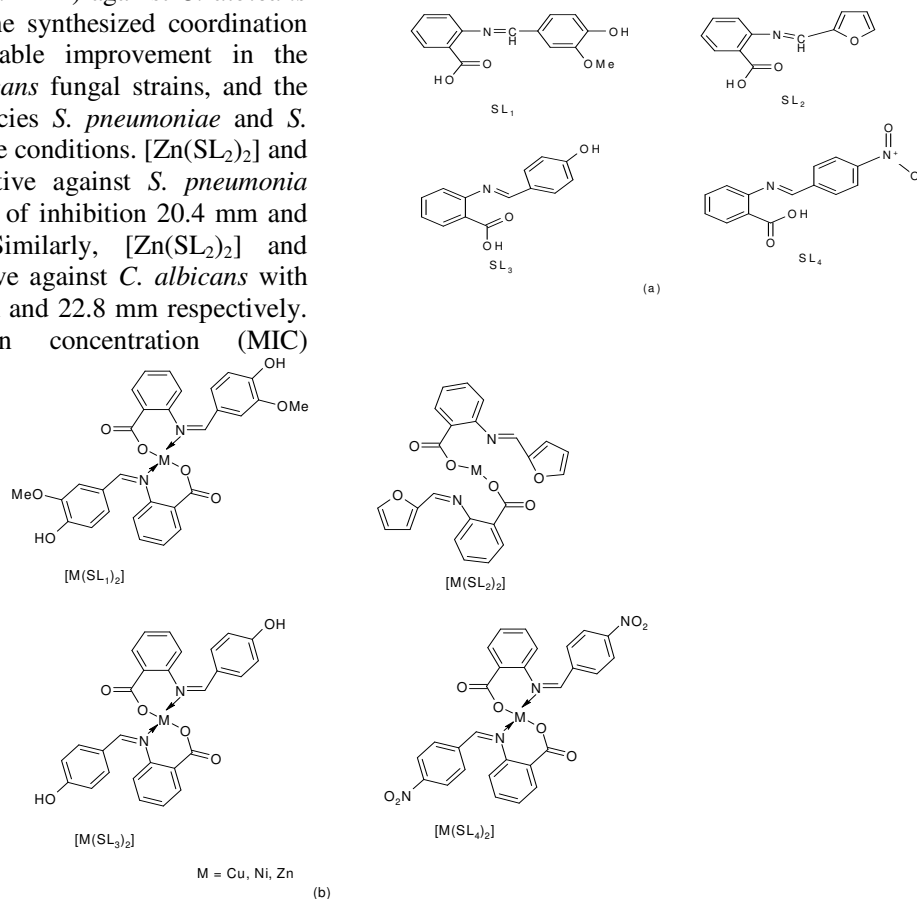


Figure 29. proposed structures of (a) ligands (b) complexes

A bidentate Schiff base, 4(1*H*-imidazole-yl)acetophenoneanthranilic acid reported a bidentate obtained by equimolar amounts of imidazoleacetophenone and 2-aminobenzoic acid under reflux has been reported in 2020 by Hussein *et al* [58]. Air stable complexes were obtained by interacting the Schiff base with Co(II), Cd(II) and Ni(II) ions (figure 30). For structure elucidation, several analytical and spectral techniques were used viz: IR, UV-visible, 1H -NMR, mass spectra as well as magnetic susceptibility measurements, elemental and thermogravimetric analyses. Magnetic moments of 3.4 and 3.8 B.M. were respectively found for the Ni(II) and Co(II) suggestive of octahedral geometry. Molar conductance measurements showed that the complexes were non-electrolyte. The *in vitro* antimicrobial screening revealed that the ligand is not active against all the tested fungal strains and some bacterial strains. However, the

complexes are active under identical experimental conditions.

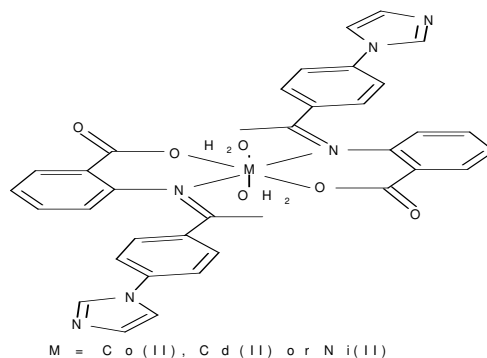


Figure 30. Proposed structure of metal complexes

Ahmad and coworkers [59] synthesized a novel Schiff base by reaction of piperonal and 2-aminobenzoic acid, which was further utilized for the synthesis of five metal complexes ultrasonically (figure 31). The products were

obtained at reduced time with high yields as compared to the conventional method of synthesis. The synthesized Schiff base and its metal complexes were characterized by UV-Visible, IR and ^1H NMR spectroscopy. The compounds were evaluated for their antibacterial and antioxidant activities. Promising antibacterial activities were recorded for these compounds against some bacterial isolates.

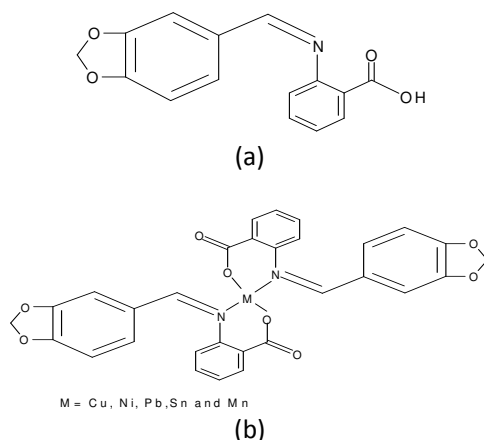


Figure 31. Structure of (a) Schiff base and (b) metal complexes

Suresh and Prakash [60] synthesized and investigated chelates of Schiff base derived from Vanillin and anthranilic acid with d-block elements such as Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). Their structures were determined on the basis of elemental analysis, infrared spectroscopy, electronic spectroscopy, thermogravimetric analyses and electron spin resonance spectroscopy (Figure 32). Molar conductivity measured revealed the 1:1 electrolytic nature for Cr(III) complexes and non-electrolytic nature for the other complexes. On the basis of the study, the coordination sites were proven to come through the nitrogen atom of azomethine and the hydroxyl group of the carboxyl group of anthranilic acid.

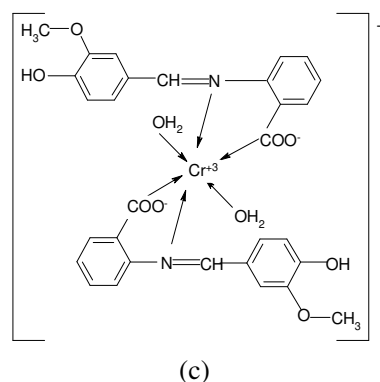
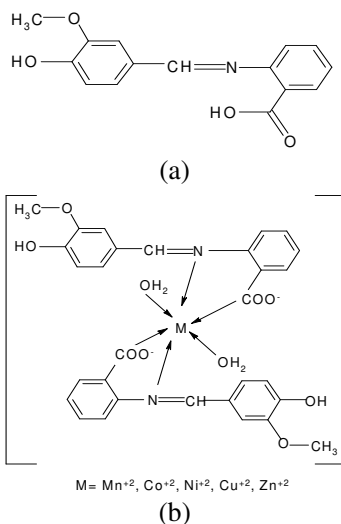
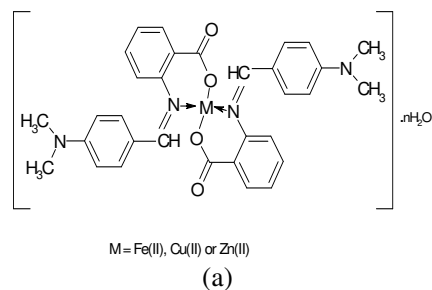


Figure 32. Proposed structure of (a) Schiff base ligand, (b) metal(II) complexes (c) metal(III) complexes

In their three different reports, Ahmed and co-workers [14,61,62] worked on a Schiff base, 2-[4-(N,N-dimethylamino)benzylidene]benzoic acid derived from condensation of 4-(N,N-dimethylamino)benzaldehyde and 2-aminobenzoic acid. The Schiff base complexes were synthesized from chloride salts of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) in an ethanolic medium, and elucidated by infrared spectroscopy, CHN microanalysis, atomic absorption spectroscopy as well as conductivity and magnetic susceptibility measurements. The metal(II) complexes were distinctly coloured solids, hydrated, non-electrolyte and thermally stable. The data from elemental analyses revealed that the stoichiometries of the synthesized complexes were of 1:2 Metal-ligand ratio type. The spectroscopic and magnetic susceptibility data revealed that Fe(II), Cu(II) and Zn(II) complexes possessed four – coordinate distorted square planar stereochemistry while Mn(II) tetrahedral geometry. On the contrary, Co(II) and Ni(II) had a six- coordinate octahedral geometry (figure 33). The Schiff base behaved as monoanionic bidentate ligand with the nitrogen atom of the azomethine ($\text{C}=\text{N}$) and carboxylate oxygen (COO^-) as donor sites. The Schiff base and its metal(II) complex were screened for antibacterial activity against *Staphylococcus aureus*, *Echerichia coli* and *Salmonellatyphi*, and antifungal activity against *Aspergillus flavus*, *Aspergillus niger* and *Aspergillus fumigatus*. All the complexes showed significant bactericidal and fungicidal activities against the tested organisms.



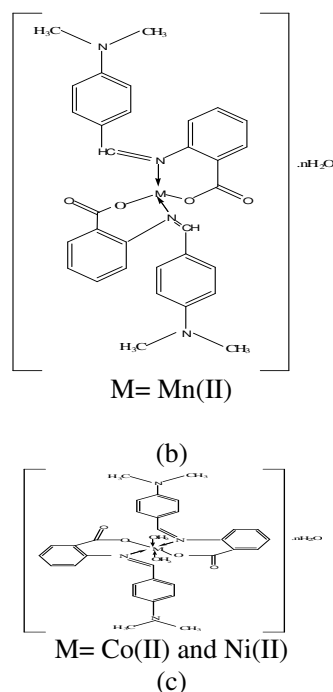


Figure 33. Geometries of the metal(II) complexes : (a) distorted square planar, (b) tetrahedral (c) octahedral

In 2021, nickel(II) complex of a Schiff base derived from 4-methoxybenzaldehyde and 2-aminobenzoic acid have been reported by Ahmed et al. [63]. The Schiff base ligand and the complex were appropriately characterized by melting point, solubility, conductance measurement, water content and infrared spectroscopy. Both the Schiff base ligand and complex were solid, air, and moisture stable. The ligand melted at 210 °C whereas the complex has high thermal stability with decomposition temperature > 340 °C. The FT-IR spectra revealed the coordination of the Schiff base *via* azomethine nitrogen and deprotonated hydroxyl oxygen of the carboxyl group, hence rendering the ligand monobasic bidentate with ON coordination sites. Moreover, the FT-IR and thermo-analytical data confirmed the presence of water lattice in the complex. Accordingly, a square planar structure was proposed for the complex (Figure 34).

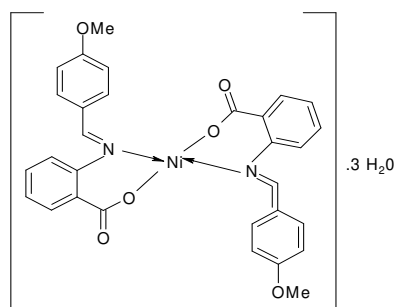


Figure 34. Proposed structure of the Ni(II) complex

Adamu et al. [64] worked on a Schiff base ligand synthesized by the condensation of 2-aminobenzoic acid and benzaldehyde. Metal complexes of the Schiff base were prepared by the reaction of the Schiff base and metal(II) chlorides of copper and zinc in ethanol. The compounds were characterized by solubility test, melting point/decomposition temperature, molar conductance, magnetic susceptibility, FT-IR, metal-ligand ratio determination and UV-Visible Spectrophotometry. Conductivity measurement values indicated the non-electrolytic nature of the metal complexes. Job's method of continuous variation suggested 1:2 metal-ligand ratio (figure 35). The *in-vitro* antibacterial activity carried out on *Staphylococcus aureus*, *Streptococcus pneumoniae*, *E. coli* and *Klebsiella pneumoniae* revealed that the metal complexes exhibited higher activity than the Schiff base. The result for the antifungal screening revealed that the Schiff base and Zn(II) complex showed appreciable activity against *Aspergillus fumigatus* and *Aspergillus flavus* whereas the Schiff base and Cu(II) complex were found to be inactive at all concentration against *Candida albicans*. The cytotoxic results showed that the Schiff base and Zn(II) complex were highly toxic with LC₅₀ values of 63.191 μg/mg and 76.684 μg/mg while Cu(II) complex was non-toxic with LC₅₀ of 1175.79 μg/mg.

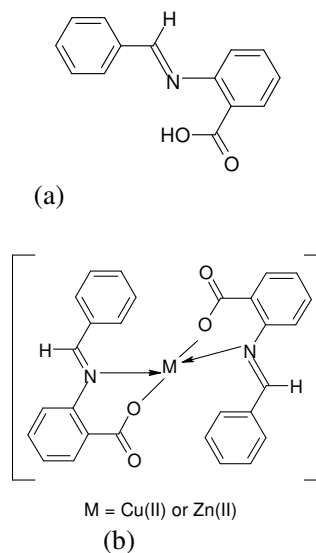


Figure 35. Structure of (a) Schiff base and (b) metal complexes

The antibacterial activity of some Schiff base chelates (figure 36), where the Schiff bases were obtained by condensation process of 2-hydroxyacetophenone with tyrosine as the main ligand (HL¹) and 4-dimethylaminobenzaldehyde with 2-aminobenzoic acid as a secondary ligand (HL²) against five pathogenic bacteria species, like *Staphylococcus aureus* and *Enterococcus faecalis*, *Pseudomonas aeruginosa*,

Klebsiella sp. and *Escherichia coli* using the agar well diffusion assay was reported in 2021 by Al-braki et al [65]. Schiff base HL¹ exhibited the higher antibacterial activity than Schiff base HL² against all the bacterial species. The chelates of Ni(II) and Zn(II) ions showed a good inhibitory effect against all the tested bacterial species while the chelates Co(II), Cu(II) and Fe(III) ions did not reveal any effect on all tested bacteria. Schiff base HL¹, Ni(II) and Zn(II) chelates were the most effective compounds that showed bacteriostatic and bactericidal activities against all the tested pathogenic bacteria species with MIC ranged from 3.1 to 25 mg/ml and MBC from 6.2 to 50 mg/ml.

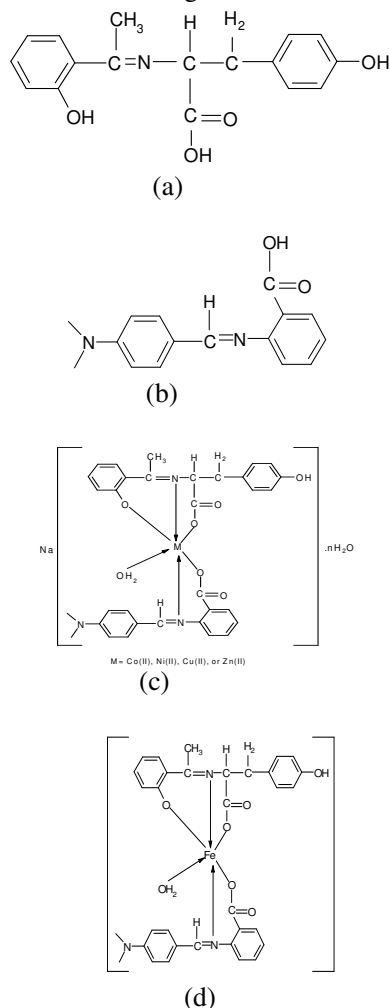


Figure 36. Structure of Schiff base (a) HL¹ (b) HL² (c) and (d) Schiff base chelates

Imran et al. [66] reported the condensation reactions of biacetyl with ortho-hydroxyaniline and 2-aminobenzoic acid to bidentate NO donor Schiff base. The prepared Schiff base ligands were further utilized for the formation of metal chelates having the general formula [ML₂(H₂O)₂] where M= Co(II), Ni(II), Cu(II) and Zn(II) and L=HL¹ and HL². These new compounds were characterized by conductance measurements, magnetic

susceptibility measurements, elemental analysis and IR, ¹H NMR, ¹³C NMR and electronic spectroscopy. Both Schiff bases were found to have mono-anionic bidentate nature and octahedral geometry was assigned to all the complexes (Figure 37). These compounds were also screened for their *in vitro* antibacterial activity against four bacterial species, namely *Escherichia coli*, *Staphylococcus aureus*, *Salmonella typhi* and *Bacillus subtilis*. The metal complexes were found to have greater antibacterial activity than the Schiff base ligands.

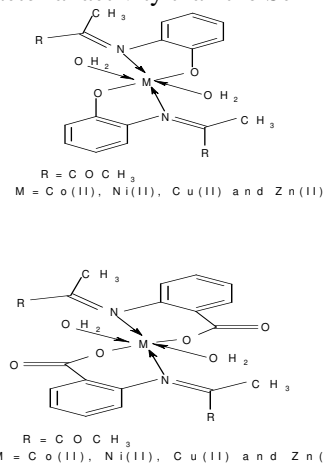
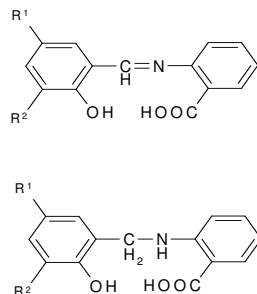


Figure 37. Proposed structures of metal complexes with HL¹ and HL²

4.2 Tridentate Schiff bases and their Complexes

Poly(5-vinyl salicylidene anthranilic acid) homopolymer and polymer complexes of 5-vinyl salicylidene anthranilic acid with some transition metal salts have been prepared and characterized by Diab et al [67]. In 1990 and 1992, Hassaan reported Ni(II) and Fe(III) complexes, respectively of Schiff bases derived from isatin or chromone with glycine, β -alanine, anthranilic acid, S-methyl hydrazine carbodithioate, ammonium salt of hydrazine carbodithioate, thiosemicarbazide, semicarbazide and benzoyl hydrazine; and 6-formyl-7-hydroxy-5-methoxy-2-methyl chromonolide S-methyl hydrazine carbodithioate and benzoyl hydrazine. Characterization of these compounds was achieved by elemental analysis, IR, UV-visible spectra and magnetic moment measurements. Octahedral structures have been assigned to the complexes [68,69]. Organotin(IV) complexes of dibasic tridentate ligand N(salicylidene)anthranilic acid have been synthesized in different metal-ligand ratios. These compounds were characterized using elemental analyses, IR, ¹H NMR, and ¹¹⁹Sn NMR spectral analysis by Rao and wankhade in 1995 [70]. Copper(II) complexes of N-salicylideneanthranilic acid (I) and its derivatives (II, III) as well as their NaBH₄ reduction products, namely N-(2-hydroxybenzyl) anthranilic acids (IV-VI) have been prepared and their structures have been determined analytically. Tetra-coordinated planar

structures of the Cu(II) complexes of the Schiff bases and distorted tetrahedral structures of the Cu(II) complexes of compounds V-VI have been elucidated by ESR and other spectral methods (figure 38). During the preparation of the complex the hydrolysis of the Schiff base often takes place in the presence of water giving anthranilates and salicylaldehydes of metals to some extent along with the complexes of the Schiff base. The kinetic data for the hydrolysis of N-salicylideneanthranilic acid (I) in methanol-water solution also are reported by Taşcıoğlu and Ismailov in 1996 [71].



Where:

	I, IV	II, V	III, VI
R ¹	H	Br	Br
R ²	H	H	Br

Figure 38. Structure of N-Salicylideneanthranilic acid

Anhydrous, dimeric vanadyl(IV) complexes of Schiff bases derived from [1 + 1] condensation of salicylaldehyde (or its derivatives) and anthranilic acid, have been synthesized from CH₃CN and were characterized by elemental analysis, FTIR, EPR, absorption, TGA, cyclic voltammetry and room temperature magnetic susceptibility measurements as reported by Asgedom et al in 1997 [72]. These complexes were found to be oxidized by air in polar solvents like MeOH and DMF to V^V products. The E_{1/2} values were found to be around 660 mV indicating that the carboxylate group favours vanadyl(IV) binding when compared to the alkoxo-bound vanadium complexes. Oxidative instability of these complexes were dependent on the substituent on the salicylaldehyde ring and follow an order: 5,6-benzo > H ≥ 3-OMe in MeOH and DMF. Attempted recrystallization of the dimeric vanadyl(IV) complex

from pyridine led to products of oxidation, polymerization and loss of Schiff base ligand. Single crystal X-ray diffraction showed the oxidation product to be a decavanadate with the pyridinium counter cation, [C₅NH₆]₆V₁₀O₂₈·2H₂O. When the dinuclear vanadyl(IV) complex was recrystallized from MeOH, it gave a product of mononuclear carboxylate bound octahedral VO³⁺ moiety along with the presence of both MeOH and OMe units in the coordination sphere with a formula, VO(L)(OMe)(MeOH), where L = 1+1 Schiff base derived from 5,6-benzosalicylaldehyde and anthranilic acid, as studied through single crystal X-ray diffraction. The structures are shown in figure 39.

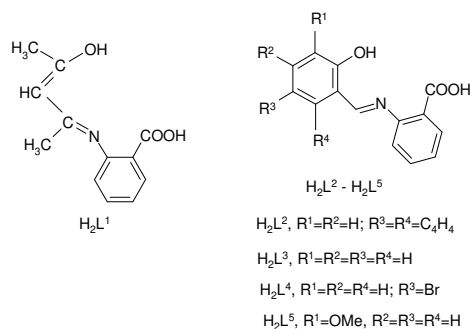


Figure 39. Structure of Schiff bases

In 2002, Jayabalakrishnan et al prepared a hexa-coordinated ruthenium(II) complexes of the type [Ru(CO)(PPh₃)(Z)(L)] {Z=PPh₃, pyridine (py) or piperidine (pip); L= anion of the Schiff base} by reacting [RuHCl(CO)(PPh₃)₂(Z)] with tridentate Schiff bases derived by condensing anthranilic acid with acetylacetone, salicylaldehyde, *o*-vanillin and *o*-hydroxyacetophenone (figures 40 and 41). The complexes were characterized by analytical and spectral (IR, electronic, ¹H- and ³¹P-NMR.) data. Interestingly, they were found to be effective catalysts for oxidising primary alcohols to aldehydes in the presence of N-methylmorpholine-N-oxide (NMO) as co-oxidant. The Schiff bases and their ruthenium(II) complexes showed growth inhibitory activity against pathogenic fungi *Aspergillus flavus*, *Fusarium oxysporium* and *Rhizoctonia solani* [73].

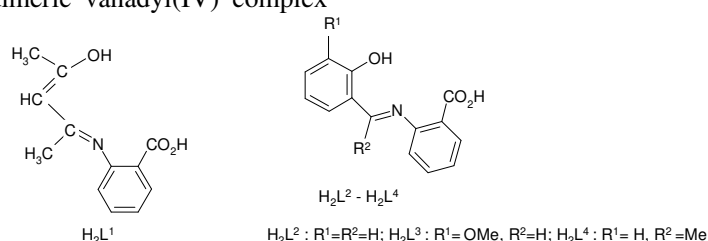
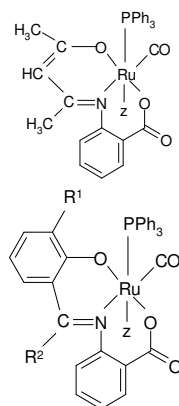


Figure 40. Structure of Schiff bases



Where R^1 , R^2 and Z are as previously defined.

Figure 41. Proposed structures of the Ru^{II} Schiff base complexes

In 2005, Mohamed et al. [74] synthesized metal complexes of Schiff base derived from 2-thiophenecarboxaldehyde and 2-aminobenzoic acid (HL); and characterized based on elemental analyses, IR, 1H NMR, solid reflectance, magnetic moment, molar conductance and thermal analysis (TGA). The ligand dissociation as well as the metal-ligand stability constants were calculated pH metrically at 25 °C and ionic strength $\mu = 0.1$ (1 M NaCl). The molar conductance data revealed that Fe(III) and Co(II), Ni(II) and $VO_2(II)$ chelates are ionic in nature and are of the type 3:1 and 2:1 electrolyte, respectively, while Cu(II) and Zn(II) complexes are non-electrolytes. IR spectra showed that HL coordinated to the metal ions in

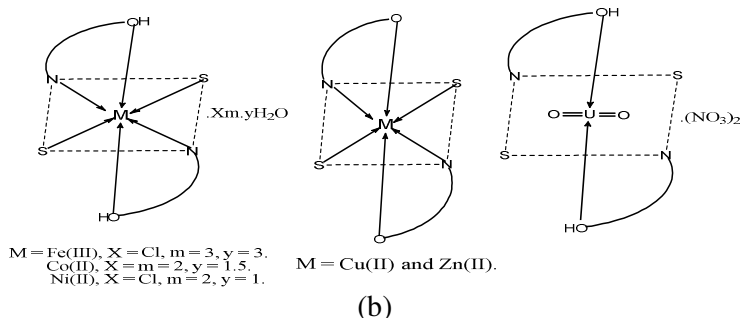


Figure 42. Structural formulas of (a) Schiff base (b) HL-metal complexes

Metal complexes of Schiff base derived from 2-furancarboxaldehyde and 2-aminobenzoic acid (HL) are reported and characterized in 2006 by Omar et al [75] based on elemental analyses, IR, 1H NMR, UV-Vis, solid reflectance, magnetic moment, molar conductance and thermal analysis (figure 43). The ligand dissociation as well as the metal-ligand stability constants have been calculated pH-metrically at 25 °C and ionic strength $\mu=0.1$ (1 M NaCl). The complexes were found to have the formulae $[M(HL)_2](X)_n \cdot yH_2O$ (where $M=Fe(III)$ ($X=Cl$, $n=3$, $y=4$), $Co(II)$ ($X=Cl$, $n=y=2$), $Ni(II)$ ($X=Cl$, $n=y=2$), $Cu(II)$ ($X=Cl$, $n=y=2$) and $Zn(II)$ ($X=AcO$, $n=y=2$)) and $[UO_2(L)_2] \cdot 2H_2O$. The thermal behaviour of

a terdentate manner with ONS donor sites of the carboxylate O, azomethine N and thiophene S. From the magnetic and solid reflectance spectra, it was found that the geometrical structure of these complexes were octahedral (figure 42). The metal complexes showed a good antibacterial activity against *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus pyogenes*. Fe(III), Cu(II), Zn(II) and $UO_2(II)$ complexes caused inhibition for *E. coli*. The importance of this lies in the fact that these complexes could be applied fairly in the treatment of some common diseases caused by *E. coli*. However, Fe(III), Co(II), Cu(II), Zn(II) and $UO_2(II)$ complexes were specialized in inhibiting Gram-positive bacterial strains (*Staphylococcus pyogenes* and *P. aeruginosa*). The importance of this unique property of the investigated Schiff base complexes lies in the fact that, it could be applied safely in the treatment of infections caused by any of these particular strains.

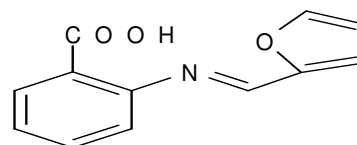
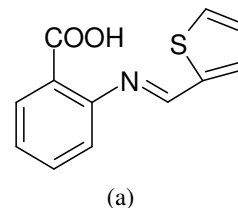


Figure 43. Structure of Schiff base ligand

Abbas in 2007 obtained a Schiff base LH₂ (figure 44) by condensation of salicylaldehyde with anthranilic acid and have been reacted with AlCl₃.6H₂O in neutral and basic medium. A cationic complex formulated as [M(LH₂)Cl] separated out. The characterization of the complex was carried out by use of infrared spectrophotometer and molar conductivity [76].

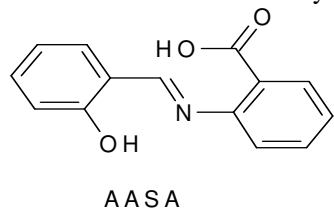


Figure 44. Structure of Schiff base

A series of oxovanadium complexes with mixed ligands, a tridentate ONO-donor Schiff base ligand [viz., salicylidene anthranilic acid (SAA)], and a bidentate NN ligand [viz., 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), dipyrdo[3,2-d:20,30-f]quinoxaline (dpq), dipyrdo [3,2-a:20,30-c]phenazine (dppz), or 7-methyldipyrdo[3,2a:20,30-c]phenazine (dppm)], have been synthesized and characterized by elemental analysis, electrospray ionization mass spectrometry, UV-vis spectroscopy, Fourier transform IR spectroscopy, EPR spectroscopy, and X-ray crystallography [77]. Crystal structures of both complexes, [V^{IV}O(SAA)(bpy)].0.25bpy and [V^{IV}O(SAA)(phen)]. 0.33H₂O, revealed that oxovanadium(IV) is coordinated with one nitrogen and two oxygen atoms from the Schiff base and two nitrogen atoms from the bidentate planar ligands in a distorted octahedral geometry (VO₃N₃) (figure 45).

The oxidation state of V(IV) with *d*¹ configuration was confirmed by EPR spectroscopy. The speciation of VO-SAA-bpy in aqueous solution was investigated by potentiometric pH titrations, and the results revealed that the main species are two ternary complexes at a pH range of 7.0–7.4, and one is the isolated crystalline complex. The complexes have been found to be potent inhibitors against human protein tyrosine phosphatase 1B (PTP1B) (IC₅₀ approximately 30–61 nM), T-cell protein tyrosine phosphatase (TCPTP), and Src homology phosphatase 1 (SHP-1) in vitro.

Interestingly, the [VIVO(SAA)(bpy)] complex selectively inhibits PTP1B over the other two phosphatases (approximate nine-fold selectivity against SHP-1 and about twofold selectivity against TCPTP). Kinetics assays suggest that the complexes inhibit PTP1B in a competitive and reversible manner. These suggest that the complexes may be promising candidates as novel antidiabetic agents.

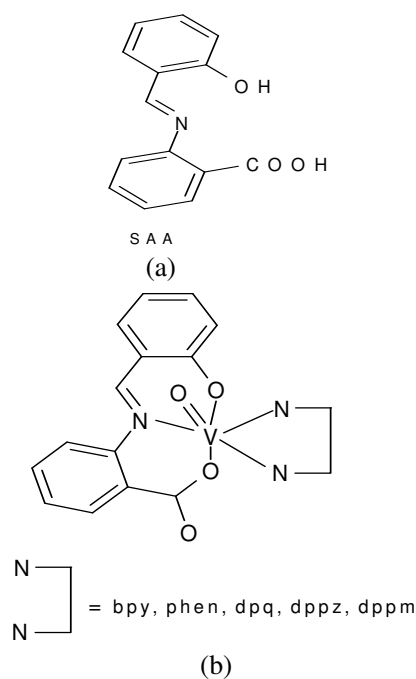
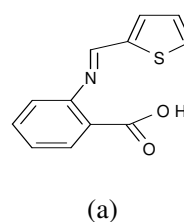


Figure 45. Structure of (a) Schiff base and (b) mixed ligand complexes

In 2009, Saghatforoush et al. reported tridentate Schiff base ligands prepared by the condensation reaction of anthranilic acid with salicylaldehyde, furfural, thiophen-2-carboxaldehyde and pyridine-2-carboxaldehyde in ethanol. Cobalt(II) complexes of related Schiff base ligands were prepared by the reaction of the respective ligand with cobalt(II) acetate [78]. The prepared ligands and oxalato-bridged cobalt complexes have been characterized by UV-vis, IR and ¹H NMR spectral data and elemental analysis. In all the cobalt(II) complexes, the central metal has five coordination number and coordinated by a tridentate Schiff base ligand and two oxygen atoms of the oxalate ligand (figure 46). The electrochemical properties of four Schiff base complexes have been investigated in the presence of tetrabutyl ammonium perchlorate as supporting electrolyte and by using a glassy carbon (GC) electrode. It has been found that all the cobalt complexes showed Co(II) oxidation process irreversibility. Cyclic voltammetry studies indicated that these processes are diffusion-controlled reactions. The obtained data from cyclic voltammetry and chronoamperometry studies showed that, the total limiting current of each of the studied compounds corresponds to one-electron transfer process.



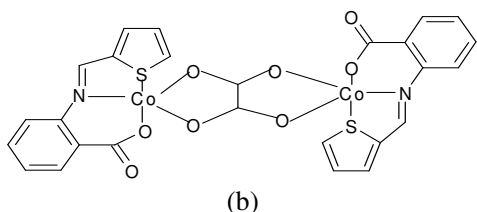
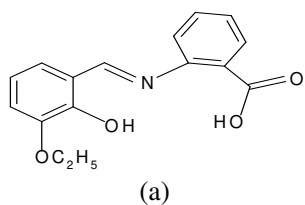


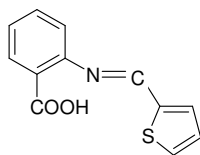
Figure 46. Structure of (a) Schiff base derived from thiophen-2-carboxaldehyde (b) metal complex

In 2010, Mounika et al. [79] synthesized a new Schiff base, 3-ethoxy salicylidene aminobenzoic acid (ETSAN) from 3-ethoxysalicylaldehyde and 2-aminobenzoic acid. Ni(II), Co(II), and Zn(II) complexes of the Schiff base ligand were synthesized from metal(II) nitrate/chloride in an alcoholic medium. The chemical structures of the Schiff base ligand and its metal complexes were confirmed by various spectroscopic techniques such as IR, UV-visible, ^1H NMR, ^{13}C NMR, electrospray ionization (ESI) - mass spectra, elemental analysis, molar conductance, thermogravimetric studies and magnetic susceptibility measurements. Elemental analysis showed 1:1 Metal to ligand ratio. Molar conductance value revealed non-electrolytic nature of the complexes. The IR spectra show that the ligand is tridentate coordinating to each metal atom through azomethine nitrogen and oxygen atoms of hydroxyl group of 3-ethoxy salicylaldehyde. Besides, the hydroxyl group of the carboxyl group of 2-aminobenzoic acid (Figure 47).

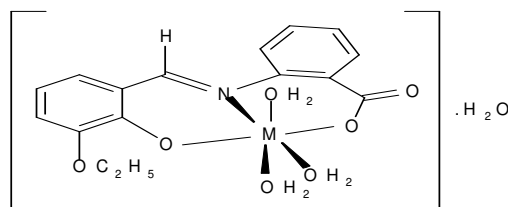
The mass spectra data confirmed the monomeric structure of the metal complexes while the thermogravimetric analysis (TGA) confirmed the presence of water molecule in the complexes. The free ligand and its complexes were tested for their antibacterial and antifungal activity by using disc diffusion method. The complexes showed enhanced activities compared to the free ligand.



(a)



(b)

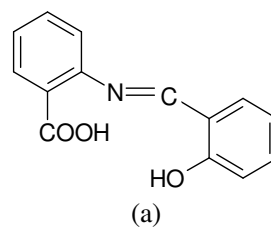


M = Ni(II), Co(II), Cu(II) or Zn(II)

(b)

Figure 47. Structure of (a) Schiff base derived from 3-ethoxysalicylaldehyde and 2-aminobenzoic acid and its (b) metal(II) complexes

El-Shafiey and coworkers in 2010 prepared two Schiff base ligands of organic acid moiety, viz., N-(2-carboxyphenyl) salicylideneimine, (H_2L^1) and N-(2-carboxyphenyl) thiopheneimine, (HL^2) by the interaction of salicylaldehyde and 2-thiophenecarboxaldehyde with 2-aminobenzoic acid. Co(II), Ni(II), Cd(II), Fe(III) and $\text{UO}_2(\text{II})$ complexes of these ligands have been prepared [80]. Also, the ternary complexes were prepared by using pyridine (Py) as a secondary ligand. All synthesized compounds were identified and confirmed by elemental analysis, molar conductance, IR, ^1H NMR, UV-Vis, mass spectra, magnetic measurements, and thermal analysis. The molar conductance data revealed that these complexes are non – electrolytic, 1:1 and 1:2 electrolytic nature of the metal complexes. The ligands are coordinated to the metal ions in a terdentate manner with ONO/ONS donor sites of the carbonyl oxygen, azomethine nitrogen and phenolic oxygen or thiophenic Sulphur (figure 48). An octahedral structure was proposed for the prepared metal complexes. The synthesized ligands, in comparison to their metal complexes also were screened for their antibacterial activity against bacterial species, *Bacillus cereus*, *Bacillus subtilis* and *Escherichia coli*. The activity data showed that some of the metal complexes were more potent antibacterial than the parent organic ligands against one or more bacterial species.



(a)

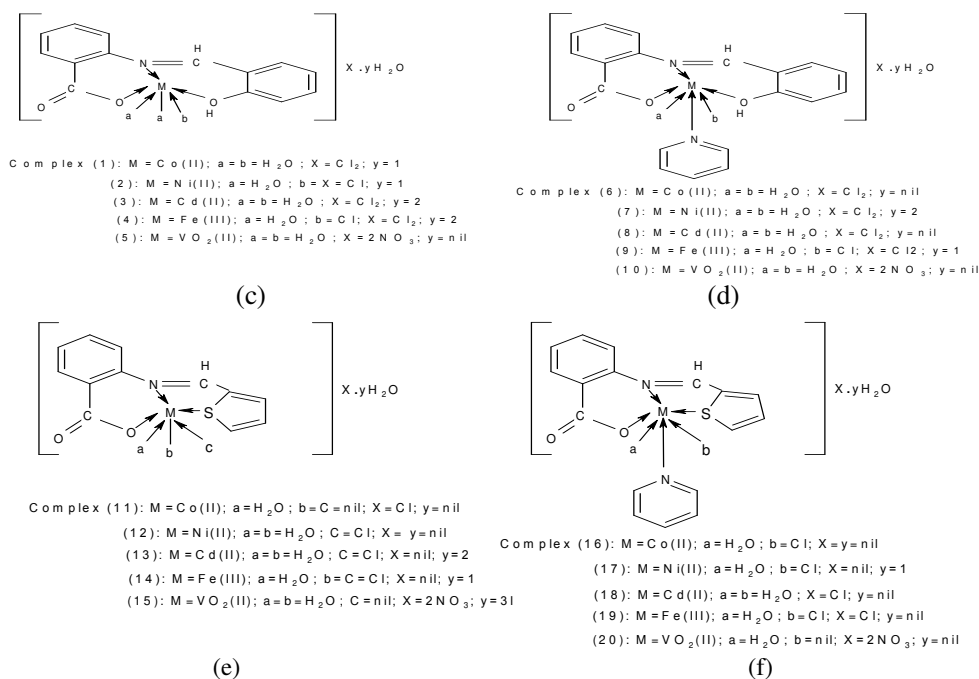


Figure 48. suggested structure of (a) N-(2-carboxyphenyl) salicyldeneimine, HL^1 (b) N-(2-carboxyphenyl) thiopheneimine, HL^2 (c) binary complexes H_2L^1 (d) ternary complexes of H_2L^1 ligand (e) binary complexes of HL^2 (f) ternary complexes of HL^2 ligand

In 2011, Singh et al. [81] reported a solid complex of Ni(II) with tetradentate Schiff base (PDMBA) derived from *p*-dimethylaminobenzaldehyde and *o*-aminobenzoic acid. Characterization by molar conductivity, elemental analysis, IR, ^1H NMR, magnetic susceptibility, electronic spectra and X-ray diffraction demonstrated a 1:1 metal-ligand stoichiometry for the complex with a formula $[\text{Ni}(\text{PDMBA})\text{H}_2\text{O}]$. A monobasic tetradentate behavior of the ligand with N,N,O,O' donor sites was ascertained from IR spectral data. Paramagnetic and non-ionic behavior of the complex were respectively observed from the results of magnetic susceptibility and conductivity molar measurements. The structures of these compounds are shown in Figure 49.

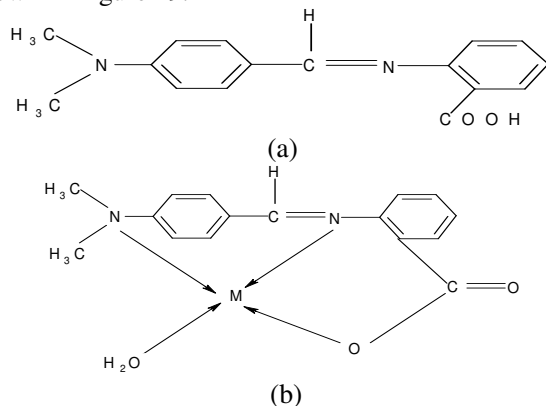


Figure 49. Structure of (a) Schiff base derived from *p*-dimethylaminobenzaldehyde and (b) its Ni complex
 Ciolan et al [82] synthesized new Schiff base, H_2L ($\text{C}_{31}\text{H}_{26}\text{O}_6\text{N}_2$), starting from a dialdehyde, [1,3-bis(2'-

formylphenyl)1,3-dioxapropane] and 2-aminobenzoic acid. Corresponding metal complexes of Cu(II), Ni(II) and Co(II) were also prepared. The structure of the Schiff base was characterized using spectroscopic data and by elemental analysis. The complexes of $[\text{M}_2\text{L}(\text{OH})_2(\text{H}_2\text{O})_4]$ type, where $\text{M} = \text{Cu(II)}$, Ni(II) or Co(II) , were characterized using the data obtained from elemental analyses, molar conductance, IR and electronic spectra, magnetic susceptibility measurements and thermal analysis. These studies support the binuclear formulations of the complexes, of M(II):L (2:1) type (figure 50).

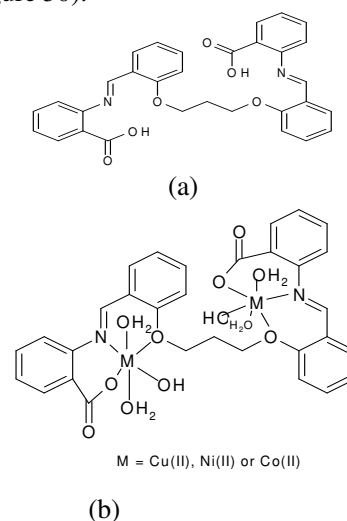


Figure 50. Structure of (a) dialdehyde Schiff base 1,3-bis[ortho-(2-carboxy-phenyliminomethyl)-phenoxy]propane (b) proposed structure of its complexes

In 2013, Jarad and coworkers [83] produced a Schiff base ligand, benzoic acid-2-salicylidene (L) by reacting 2-aminobenzoic acid with salicylaldehyde in ethanolic medium. Complexation of the Schiff base ligand (L) with Co(II), Ni(II), Cu(II) and Zn(II) metal ions in 1:1 M-L ratio in aqueous ethanol at optimum pH yielded a series of neutral complexes with the general formula $[M(L)H_2O]$ (Figure 51). The complexes were characterized by flame atomic absorption, elemental analysis, FT-IR and UV-Visible spectroscopic methods, as well as magnetic susceptibility and conductivity measurements. From the data obtained, tetrahedral structure was suggested for all the complexes prepared.

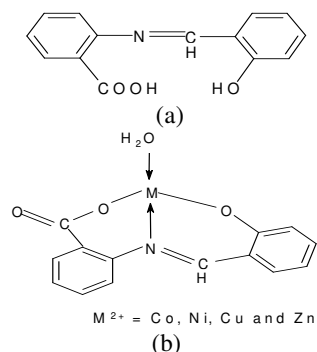


Figure 51. Structure of (a) Schiff base derived from salicylaldehyde and 2-aminobenzoic acid and (b) its metal complexes

Three oxovanadium complexes, namely $[VO(NOSAA)(bpy)]$, (NOSAA = 2-hydroxy-5-nitrosalicylidene anthranilic acid, bpy = 2,20-bipyridyl), $[VO(NOSAA)(4,40-dimebpy)]$, (4,40-dimebpy = 4,40-dimethyl-2,20-bipyridyl), and $[VO(NOSAA)(phen)]$ (phen = 1, 10-phenanthroline), have been prepared and characterized by Lu et al in 2013 [84]. The binding modes and strengths of these complexes with calf thymus DNA (CT-DNA) were studied using various techniques. The chemical nuclease activities and photocleavage reactions of the complexes were also tested. All three complexes interact with CT-DNA through intercalative modes, and complex $[VO(NOSAA)(phen)]$ possesses the largest binding affinity. All three complexes can efficiently cleave pBR322 DNA upon irradiation or under physiological conditions in the presence of H_2O_2 , and complex $[VO(NOSAA)(phen)]$ has the best cleaving ability. In vitro experimental results showed that the three complexes are cytotoxic against myeloma (Ag8.653) and gliomas (U251) cell lines and complex $[VO(NOSAA)(phen)]$ again showed the highest efficacy. Mononuclear complexes $[ML_2]^0$ ($M = Co, Ni, Zn$; HL – Schiff base ligand formed in situ from 2-pyridinecarbaldehyde and anthranilic acid, AA) interacted with AA molecules to produce $CoL_2 \cdot AA \cdot H_2O$ (1), $NiL_2 \cdot AA \cdot H_2O$ (2) and

$ZnL_2 \cdot AA \cdot 0.25CH_3OH \cdot 0.5H_2O$ (3) cocrystals as reported by Buvaylo et al in 2014 [85]. Compounds 1–3 have been obtained as single crystals and characterized by elemental analysis, IR spectroscopy, thermal analysis, and single-crystal X-ray diffraction techniques (Figure 52). The compounds crystallize in the triclinic space group 1 P, with 1 and 2 being isomorphous. Neutral ML_2 molecules in 1–3 showed no crystallographically imposed symmetry with the metal atoms octahedrally surrounded by two anionic ligands in a *mer* configuration. Of the two crystallographically distinct AA molecules, one molecule only is engaged in H-bonding $N/O-H \cdots O$ interactions with ML_2 units. The solid-state organization of the cocrystals was described as an insertion of the organic molecules between the layers of ML_2 complexes as they occurred in the reported native $NiL_2 \cdot H_2O$ structure.

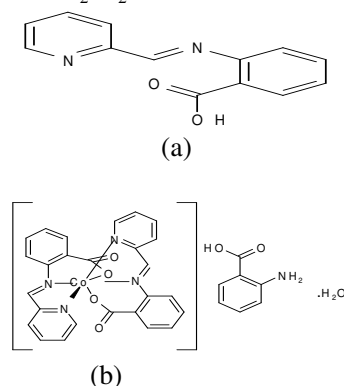
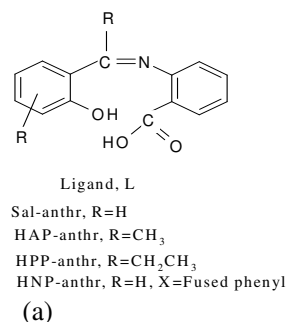


Figure 52. Chemical structure of (a) 2-(2'-pyridylimine)benzoic acid, HL and (b) its metal complex

In 2015, Hasan et al [86] reported the synthesis of dibasic tridentate Schiff bases by condensation of monoketone or diketone with 2-aminobenzoic acid. Subsequently, Ni(II) complexes of the Schiff bases were prepared and characterized by IR, 1H -NMR, mass and electronic spectra as well as magnetic susceptibility and molar conductivity measurements. The complexes have been found to possess 1:1 stoichiometry with a four-coordinate geometry (Figure 53). The bio-efficacy of the synthesized complexes has been evaluated against some human pathogens. The results show effectiveness of most of the prepared compounds against most of the bacteria and fungi studied.



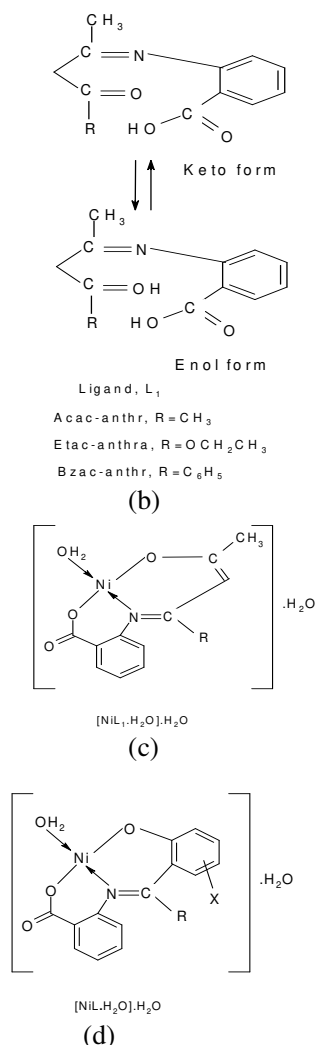


Figure 53. Proposed structure of (a) Schiff base ligands (b) keto and enol form (c) and (d) their metal complexes

Copper(II) complexes containing mixed ligands, Schiff bases ($L_1 = (2\text{-carboxyphenyl})\text{-pyridine-2-ylethyleneamine}$ and $L_2 = 5\text{-NO}_2\text{-(2-carboxyphenyl)-pyridine-2-ylethyleneamine}$) and 1,10-phenanthroline has been synthesized through conventional and microwave methods by Giri et al. in 2015 [87]. These copper(II) complexes have been characterized by elemental analysis, molar conductance, magnetic moment, IR, UV-Visible spectra and thermal analysis. The copper(II) complexes were green and brownish green colored and stable in air. On the basis of these spectral studies, it was revealed that all the complexes exhibited 1:1 (metal: ligand) ratio with the coordination number 6. Thermal data showed degradation pattern of the complexes. The thermal behavior of metal complexes showed that the hydrated complexes loses water molecules of hydration in the first step; followed by decomposition of ligand molecules in the subsequent steps. The Schiff base ligands and its copper(II) complexes have been tested for their antimicrobial behavior against various microorganisms. The

antimicrobial analysis revealed that copper(II) complex prepared by Schiff base ($L_2 = 5\text{-NO}_2\text{-(2-carboxyphenyl)-pyridine-2-ylethyleneamine}$) and 1,10-phenanthroline is more active than copper(II) complex prepared by Schiff base ($L_1 = (2\text{-carboxyphenyl})\text{-pyridine-2-ylethyleneamine}$) and 1,10-phenanthroline. The structure of Schiff base is shown in figure 54.

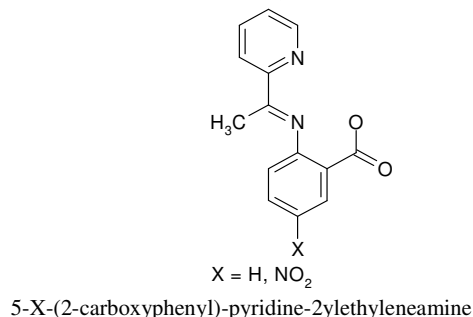
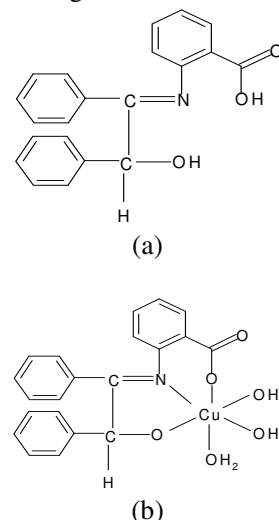


Figure 54. Structure of ligands

In 2017, Gayathri et al. [88] synthesized and characterized oxovanadium VO(IV) and Cu(II) complexes with a tridentate Schiff base derived from benzoin and 2-aminobenzoic acid. The structures of the compounds were deduced from elemental and thermal analyses, UV-visible, FTIR and ESR spectral analysis cum magnetic susceptibility and molar conductivity measurements. On the basis of electronic spectra and magnetic moment, an octahedral geometry have been assigned for both complexes with $[\text{VOL}(\text{H}_2\text{O})_2]$ and $[\text{CuL}(\text{H}_2\text{O})_3]$ formulation (Figure 55). The IR spectra revealed the participation of azomethine nitrogen ($-\text{C}=\text{N}-$), oxygen atom from hydroxyl group and carboxylate ion in coordination with coordinated water molecule. The metal complexes have been assayed for their antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Serratia sp.* *Pseudomonas aeruginosa* and *Bacillus cereus* and found to be more potent than the free ligand.



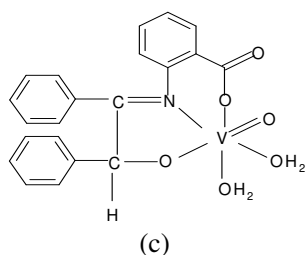
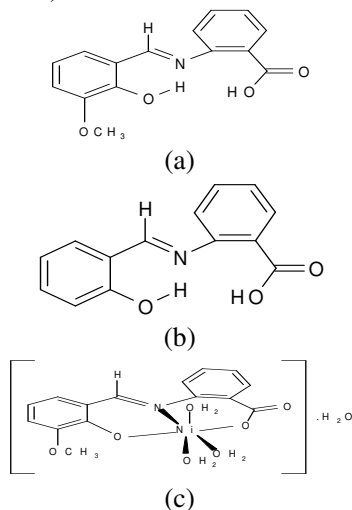


Figure 55. Structure of (a) Schiff base (b) metal complexes

In 2018, Govindaraj et al. [89] reported synthesis and characterization of Ni(II) complexes with two Schiff bases: L^1 , 2-((2-hydroxy-3-methoxybenzylidene)amino)benzoic acid obtained by condensation of *o*-vanillin and 2-aminobenzoic acid and L^2 , 2-((2-hydroxybenzylidene)amino)benzoic acid obtained by the condensation of salicylaldehyde and 2-aminobenzoic acid. The ligands and complexes were characterized by a number of spectral and analytical techniques. The data showed the composition of the complexes to be $[(NiL^1-2H)(H_2O)_3].H_2O$ or $[(NiL^2-2H)(H_2O)_3].H_2O$ (Figure 56). The complexes were observed to be more active compared to the ligands against all pathogens. The biologically active $[(NiL^2-2H)(H_2O)_3].H_2O$ complex showed excellent cytotoxicity towards (MG-63) cancer cell line.



(c)

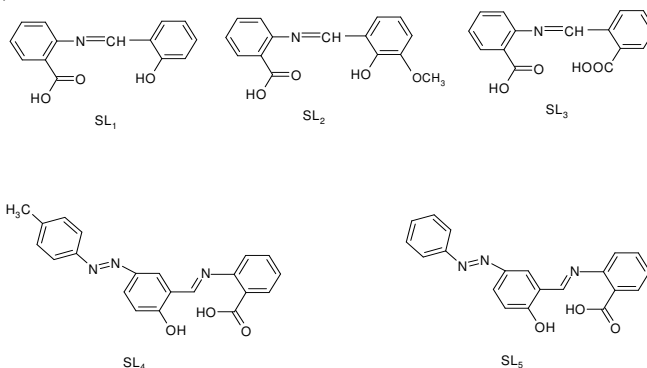


Figure 57. Schiff bases SL_1 , SL_2 , 1-(2-carboxyphenylimino)-2-hydroxy-3-methoxybenzene; SL_3 : SL_4 : 1-(2-carboxyphenylimino)-1-(3-formyl-4-hydroxyphenylazo)-4-methylbenzene SL_5 : 1-(2-carboxyphenylimino)-1-(3-formyl-4-hydroxyphenylazo)benzene

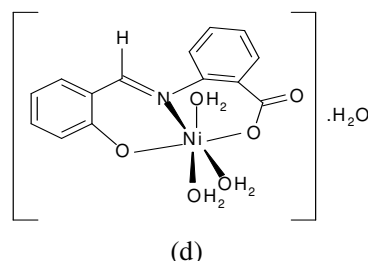


Figure 56. structure of (a) L^1 , 2-((2-hydroxy-3-methoxybenzylidene)amino)benzoic acid and (b) L^2 , 2-((2-hydroxybenzylidene)amino)benzoic acid (c) Ni(II) complex with L^1 (d) Ni(II) complex with L^2

Alzahrani et al. [90] reported bivalent Cu(II), Ni(II) and Zn(II) complexes synthesized using the prepared tridentate Schiff base ligands derived from 2-aminobenzoic acid as the primary amine condensed with different substituted aldehydes (salicylic acid, *o*-vaniline, 2-carboxybenzaldehyde, 1-(3-formyl-4-hydroxyphenylazo)-4-methylbenzene and 1-(3-formyl-4-hydroxyphenylazo benzene) (figure 57). The ligands and their corresponding complexes have been characterized using analytical, spectroscopic, conductivity and magnetic moment measurements. The analytical data showed the stoichiometry of the metals to ligands was (1:1). The conductivity data showed that all the complexes were non-electrolytes. The geometry of Cu(II) complexes were suggested to be distorted square planer. Ni(II) complexes were square-planar and Zn(II) complexes were tetrahedral (Figure 58). The antimicrobial investigation showed that the metal complexes had remarkable enhancement of activity with zinc complexes and were having highest susceptibility. The complex $[ZnSL_4.H_2O]$ showed MIC value of 12.5 $\mu\text{g}/\text{disc}$ against *Candida albicans* and the complex $[ZnSL_5.H_2O]$ indicated MIC value of 50 $\mu\text{g}/\text{disc}$ against *Streptococcus pneumonia*. The molluscicidal activity tests against the land snail *Eobania vermiculata* showed that complexes were more toxic with LC_{50} of 0.4 mg/L, while the LC_{50} of the ligands was at 0.5 mg/L.

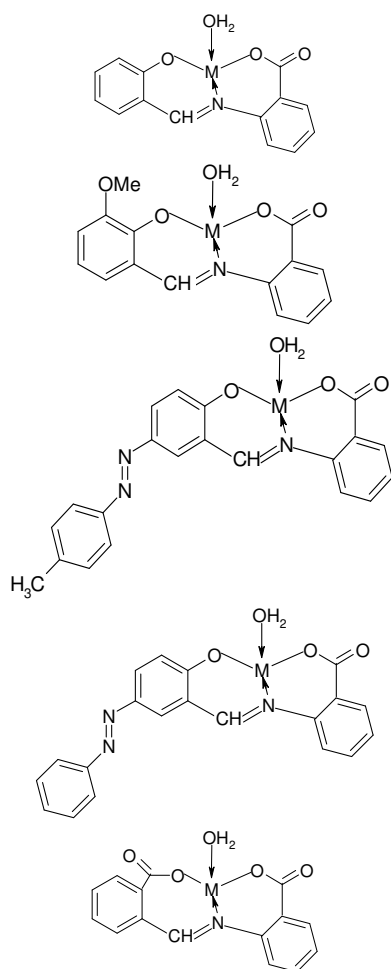


Figure 58. Proposed structures of the metal complex

In 2019, Ali and coworkers [91] prepared a Schiff base ligand from 2-furancarboxaldehyde and 2-aminobenzoic acid and its complexes with Cu(II), Ni(II), Co(II), Zn(II), Hg(II), Fe(III), La(III) and Sm(III); and were characterized based on microanalysis, IR, ^1H NMR, solid reflectance, magnetic susceptibility as well as molar conductance measurements and thermogravimetric analyses (TG and DTG). The data suggested the variable formulation of the complexes (Figure 59). The molar conductance data of the chelates revealed non-electrolytic nature. Thermal analysis indicated the presence of water of hydrations. The ligand and its complexes were tested by weight loss method and found corrosion inhibition for stainless steel type 410 in 1 M H_2SO_4 medium. Fluorescence and antibacterial sensitivity of the synthesized compounds were investigated revealing photoactive materials and considerable biological activity with the Hg(II) complex been more potent than the standard antibiotics drug (tetracycline) against *Bacillus subtilis* and as the standard drug in the case of *Pseudomonas aeruginosa*.

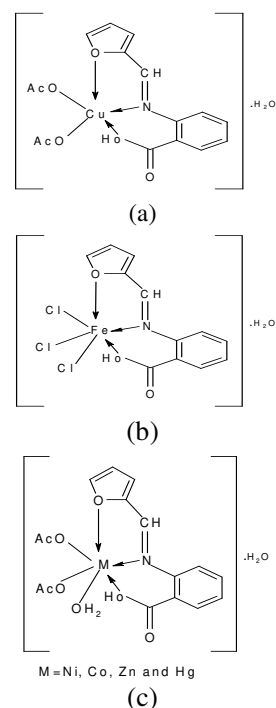
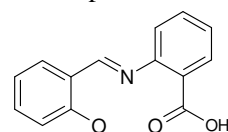


Figure 59. Structures of the metal complexes

In 2019, Prajapati et al. [92] reported three metal chelates synthesized by using metal perchlorates of divalent nickel, cobalt and copper with Schiff base (HL). The Schiff base ligand (HL) furnished O and N donor atoms for ligation was prepared from anthranilic acid and ortho-hydroxybenzaldehyde in ethanol. Techniques like elemental analysis, FT-IR, UV-Visible and mass spectrometry, thermal analysis, molar conductance and magnetic susceptibility were carried out to identify the chelate compounds. General formula of $[\text{M}(\text{HL})\text{OH}]$ type in all cases was proposed by the spectral and elemental analysis. The ratio of ligand to metal has been found as 1:1 for all metal chelates (Figure 60). Infrared spectral data implied the inclusion of oxygen (of COOH and phenolic OH) and azomethine nitrogen in tridentate coordination mode with central metal ion. The study of conductivity measurement indicated the non-electrolytic nature of the chelates. Catalysis by these chelates was studied. The activation energy for the synthesized metal chelates were evaluated by the broido method. Antibacterial property was examined for all metal chelates and its parent ligand against gram positive (*B. subtilis*, *B. cereus*) and gram negative (*E. coli*, *P. aeruginosa*) bacterial species.



2-[(E)-(2-hydroxybenzylidene)amino]benzoic acid
(a)

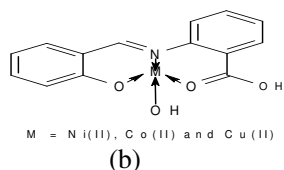


Figure 60. structure of (a) Schiff base (b) metal complexes

In 2020, Biswas et al [93] synthesized two monomeric copper complexes [Cu(Pymab)CCl₃COO(H₂O)].H₂O (**1**) and [Cu(Pymaib)(H₂O)Cl₂] (**2**) by reacting copper(II) trichloroacetate and copper(II) chloride with the monobasic tridentate Schiff base ligands (HPymab = (E)-2-((Pyridine-2-yl)methyleneamino)benzoic acid and HPymaib = 4-iodo-2-((E)-[(Pyridine-2-yl)methyleneamino]benzoic acid) and characterized by elemental analysis, IR, UV-Visible, mass spectrometry, CV and single crystal XRD analysis. Both complexes were monomeric in both solid state and solution. A distorted square pyramidal coordination of metal ions was observed in the XRD (Figure 61). Strikingly, both complexes behave as effective catalyst for the oxidation of 3,5-di-*tert*-butyl catechol to the corresponding quinone derivative in aerial oxygen. The reactions follow the Michaelis-Menten enzymatic reaction kinetics with *K_{cat}* values of 1452 h⁻¹ and 1458 h⁻¹ respectively in DMSO and 1590 h⁻¹ and 1636 h⁻¹ respectively in THF.

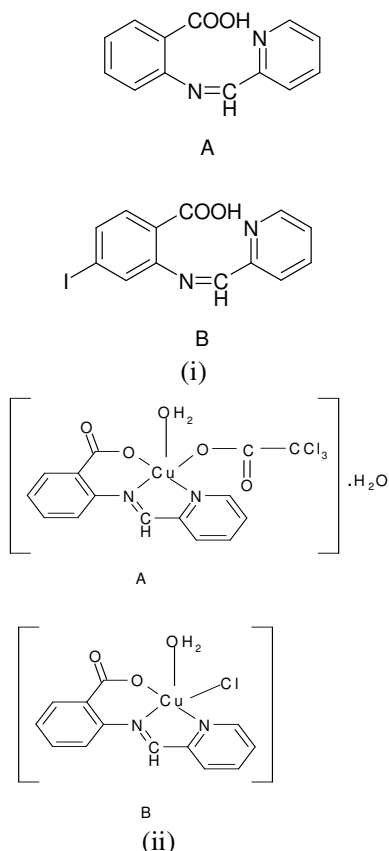
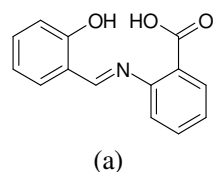


Figure 61. structures of (i) Schiff bases (ii) metal complexes

New Schiff base ligand 2-(imine-2-anthranilic acid)-3-hydroxyiminobutane [L] and its Mn(II) and Fe(II) metal complexes were prepared by Rajurkar [94] through condensation of 2,3-Butanedione-3-monoxime, anthranilic acid and metal salts. The ligand and metal complexes were characterized by elemental analysis, magnetic susceptibility measurements and spectral (I.R., UV-Visible, ¹H NMR) analysis. Based on electronic spectral data and magnetic susceptibility measurement, the octahedral geometry has proposed for both the metal complexes. The ligand and metal complexes were screened for their antimicrobial activity against microorganisms *S. aureus* (gm positive), *P. aeruginosa* (gm negative), *Aspergillus niger* and *Candida albicans* which showed moderate activity against all microorganisms as compared to the standard drugs. Metal complexes behaved as good antimicrobial agent as compared to its ligand.

Mohammad and coworkers in 2021 [95] reported a Schiff base ligand (H₂L), {2-((2-hydroxybenzylidene)amino)benzoic acid} (C₁₄H₁₁NO₃) containing nitrogen-oxygen donor atom prepared by the condensation of salicylaldehyde and anthranilic acid and coordinated with Cu(II), Ni(II), Cd(II), Mn(II) and Co(II) ions. The Schiff base and its metal complexes were characterized by elemental analysis, FT-IR, ESI-MS, electronic absorption spectroscopy and some of their physicochemical properties were determined. The overall reaction was monitored by TLC analysis. The analytical and theoretical data showed that the metal ligand stoichiometry in the complexes was 1:1. Molar conductance study have shown that all the complexes were non-electrolytic in nature. FT-IR studies suggested that Schiff base acted as deprotonated tridentate ligand and metal ions are attached with the ligand by azomethine nitrogen, oxygen atom of deprotonated hydroxyl group and deprotonated oxygen of the carboxyl group of ligand respectively (Figure 62). Thermal analysis (TGA and DTG) data suggested that, a small weight loss occurred in the range of 40 °C – 80 °C from the complex which is assigned to the loss of lattice water and maximum weight loss in the range of 280-450 °C was attributable to the loss of coordinated water present in all complexes. These data also showed that most of the complexes were thermally stable up to 200 °C. All the complexes showed good antimicrobial activity compared to ligand and commercial standard.



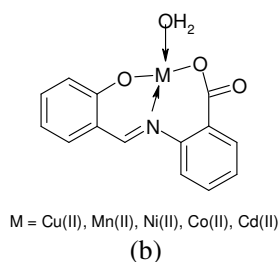


Figure 62. structure of (a) {2-((2-hydroxybenzylidene)amino)benzoic acid} (b) metal complexes

Mostafa et al. in 2021 [96] fabricated two new ligands, namely: 2-((2-hydroxybenzylidene)amino)benzoic acid (L_1) (Figure 63) and 2-(furan-2-ylmethyleneamino)phenol (L_2); and were employed to coordinate Cu(II) producing the characteristically stable complexes that performed as the ionophores in the fabricated electrodes A and B. Thus it was possible to build these electrodes that have attractive properties and expected behavior, namely, low detection limits: 2.32×10^{-7} and 1.14×10^{-6} M Cu(II), Nernstian slope of 29.13 and 30.85 mV/decade Cu(II), broad concentration ranges from 3.98×10^{-7} – 1.00×10^{-2} and 1.52×10^{-6} – 1.00×10^{-2} M for sensors A and B, respectively, as well as short response time (ca. 3 – 5 s) with distinct selectivity toward Cu(II) over the other cations and applicability over the pH range 1.5–5.5 for miscellaneous samples: aqueous solutions, urine, and blood serum. Thus, these sensors surpassed many others towards fulfilling the intended function of Cu(II) determination in various applications.

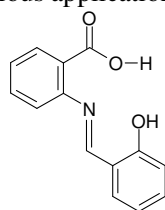
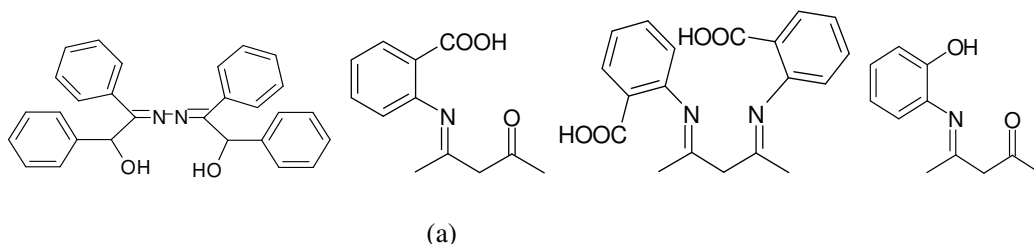


Figure 63. The chemical structure of ligand [2-((2-hydroxybenzylidene)amino)benzoic acid]

In 2022, Yasseen [97] synthesized a simple and easily fluorescent sensor, Schiff base sensor (SBS), produced by condensation reaction of equal amounts of anthranilic acid and salicylaldehyde. It was synthesized and characterized systemically. Both UV-vis and fluorescence spectroscopic studies indicated that the



SBS sensor showed good selectivity toward the studied ions: Na^+ , K^+ , Cu^{2+} , Co^{2+} , Fe^{3+} , Al^{3+} and Cr^{3+} . Whereas, chromium(III) and copper(II) exhibited the largest fluorescence enhancement over the other investigated ions. Chelation-enhanced fluorescence was shown upon the interaction of SBS sensor with some metal ions studied forming inclusion complexes (Figure 64). The fluorescent sensor in aqueous ethanolic solution exhibited high selectivity towards Cu^{2+} and Cr^{3+} ions, forming 2:1 (L:M) complex as determined by Job's plot. The formation constants of the inclusion complexes (Mn^+/SBS) were measured via spectrofluorometric method applying Benesi-Hildebrand.

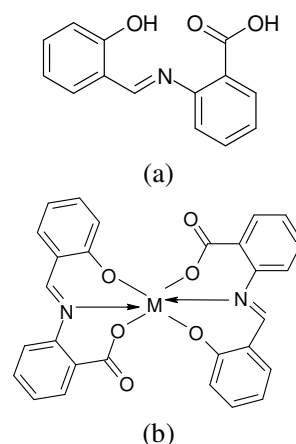


Figure 64. structure of (a) Tridentate sensor (SBS) and (b) proposed structure of the M^+/SBS inclusion complex

Raouf et al. [98] reported six types of chromium complexes were prepared via the reaction mixture of four ligands. The prepared ligands and chromium complexes were characterized using Fourier transform spectroscopy (FT-IR), elemental analysis, molar conductivity, and magnetic moment, as well as UV-Vis spectroscopy (Figure 65). Different benzyl bromide derivatives were selected with both electron-donating groups and electron-withdrawing groups at -ortho-, -meta-, and - para positions. Under the optimum conditions, the corresponding benzaldehyde derivatives were obtained in moderate to excellent yields. In addition, the biological activity of the prepared chromium complexes was checked.

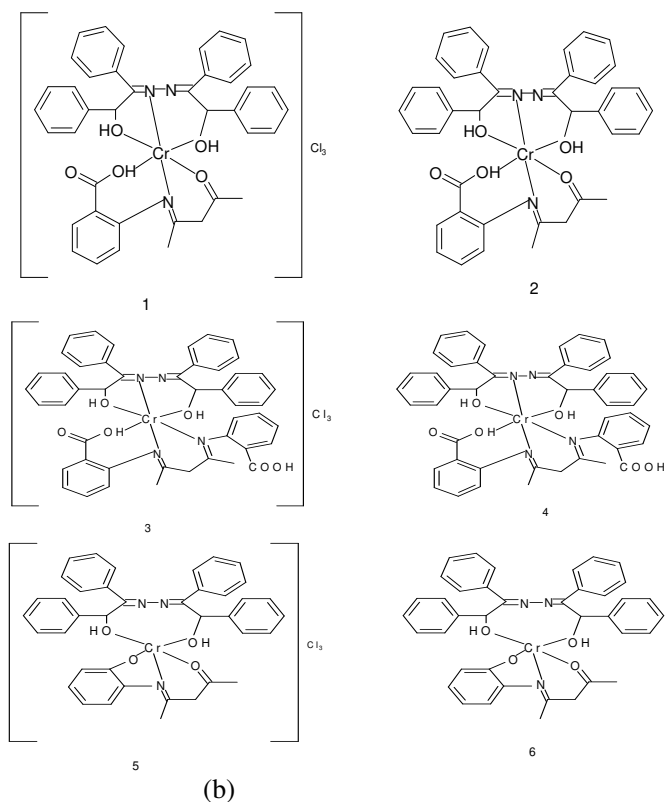
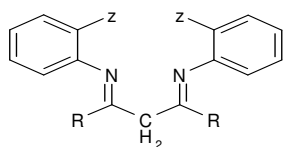


Figure 65. chemical structures of (a) Schiff bases (b) octahedral chromium complexes

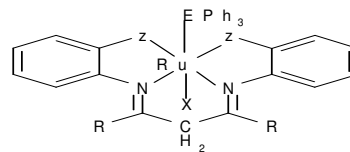
4.3 Tetradentate Schiff bases and their Complexes

Thangadurai and Natarajan [99] synthesized several hexa-coordinated ruthenium(III) complexes of the type $[\text{RuX}(\text{EPh}_3)(\text{L-L})]$ ($\text{X}=\text{Cl}, \text{Br}$; $\text{E}=\text{P}, \text{As}$; $\text{L-L}=\text{anthracac}$, anthdibm, 2-amtpacac or 2-amtpdibm) by reacting $[\text{RuCl}_3(\text{PPh}_3)_3]$, $[\text{RuCl}_3(\text{AsPh}_3)_3]$, $[\text{RuBr}_3(\text{AsPh}_3)_3]$ or $[\text{RuBr}_3(\text{PPh}_3)_2(\text{MeOH})]$ with tetradentate Schiff bases such as bis(anthranilic acid)acetylacetimine ($\text{H}_2\text{-anthacac}$), bis(anthranilic acid)dibenzoylmethimine ($\text{H}_2\text{-anthdibm}$), bis(2-aminothiophenol)acetylacetimine ($\text{H}_2\text{-amtpacac}$) or bis(2-aminothiophenol)dibenzoylmethimine ($\text{H}_2\text{-2-amtpdibm}$) (Figure 66). All the complexes were characterized by elemental analyses, IR, electronic spectra, EPR, magnetic moment and cyclic voltammetric data. An octahedral structure has been tentatively proposed for the complexes. These complexes were also tested for their antibacterial properties.



$\text{H}_2\text{-anthacac}$: $\text{Z} = \text{COOH}$, $\text{R} = \text{CH}_3$; $\text{H}_2\text{-anthdibm}$: $\text{Z} = \text{COOH}$, $\text{R} = \text{C}_6\text{H}_5$; $\text{H}_2\text{-2-amtpacac}$: $\text{Z} = \text{SH}$, $\text{R} = \text{CH}_3$; $\text{H}_2\text{-2-amtpdibm}$: $\text{Z} = \text{SH}$, $\text{R} = \text{C}_6\text{H}_5$

(a)



$\text{X} = \text{Cl}$ or Br ; $\text{E} = \text{P}$ or As ; $\text{R} = \text{CH}_3$ or C_6H_5 ; $\text{Z} = \text{COO}^-$ or S^-

(b)

Figure 66. Structures of (a) Schiff base ligands (b) ruthenium(III) complex

Yuhua et al [100] synthesized and characterized two solid binuclear complexes of the compositions $[(\text{UO}_2)_2(\text{HL})_3]\text{NO}_3$, and $[\text{Th}_2(\text{HL})_3(\text{NO}_3)_2](\text{NO}_3)_3$ ($\text{H}_2\text{L} = o\text{-vanillylidene anthranilic acid}$) elemental analyses, DTA-TG, IR spectra, UV spectra and molar conductance. Possible structures of the two complexes have been proposed.

Raman et al. [101] synthesized N_2O_2 donor Schiff base synthesized by condensing 2-aminobenzoic acid and acetoacetanilido-4-aminoantipyrine in ethanol. Solid metal complexes of the Schiff base with $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Co}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Zn}(\text{II})$, $\text{VO}^{2+}(\text{IV})$, $\text{Hg}(\text{II})$ and $\text{Cd}(\text{II})$ metal ions were synthesized and characterized by elemental analysis, magnetic susceptibility, molar conductance, fast atom bombardment (FAB) mass, IR, UV-Vis and ^1H NMR spectral studies. The data showed that the complexes have the composition of ML type. The UV-visible and magnetic susceptibility data

suggested a square planar geometry around the central metal ion for all the complexes except $\text{VO}^{2+}(\text{IV})$ complex which has square-pyramidal geometry (Figure 67). Then *in vitro* antifungal activities of the compounds were tested against *Aspergillus niger*, *Aspergillus flavus*, *Rhizopus stolonifer*, *Candida albicans*, *Rhizoctonia bataicola* and *Trichoderma harizanum*. All the metal complexes showed stronger activities than the free ligand. The minimum inhibitory concentrations (MIC) of the metal complexes were found in the range of 10–31 $\mu\text{g}/\text{ml}$.

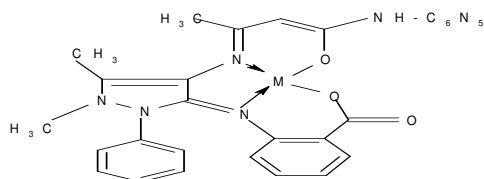


Figure 67. structure of Schiff base Cu(II) complex

Four neutral complexes of Cu(II), Ni(II), Co(II) and Zn(II) have been prepared by Raman and coworkers from a tridentate Schiff base (HL) derived from anthranilic acid and acetoacetanilide [102]. The analytical data show that the metal to ligand ratio is 1:2. The structural features have been determined from IR, UV-Vis, ^1H -NMR, ESR and mass spectral data. All the complexes exhibited octahedral geometry around the central metal ion. Their low electrical conductance values supported their neutral nature. The magnetic moment data provided evidence for the monomeric nature of the complexes. Absorption experiments have been carried out on the interaction of the complexes with calf thymus DNA (CT-DNA). The results suggested that all the complexes can bind to CT-DNA by intercalation between chromophore and DNA base pairs. An electrochemical study of the copper complex revealed that it preferred to bind to DNA in the Cu(II) rather than the Cu(I) oxidation state. The nucleolytic cleavage activity of all the complexes was examined on CT-DNA by using a gel electrophoresis experiment in the presence and absence of oxidant, H_2O_2 . In the absence of the oxidant, a less discernible DNA cleavage was observed, whereas in the presence of the oxidant, all complexes showed enhanced nuclease activity.

In 2010, Abdallah et al. [103] prepared Schiff base ligand (H_2L) via the condensation of *o*-phthalaldehyde and 2-aminobenzoic acid in 1:2 ratio. Metal complexes were prepared and characterized. The complexes were proposed to have the general formula $[\text{MCl}(\text{L})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (where $\text{M} = \text{Cr}(\text{III})$ and $\text{Fe}(\text{III})$); $[\text{M}(\text{L})] \cdot y\text{H}_2\text{O}$ (where $\text{M} = \text{Mn}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$, $y = 1 - 2$) and $[\text{M}(\text{L})(\text{H}_2\text{O})_n] \cdot y\text{H}_2\text{O}$ (where $\text{M} = \text{Co}(\text{II})$ ($n=y=2$), $\text{Co}(\text{II})$ ($n=y=1$), $\text{Ni}(\text{II})$ ($n=2$, $y=1$)). The molar conductance data revealed that all the metal chelates were non-electrolytes. IR spectra

showed that H_2L is coordinated to the metal ions in a bi-negative tetradentate manner with NOON donor sites of the azomethine-N and carboxylate-O. From the magnetic and solid reflectance spectra, it was found that the geometrical structure of these complexes are octahedral ($\text{Cr}(\text{III})$, $\text{Fe}(\text{III})$, $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$), square planar ($\text{Cu}(\text{II})$), trigonal bipyramidal ($\text{Co}(\text{II})$) and tetrahedral ($\text{Mn}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$) (Figure 68). The thermal behaviour of these chelates showed that the hydrated complexes losses water molecules of hydration in the first step followed immediately by decomposition of the ligand molecule in the subsequent steps. The biological activity data showed that the metal complexes to be more potent/antibacterial than the parent Schiff base ligand against one or more bacterial species.

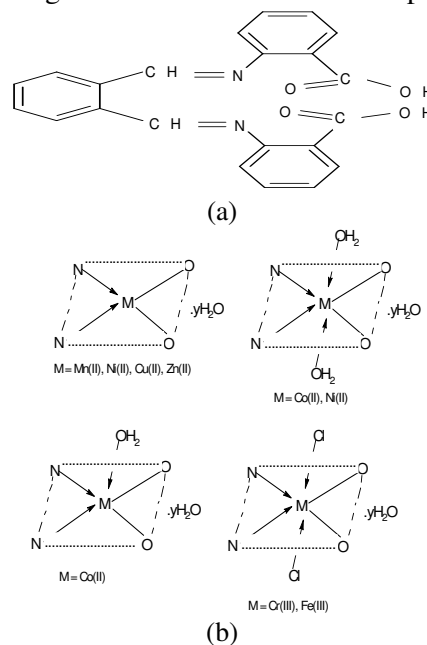


Figure 68. Structure of (a) Schiff base ligand, H_2L , (b) metal complexes

In a work conducted in 2015, Muhammad and Shedewo [104] synthesized and diagnosed the complex of Ni(II) with Schiff base derived from benzoin and *o*-aminobenzoic acid by infrared spectral analysis, conductance measurement, UV- visible spectral studies and elemental analysis (Figure 69). The melting point of the Schiff base determined was 120 $^{\circ}\text{C}$. The decomposition temperature of Ni(II) complex was 155 $^{\circ}\text{C}$, while the molar conductance value was 10.7 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Antibacterial screening of the compounds was carried out *in vitro* against *Escherichia coli*, *Salmonella typhi* (Gram negative) and *Staphylococcus aureus*, *Streptococcus species* (Gram positive). The bioassay revealed a considerable activity of the Schiff base complex against the bacteria.

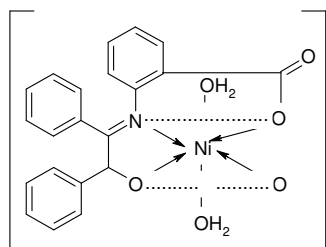


Figure 69. proposed structure of Ni(II) Schiff base complex

Tetradentate N_2O_2 type Schiff base, synthesized from benzil and 2-aminobenzoic acid in the ratio 1:2 formed stable complexes with transition metal ions such as VO(IV), Cu(II), Ni(II) and Co(II) in ethanol have been reported in 2017 by Gayathri and Suresha [105]. Micro-analytical data, magnetic susceptibility, molar conductance measurements, FTIR, UV-visible, ESR spectroscopic techniques and thermal analysis were used to confirm their structures. These complexes showed very low conductance values supporting non-electrolytic nature. The infrared spectra supported the involvement of azomethine nitrogens and oxygen from carboxylate ion are coordinated to the metal. Electronic spectra of the complexes suggested a square pyramidal geometry for oxovanadium(IV) complex $[VO(L)]$, distorted octahedral geometry for Cu(II) and Co(II) complexes and octahedral geometry for Ni(II) complexes with general formula $[M(L)(H_2O)_2]$ where $M = Cu(II), Ni(II), Co(II)$ (Figure 70). The X-band ESR spectra of VO(IV) and Cu(II) complexes were recorded in DMSO at LNT and their parameters were calculated. All these complexes were paramagnetic and thermal studies showed that in all the cases a stable metal oxide was obtained as the residue.

The metal complexes have been screened for their antibacterial activity against organisms like *E. coli*, *S. aureus*, *Serratia sp.*, *P. aeruginosa* and *B. cereus* and it was found that the complexes were more active than the corresponding ligand.

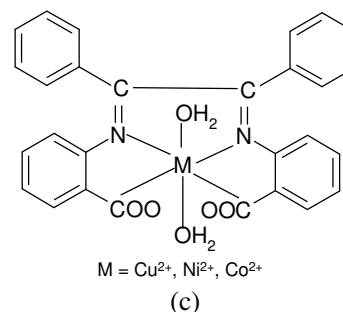
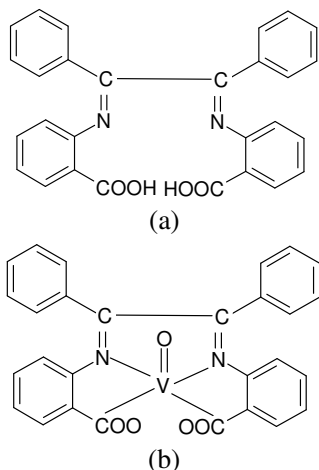


Figure 70. structures of (a) Schiff base, (b) vanadate complex and (c) other complexes

In 2020, Jirjees et al. [106] prepared complexes prepared from the ligand [2,20(5,5-dimethylcyclohexane-1,3-diylidene)bis(azan-1-yl-1-ylidene)dibenzoic acid] derived from 5,5-dimethylcyclohexane-1,3-dione and 2-aminobenzoic acid. Accordingly, its mono and binuclear Mn(II), Co(II), Cu(II), Zn(II), and Cd(II) complexes were prepared (Figure 71). The prepared components have been characterized by various spectroscopic techniques and elemental analysis. The thermal stability of the ligand and its complexes were determined by TGA. It was found that all the complexes have excellent thermal stability and do not contain water molecules within their structure, but the ligand has little stability. Additionally, theoretical chemical calculation was performed of both electronic structure and spectroscopic properties of prepared Schiff base and its complexes. Moreover, the consequences predicted that the structure will be played a critical role in biological, liquid-liquid extraction, active transport applications.

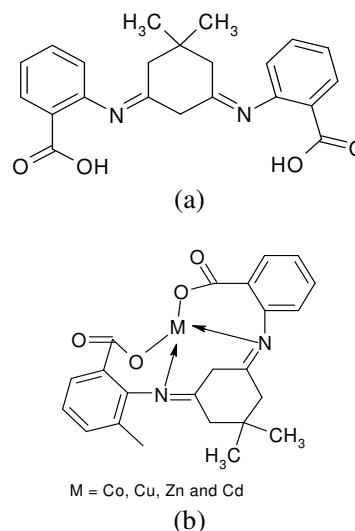


Figure 71. Structure of (a) Schiff base (b) metal complexes

Complexes of Co(II), Mn(II) and Ni(II) with Schiff base derived from condensation of pentane-2,4-dione and 2-aminobenzoic acid have been synthesized by Uba *et al* [107]. The synthesized compounds were characterized by molar conductivity, infrared and elemental analyses

(Figure 72). The solubility study revealed that the compounds are soluble in most organic solvents except chloroform and diethyl ether. The molar conductance measurement values of the complexes were small suggestive of their non-electrolytic nature. Biological studies showed the non-electrolytic nature of the complexes. The compounds were assayed for antibacterial activity and were found to have good activity except Ni(II) complex.

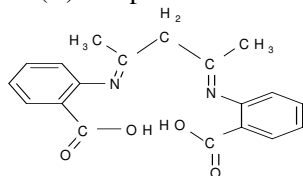
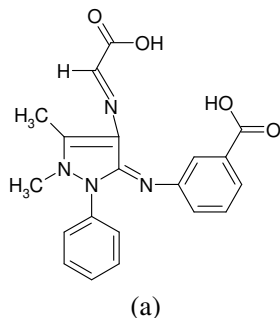
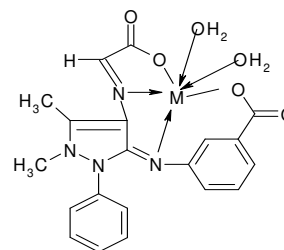


Figure 72. structure of Schiff base derived from pentane-2,4-dione and 2-aminobenzoic acid

In 2021, Abdul Rahman and Alshemary [108] synthesized new Co(II), Cu(II), Mn(II), Zn(II), and Ni(II) complexes, including H₂DAPB by reacting 2-aminobenzoic acid with 4-amino antipyrine and glyoxylic acid. The new complexes were recognized by diverse spectroscopic methods, and the arrangement of the complexes was assured by Mass spectra and (TGA and DTG) thermal analyses (Figure 73). The *in vitro* antifungal and antibacterial efficiencies of the compounds were screened versus fungi like *C. Albicans*, *A. niger*, *R. stolonifer*, and *A. flavus*, and bacteria such as *S. aureus*, *E. coli*, *P. aeruginosa*, *B. subtilis*. All the metal complexes offered powerful antifungal and bacterial efficiencies than the ligand. The linking ability of CT-DNA with the complexes was carried out by photophysical (emission titration /absorption) methods in which an interactive mode of binding was observed. Moreover, outcomes of the DNA cleavage efficacy proposed which the ligand and its metal complexes may cleave CT-DNA at various degrees. Then, the study of interaction for complexes with CT-DNA has been inspected by viscometric and absorption spectral titration determinants. Cytotoxicity studies of complexes on (MCF-7) cell line of human breast cancer were screened by EtBr in (MTT) test. Cell viability 50 % was given at 25 µg for Cu(II), 50 µg for Co(II), 100 µg for Mn(II), 150 µg for Co(II) and 250 µg for Ni(II). The compounds showed significant activity in the biological studies.



(a)

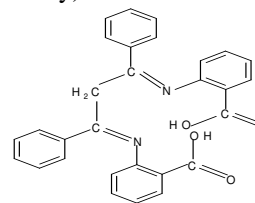


M=Ni(II), Co(II), Cu(II), Mn(II) and Zn(II)

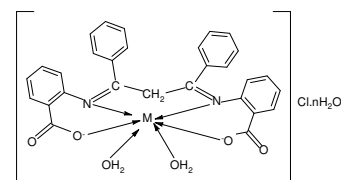
(b)

Figure 73. proposed structure of (a) ligand (b) complexes

Schiff base ligand, 2,2'-((1Z-1'Z)-(1,3-diphenylpropane-1,3-diylidene) bis(azanylylidene)) dibenzoic acid (H₂L) obtained via condensation reaction between anthranilic acid and dibenzoyl methane in 2:1 ratio was reported by Abd El-Halim et al. in 2021 [109]. A series of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes resulted from 1:1 (ligand: metal salt) reaction. The structural features of the synthesized ligand and its metal complexes was determined by elemental analyses, IR, ¹H NMR, UV-Vis, ESR, mass spectra, conductivity and magnetic susceptibility measurements as well as thermal (TG/DTG) analyses (Figure 74). The analytical and spectroscopic tools showed that the complexes had composition of ML type with octahedral geometry. The IR results confirmed the tetradentate binding of the ligand involving two azomethine nitrogen atoms and two carboxylate oxygens. The Schiff base and its complexes have been screened for their antimicrobial activity against several bacterial organisms (*Streptococcus pneumonia* and *Bacillus subtilis*; *Pseudomonas aeruginosa* and *Escherichia coli*) and fungi (*Aspergillus fumigatus*; *Syncephalus trumracemosum*; *Geotricum candidum* and *Candida albicans*) by disc diffusion method. All the metal complexes have potent antimicrobial activity than the free ligand. Anticancer activity of the ligand and its metal complexes was evaluated against human cancer (MCF-7 cells viability).



(a)



(b)

Figure 74. structure of (a) Schiff base (b) metal complexes

4.4 Pentadentate Schiff bases and their Complexes

A potential active Schiff base ligand and its binuclear copper complexes have been synthesized by Shakila *et al.* [110]. This was accomplished by condensation of 2,6-diformyl-4-methyl phenol and 2-amino benzoic acid in 1:2 stoichiometric ratios. The Schiff base coordinated with two copper ions after deprotonation of the phenol group forming binuclear complexes (Figure 75). These compounds were characterized by several techniques including molar conductance, elemental analysis as well as $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, UV-Visible, FT-IR and ESR spectral studies. The complexes were non-electrolytic in nature as suggested by molar conductance values. The redox behavior of the complexes has been investigated by cyclic voltammetry. Furthermore, the Schiff base and the complexes were screened for their antibacterial, antifungal and antioxidant activities. The results show the metal complexes to be more antifungal and more antioxidant as compared to free ligand.

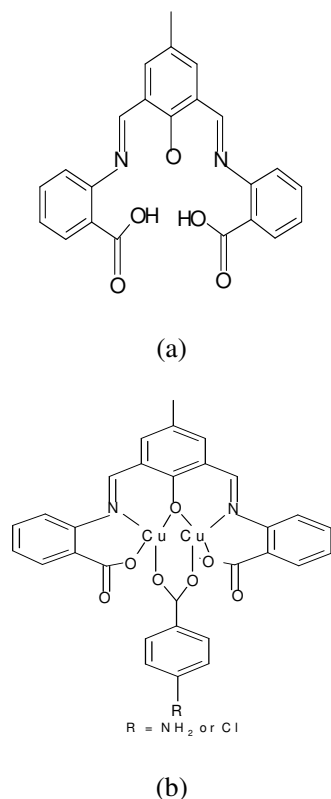


Figure 75. Structure of (a) Schiff base (b) binuclear complex

In 2021, Moubeen *et al.* [111] reported series of mononuclear octahedral Ru(III) complexes of general formula $[\text{RuL}_3\text{-3Cl}]$ (**1-3**) where L = dianion of Schiff bases namely:

2,2'-(((1E,1'E)-thiophene-2,5-diylbis(methaneylylidene))bis(azaneylylidene))diphenol (H_2L_1), 2,2'-(((1E,1'E)-thiophene-

2,5-diylbis(methaneylylidene))bis(azaneylylidene))dibenzenethiol (H_2L_2) and 2,2'-(((1E,1'E)-thiophene-2,5-diylbis(methaneylyli-dene))bis(azaneylyli-dene))-dibenzoic acid (H_2L_3), respectively synthesized and characterized by different physicochemical techniques (Figure 76). The results of interaction of complexes with CT-DNA supported that, the Ru(III) complexes bind to DNA via an intercalative mode. The interaction has also been investigated by gel electrophoresis. Interestingly, it was found that all Ru(III) complexes cleave super coiled (SC) pUC19 plasmid DNA efficiently in the absence of an external agent. Further, the antiproliferative activity of the complexes on Human Cervical Cancer Cells (HeLa) and Human Breast Cancer Cells (MCF-7) were evaluated by MTT assay, which revealed that, all the complexes showed more intense inhibition against HeLa and MCF-7 cell lines, particularly Ru(III) complex (**3**) attenuated the strongest proliferation, allowing its use as chemotherapeutic agent for cancer treatment.

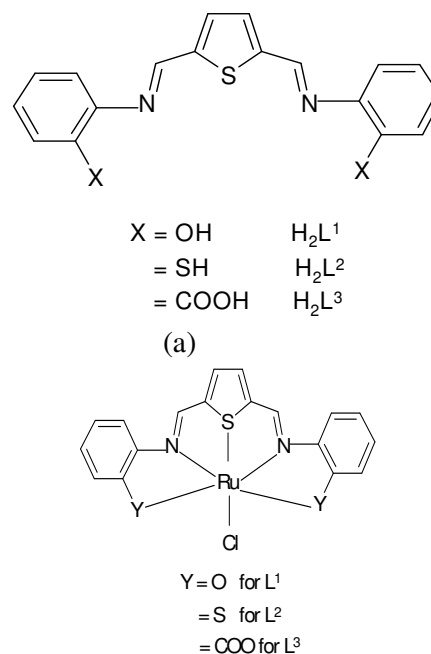


Figure 76. structure of (a) Schiff base (b) Ru(III) complex

3.5 Hexadentate Schiff bases and their Complexes

In 2014, Zayed *et al.* [112] reported new Schiff base complexes synthesized using bioactive bis-Schiff base ligand derived by condensation of 2-aminobenzoic acid and 2,2'-(ethylenedioxy)bis(benzaldehyde) (Figure 77a). The pKa of the bis-Schiff base was spectrophotometrically determined and stability constants of the complexes were investigated. The structures of the compounds were elucidated from their elemental analyses, magnetic susceptibility and molar measurements cum IR and $^1\text{HNMR}$ spectral studies. Powder XRD gave a clear idea about the crystallinity of

Cr(III) and Cu(II) complexes and amorphousness of all other complexes. The investigation revealed that the stoichiometries of the chelates are of 1:1 M-L type with octahedral geometry (Figure 77b and c). In order to assess their bioactivity, bacterial and fungal isolates were used. The results show more potency of most complexes against the bacterial isolates as compared to the bis-Schiff base ligand while Ni(II) complex have antifungal activity against *Candida albicans* as opposed to the bis-Schiff base. Fe(III) recovery was tested by spectrophotometry.

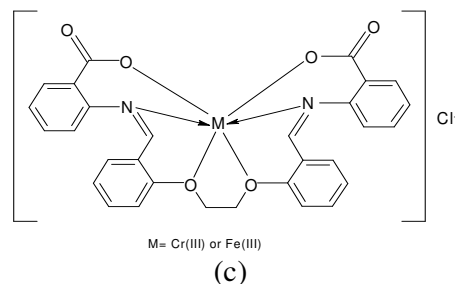
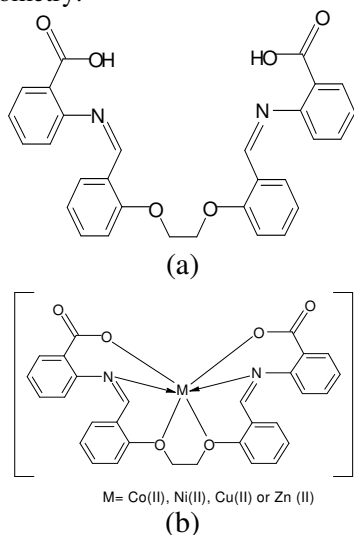


Figure 75. Proposed structure of (a) bis-Schiff base (b) metal(II) complexes (c) metal(III) complexes

5. Applications

Schiff bases and coordination complexes derived from anthranilic acid have broad range of multidisciplinary applications as antifungal, antibacterial, anticancer, antidiabetic, antioxidant, antiulcer, anti-inflammatory and molluscicidal agents. They also act as catalysts for different organic transformation reactions, chemo sensors as well as fluorescents. A recap of the various aldehydes/ketones used in the formation of different Schiff bases of anthranilic acid and their metal complexes as well as plethora of applications and their references are provided in Table 1.

Table 1. Different aldehydes/ketones used in the synthesis of Schiff bases of o-aminobenzoic acid and their applications

Entry	Aldehydes/ketones	Reported Application	Reference
1.	Salicylaldehyde	Fluorimetric monitoring of small pH changes Antimicrobial activity Nil Anti-inflammatory and antiulcer activity Catalyst Antidiabetic agents Electrochemical properties Antibacterial activity Cytotoxicity Molluscicidal activity Chemosensor, fluorescent sensor	[20] [21,23,51,73,86,90,95] [35,37,46,53,54,67,70,71,72,76,83] [36] [38,73,92] [77] [78] [80,92] [89] [90] [96,97]
2.	5-bromo-2-hydroxybenzaldehyde	Nil	[71,72]
3.	2-hydroxy-1-naphthaldehyde	Antimicrobial activity	[86]
4.	2-hydroxy-5-nitrosalicylaldehyde	Cytotoxic activity	[84]
5.	3,5-dibromo-2-hydroxybenzaldehyde	Nil	[71]
6.	Acetylacetone	Nil Catalyst Antimicrobial activity Antibacterial activity	[72] [73,98] [73,86] [99]
7.	Dibenzoylmethane	Antibacterial activity Anticancer	[99,109] [109]
8.	5,6-benzosalicylaldehyde	Nil	[72]
9.	4-hydroxybenzaldehyde	fluorimetric monitoring of small pH changes Corrosion inhibitor	[20,23] [28]

		Nil	[34,35]
		Antimicrobial activity,	[57]
		molluscicidal activity	
10.	4-nitrobenzaldehyde	Fluorimetric monitoring of small pH changes	[20,23]
		Nil	[34,35]
		Antimicrobial activity,	[57]
		molluscicidal activity	
11.	4-(dimethylamino)benzaldehyde	Fluorimetric monitoring of small pH changes	[20]
		Nil	[34,35,44,81]
		Antimicrobial activity	[14,61,62]
		Antibacterial activity	[65]
12.	Isatin	Biological activities such as acute neurological disorder, gastrointestinal hemorrhage, superoxide dismutase inhibitor and, hypothermia	[22]
		Nil	[68,69]
13.	Fluorenone	Nil	[39]
14.	Chromone	Nil	[68,69]
15.	Citronellal	Nil	[40]
16.	Furfuraldehyde	Antimicrobial activity	[23,57,91]
		Molluscicidal activity	[57]
		Antibacterial activity	[75]
		Electrochemical properties	[78]
		Fluorescence	[91]
17.	5-bromo-citronellal	Nil	[40]
18.	4- hydroxy-3-methoxy benzaldehyde	Nil	[24]
19.	pyridine-4-carbaldehyde	Antioxidant, DNA binding interactions	[25]
20.	Anisaldehyde	Antimicrobial activity, Odorant	[26]
		Antibacterial activity	[41]
21.	Cinnamaldehyde	Antimicrobial activity, Odorant	[26]
		Antibacterial activity	[41]
		Chemosensor	[55]
22.	<i>p</i> -tolualdehyde	Antibacterial activity	[41]
23.	α -ionone	Antimicrobial activity, Odorant	[26]
24.	Cuminaldehyde	Antimicrobial activity, Odorant	[26]
25.	Citronellal	Antimicrobial activity, Odorant	[26]
26.	Citral	Antimicrobial activity, Odorant	[26]
27.	Veratraldehyde	Antimicrobial activity, Odorant	[26]
28.	Acetophenone	Antimicrobial activity, Odorant	[26]
29.	Benzaldehyde	Antimicrobial activity, Odorant	[26]
		Nil	[35]
		Antimicrobial activity	[42,43,64]
30.	5-nitro-salicylaldehyde	Chemo sensor for cations and anions	[27]
31.	2,6-diformyl-4-methyl phenol	Selenite (Se ^{IV}) and arsenite (As ^{III}) species Detector	[29]
32.	3-formylacetylacetone	Nil	[30]
33.	4-methoxybenzaldehyde	Antimicrobial activity	[43]
34.	3-nitrobenzaldehyde	Antimicrobial activity	[43]
35.	Acetoacetinilide	Antimicrobial activity	[45]
		Nuclease activity	[102]
36.	2-thiophenecarboxylaldehyde	Nil	[47]
		Antibacterial activity	[74,80]
		Electrochemical properties	[78]
37.	Aldose	anti-inflammatory activity	[48,49]
38.	indoline-2,3-dione	Antibacterial activity	[50]
39.	2-acetyl-pyridine	Anticancer activity	[52]
40.	<i>o</i> -vanillin	Antibacterial activity	[56,73]

		Catalyst	[73]
		Cytotoxic activity	[89]
		Antimicrobial activity,	[90]
		Molluscicidal activity	
		Nil	[100]
41.	2-carboxybenzaldehyde	Antimicrobial activity,	[90]
		Molluscicidal activity	
42.	1-(3-formyl-4-hydroxyphenylazo)-4-methylbenzene	Antimicrobial activity,	[90]
		Molluscicidal activity	
43.	1-(3-formyl-4-hydroxyphenylazo)benzene	Antimicrobial activity,	[90]
		Molluscicidal activity	
44.	Vaniline	Antimicrobial activity,	[57]
		molluscicidal activity	
		Antibacterial activity	[60]
45.	4-methoxybenzaldehyde	Nil	[63]
46.	Imidazoleacetophenone	Antimicrobial activity	[58]
47.	Piperonal	Antibacterial and antioxidant activities	[59]
48.	2-hydroxyacetophenone	Antibacterial activity	[65,73]
		Catalyst	[73]
		Antimicrobial activity	[86]
49.	2-hydroxypropiophenone	Antimicrobial activity	[86]
50.	Biacetyl	Antibacterial activity	[66]
51.	Pyridine-2-carbaldehyde	Electrochemical properties	[78]
		Nil	[85]
		Catalyst	[93]
52.	3-ethoxysalicylaldehyde	Antimicrobial activity	[79]
53.	1,3-bis(2'-formylphenyl)1,3-dioxapropane	Nil	[82]
54.	Benzoylacetone	Antimicrobial activity	[86]
55.	2-acetyl-pyridine	Antimicrobial activity	[87]
56.	2,3-Butanedione-3-monoxime	Antimicrobial activity	[94]
57.	2,2'-(ethylenedioxy)bis(benzaldehyde)	Antimicrobial activity	[112]
58.	Benzoin	Antibacterial activity	[88,104]
59.	acetoacetanilido-4-aminoantipyrine	Antifungal activity	[101]
60.	4-amino antipyrine	Antimicrobial activity, cytotoxicity	[108]
61.	Benzil	Antibacterial activity	[105]
62.	5,5-dimethylcyclohexane-1,3-dione	Biological activity, liquid-liquid extraction, active transport applications (predicted theoretically)	[106]
63.	<i>o</i> -phthalaldehyde	Antibacterial activity	[103]
64.	pentane-2,4-dione	Antibacterial activity	[107]
65.	2,6-diformyl-4-methyl phenol	Antibacterial, antifungal and antioxidant activities	[110]
66.	2,5-Thiophenedicarboxaldehyde	Antioxidant and anticancer activities	[111]

6. Conclusion

The review provides details of Schiff bases derived from anthranilic acid and their applications. These Schiff bases are widely used as chemosensors not only for detection of metal ions but also for the detection of anions. Furthermore, these Schiff bases and their various coordination compounds are reported to show wide range of applicability in medicine as antibacterial, antifungal, anticancer, antidiabetic, anti-inflammatory, antiulcer, antioxidant and mulluscicidal agents. Advances in this field will require analyses of structure-activity relationship (SAR) and mechanism of actions.

From structural point of view, these Schiff bases have varying denticity - bidentate, tridentate, tetradentate, pentadentate and hexadentate. The metal chelates exhibit different geometric structures around different metal ions. Common among these are tetrahedral, square planar and octahedral.

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