

Schiff Base Metal Complexes and Their Potential Medicinal Uses: A Review

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ABSTRACT

Metal complexes of Schiff bases are frequently employed in industry as catalysts, pigments, dyes, intermediates in chemical synthesis, polymer stabilizers, and corrosion inhibitors. They are produced when an amine condenses with carbonyl compounds. Schiff bases with imine or azomethine ($-C=N-$) functional groups are valuable pharmacophores for designing and developing various bioactive chemicals. Due to their broad uses in pharmaceuticals as antiviral, antibacterial, antifungal, antimalarial, antitubercular, anticancer, anti-HIV, anti-inflammatory, and antipyretic drugs, novel chemotherapeutic Schiff bases and their metal complexes have drawn the interest of medicinal chemists. The freshly synthesized Schiff bases and their metal complexes are highlighted in this study as possible bioactive cores.

INTRODUCTION

Since primary amines and carbonyl compounds, aldehydes, or ketones are condensation products, Schiff base ligands are given preference in their synthesis. Hugo Schiff, a German scientist and Nobel Prize laureate, developed Schiff bases in 1864 and was given his name as a result. The ability of Schiff bases to form complexes with transition metal ions makes them a crucial class of substances. Almost all metal ions can form complexes with Schiff base ligands, which are simple to make and coordinate with metal ions via azomethine nitrogen. Schiff base ligands have received much attention in coordination chemistry primarily because of their accessible availability and favorable electronic characteristics. Schiff base coordination chemistry has garnered much interest because of its significant roles in analytical chemistry, chemical synthesis, metal refinement, electroplating, metallurgy, and photography. Modern coordination chemistry and the advancement of bioinorganic chemistry both rely heavily on Schiff bases. They have a wide range of medical applications because of their pharmacological characteristics. The biological activity of azomethine derivatives depends on the C=N. As a result, some azomethines were found to have diuretic, anticancer, and antimicrobial (antibacterial, antifungal) properties. Schiff bases are widely used in the food and dye industries, analytical chemistry, catalysis, fungicidal, and agrochemical activities. In biological systems, the azomethine nitrogen of Schiff bases provides a binding site for metal ions to be attached with various bio-molecules like proteins and amino acids for anti-germ activities. This is particularly important for supramolecular chemistry, catalysis, material science, separation and encapsulation processes, and biomedical applications. Schiff bases produced by human bodies catalyze numerous metabolic processes using antimicrobial activity enzymes. Numerous researchers have improved the bio-functions of Schiff bases and their metal complexes. Schiff bases have antibacterial, antifungal, antiviral, anti-ulcer, and anticancer properties based on the transition metal ions present. A review highlighting the uses of Schiff base ligands and their complexes is required because there have been numerous reports on applications, particularly in biology, including antibacterial, antifungal, anticancer, antioxidant, anti-inflammatory, antimalarial, and antiviral activities. According to review papers, Schiff base metal complexes have many applications. This review emphasizes Schiff bases and their metal complexes' biological applications from 2000 to the present.

BASES FOR SCHIFF

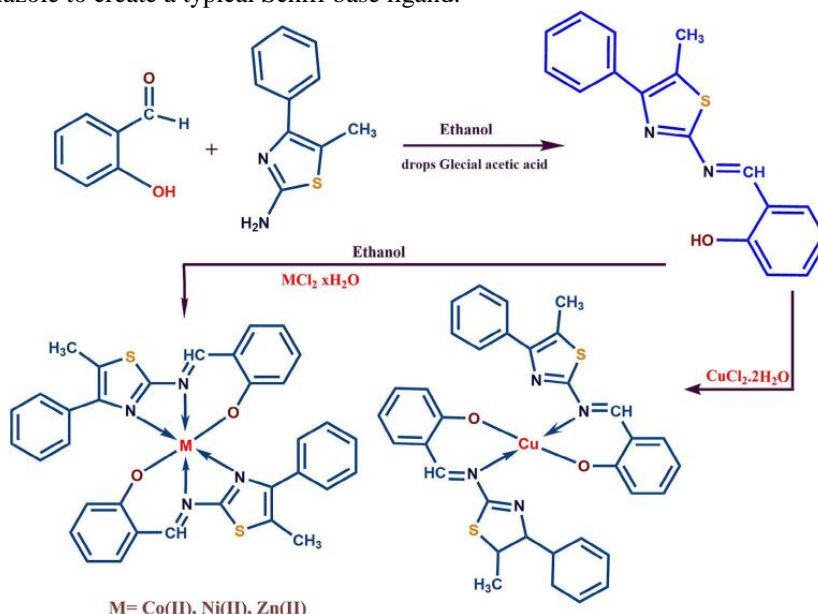
Mechanism and preparation

Nucleophilic addition is used to create Schiff bases from amines and carbonyl compounds, forming a hemi-aminal group and imine compounds that cause dehydration (Scheme 1). Since the initial manufacture of a Schiff base was recorded in the 19th century, numerous procedures for synthesizing Schiff bases have been published.

These are what they are:

Microwave irradiation for solvent-free synthesis

Schiff bases can be quickly and effectively synthesized using a microwave without solvents. Additionally, high product yield and purity. Some 4-phenylthiosemicarbazide Schiff bases with aromatic aldehydes (anisaldehyde, anthraldehyde, cinnamaldehyde, indole-3-carboxaldehyde, 1-naphthaldehyde, and o-vanillin) have been produced using microwave technology. System 1. Salicylaldehyde and its metal complexes were condensed with 2-amino-4-phenyl-5-methylthiazole to create a typical Schiff base ligand.



Utilizing the catalyst to create a solvent-free synthesis

When the reaction mixture is ground in a mortar and pestle, the efficient synthesis of Schiff bases using a catalyst, such as SnCl acetic acid, can be carried out at room temperature.

Catalyst- and solvent-free synthesis

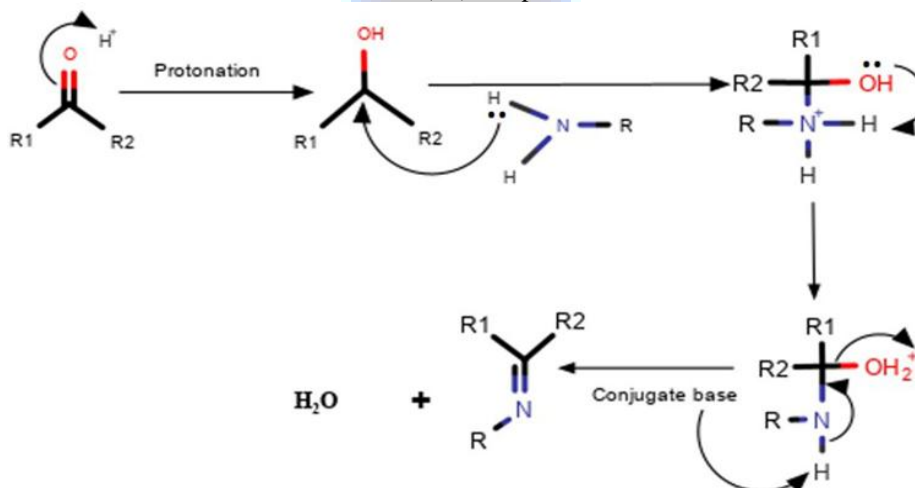
Amines, aldehydes, and ketone mixtures are ground in a mortar and pestle. The reaction takes two to three minutes to complete.

Constructed using solvents

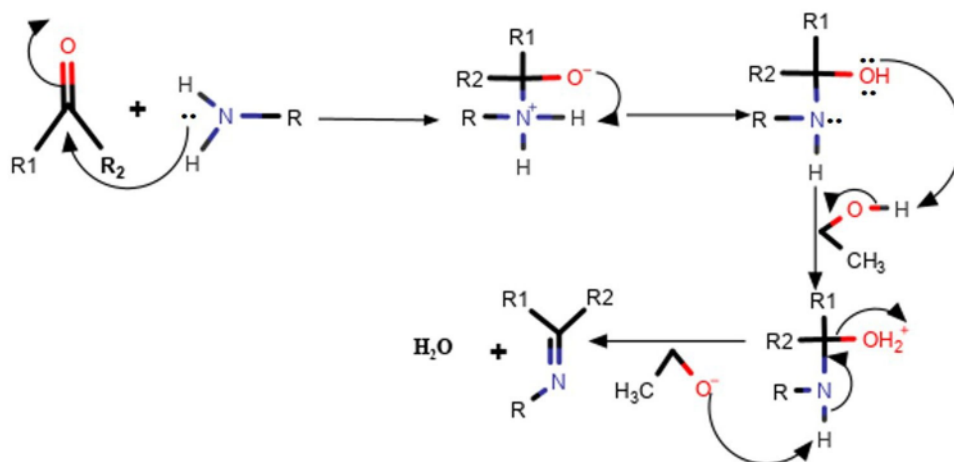
When the mixture is refluxed in an acidic, basic, or neutral medium, a suitable solvent, such as ethanol or methanol, is typically required. Purification methods for products include recrystallization, TLC, and column chromatography. Schemes 2 and 3 provide diagrams of the reaction mechanisms in various media—basic medium speeds up the nucleophilic attack, causing rapid Schiff base formation.

Schiff base types

According to various characteristics, Schiff bases are categorized, as seen in Figure 1. The number of donor atoms in a ligand determines how they are first categorized. As a monodentate ligand, the Schiff base 4-aminobenzenesulfonamide-1,3-benzodioxole-5-carbaldehyde can coordinate with transition metals. Bidentate aroyl hydrazine-based Schiff bases that form dioxouranium (VI) complexes.



Scheme 2. Schiff base ligand reaction mechanism in an acidic medium.



Scheme 3. Schiff base ligand in basic medium reaction mechanism.

(ON) have been characterized with acetone [17]. Monobasic bidentate (ON) Schiff bases of 2-((3-chlorophenyl imino) methyl)-5-(diethylamino) phenol, 2-((2,4-dichlorophenylimino)-methyl)-5-(diethylamino) phenol, 5-(diethylamino)-2-((3,5-dimethyl phenylamino) methyl) phenol, 2-((2-chloro-4-methyl phenylamino) methyl)-5-(diethyl amino) phenol, and 5-(diethylamino)-2-((2,6-diethylphenyl imino) methyl) phenol was produced and described. The tridentate Schiff base, 1-pyridin-3-ylimino-ethyl benzene-1,3-diol, was synthesized from 3-aminopyridine and 2,4-dihydroxyacetophenone and interacted with Ce (III), Pr(III) and Er(III). Tetradentate (ONNO) Schiff base ligand was produced via condensation of 1,2-di-(4-fluoro-phenyl) ethylenediamine with salicylaldehyde. Symmetrical pentadentate macrocyclic Schiff bases were produced via a template

Ligands	a. Donor atoms	i. Monodentate	
		ii. Bidentate	
		iii. Tridentate etc.	
b. No. of amino groups		i. Mono amino-aliphatic, aromatic	
		ii. Diamino-aliphatic, aromatic	Mono-condensed unsymmetrical
			Bi-condensed-bis
		iii. Triamino-	Symmetrical
			Unsymmetrical
Complexes	a. Binary (M,L)	i. Mononuclear	
		ii. Binuclear	
		iii. Trinuclear	
		Homo- M-L-M	
	Hetero- M-L-M'		
b. Ternary (M,L,L')			

Figure 1. Flow diagram demonstrating the classification of ligands and metal complexes technique based on the condensation of an amine-containing homopiperazine and 2,6-diacetylpyridine or 2,6-pyridine dicarboxaldehyde in 1:1mol ratio in the presence of metal ions. Hexadentate macrocyclic Schiff base ligands (N₆O₂) of 2-hydroxybenzaldehyde (H₂L) or 2-hydroxy-3-methoxybenzaldehyde have been produced by the condensation of polyamine, 2,20-(1,4-diazepane-1,4-diyl) aniline followed by reaction of 1-fluoro-2 nitrobenzene with homopiperazine. Schiff base ligand (N₄O₂) (6,60-((1E,11E)-5,8-dioxa-2,11-diazadodeca-1,11-diene-1,12-diyl) bis(2,4-dichlorophenol)) has been synthesized from 1,8-diamino-3,6-dioxaoctane and 3,5-dichloro salicylaldehyde. Two macrocyclic octadentate (N₆O₂) Schiff base ligands were generated by condensation of polyamine, 2,20-(ethane-1,2-diylbis(piperazine-4,1-diyl)) bis(ethan-1-amine) with 2-hydroxybenzaldehyde and 2-hydroxy-3-methoxybenzaldehyde, respectively. Schiff base ligands are also categorized depending on the amine types. Some monovalent bidentate Schiff base ligands and associated dioxouranium (UO₂) complexes were produced utilizing aniline as the main amine. Schiff bases produced from diamines are distinct sorts depending on their symmetry. The symmetrical Schiff base N₂O-bis(salicylidene)-o-phenylenediamine produced by the condensation of salicylaldehyde with o-phenylenediamine was described by X-ray diffraction. Transition metal complexes of symmetrical N₂O-bis [4-(benzene azo) salicylaldehyde]4-methyl-1,2-phenylenediamine Schiff base ligand have been described Nickel, copper and zinc complexes of the ligands formed by condensation of o-phenylene amine with salicylaldehyde, 2-hydroxy-1-naphthaldehyde or o-hydroxy acetophenone have been synthesized. By condensation of 2-((4-(2-amino benzyl)-1,4-diazepan-1-yl) methyl) benzylamine with 2-formyl pyridine, a symmetrical macrocyclic hexadentate (N₆ donor) Schiff base has been produced. An NN₂O type unsymmetrical Schiff base ligand is the mono-condensed form of the reaction between ethylenediamine or meso-1,2-diphenyl-1,2-ethylenediamine and salicylaldehyde derivatives. O-phenylenediamines and 2-hydroxyacetophenone or 2-hydroxy naphthaldehyde react to form the bis-unsymmetrical dibasic tetradentate Schiff base N-2-hydroxyacetophenon-NO-2-hydroxynaphthaldehyde-1,2 phenylene diamine. Three methoxysalicylidene and diethylenetriamine were

combined to generate the Schiff base, N1, N3-bis(3-methoxysalicylidene) diethylenetriamine. It has proven possible to create ferrocenyl-substituted Schiff bases by combining 2-acetylferrocene with 1,8-naphthalene diamine and 4-aminosalicylic acid. N, N0-bis(pyridoxyl-5,50-bis(phosphate) ethylenediamine and N, N0-bis(pyridoxal)-5,50-bis(phosphate)-100-(p-nitrobenzyl) ethylenediamine were produced by condensation of optically active C-substituted ethylenediamine and pyridoxal-5-phosphate Schiff bases. Schiff bases (4- {E-[(2-hydroxy-3-methoxyphenyl)methylidene]amino}benzene-1-sulfonamide and 4- {[(2-hydroxy-3-methoxyphenyl) methylidene] amino} -N-(5-methyl-1,2-oxazol-3-yl) benzene-1-sulfonamide were synthesized by reaction of 4-aminobenzene-1-sulfonamide and 4-amino-N-(3-methyl-2,3-dihydro-1,2-oxazol-5-yl)benzene-1-sulfonamide with 2-hydroxy-3-methoxy benzaldehyde. To create Schiff bases, E-N0-(3,4,5-trimethoxybenzylidene) benzofuran-2,6-carboxy hydrazide was reacted with ortho-phenylenediamine or 2,6-aminopyridine. Salicylaldehyde and aminoneocryptolepine were combined to create a Schiff base ligand. Both 4-(4-hydroxy-3-methoxybenzylidene amino) naphthalene-1,2-dione and 4-(3,4,5-trimethoxybenzylideneamino) naphthalene-1,2-dione have Schiff bases.

They are created from substituted benzaldehydes and 4-amino-1,2-naphthoquinone. L-alanine and 4-hydroxy salicylaldehyde have been reported to produce a Schiff base. The interaction of salicylaldehyde and benzoylhydrazide has created a Cu₂ or Fe₃ complex of the Schiff base ligand. Tetradentate Schiff bases produced from acetylacetone, benzoyl acetone, thenoyltrifluoroacetone, and dibenzoyl methane were combined with diamines (1,2-diamino propane or 1,4-diamino butane) and b-diketones (acetylacetone, benzoyl acetone, and thenoyltrifluoroacetone) in the ratio 1:2:1. Schiff base (NNO, NO) complexes comprising thiazole moiety generated from 2-amino-4-phenyl-5-methylthiazole and salicylaldehyde was produced in good yield in the metals Co (II), Ni(II), Cu(II), and Zn(II).

METAL ASSEMBLAGES

Getting complexes ready

Active imine (C 14 N) linkage in Schiff bases provides metal ion binding sites through nitrogen and other hetero-elements like oxygen and sulfur. Transition metals can create complexes with nitrogen, oxygen, and sulfur (Scheme 1). Weak acid prevents the precipitation of metals, while triethylamine is typically employed to make the medium basic, facilitating the deprotonation of ligands.

The traditional or wet chemical technique

Metal complexes can be created by stirring and refluxing a combination of prepared Schiff bases and metal salts in a suitable solvent, such as ethanol. The resulting compounds are dried after being cleaned with alcohol. The straightforward wet chemical procedure created the Fe (III) complex with carbonyl-releasing Schiff base chelate. Some ligands from benzoylhydrazine, salicyloyl hydrazine, and nicotinoylhydrazine have been produced as dioxouranium (VI) complexes with acetone in their keto and enol forms. Several dibasic tetradentate Schiff bases of the type MoO₂L dioxomolybdenum(VI) complexes of ethylenediamine, 1,2-propane diamine, trimethylenediamine with o-hydroxyaldehyde and o-hydroxyketone have been described. It has been possible to create Schiff bases produced from o-hydroxy aldehyde, ketone, and aniline as dioxouranium (VI) complexes. ONS donors from modified salicylaldehydes, 2-hydroxy-1-naphthaldehyde, and 2-aminothiophenol have been studied in Schiff bases' dioxouranium (VI) complexes.

Microwave-aided technique

Microwave-assisted synthesis has received much interest lately. Microwave irradiation applications, which are pollution-free, environmentally benign, inexpensive, and provide excellent yields with easy procedure and handling, are used to carry out chemical transformations. The preparation of metal complexes of N-(4-chlorobenzylidene)-5-methyl-1,3-thiazol-2-amine, N-[4-(dimethylamino) benzylidene]-6-nitro-1,3-benzothiazol-2-amine, and N-isonicotinamido-2-hydroxy naphthalaldimine using conventional and microwave synthesis methods has been compared.

Several kinds of metal complexes

Figure 1 illustrates the categorization of metal complexes according to the number of ligands (binary or ternary complexes) or metal ions (e.g., mono-, di-, or trinuclear complexes). The Schiff base ligand 2-((E)-(4-trifluoromethoxy) phenylimino) methyl-6-tert-butylphenol, which is produced by combining 4-trifluoromethoxyphenylamine with 2-hydroxy-3-tert-butyl benzaldehyde, has been used to generate the mononuclear binary complexes of Co (II), Ni (II), and Cu (II). An unsymmetrical tetradentate Schiff base ligand was produced using 5-chloro-2-hydroxybenzophenone, o-phenylenediamine, and salicylaldehyde. Its complexes with Cu (II), Ni (II), Zn(II), Mn(II), and Co(II) have been studied. The spectroscopy of mononuclear ternary copper (II) Schiff base complexes was studied. An NNOO type unsymmetrical tridentate Schiff base and secondary N-donor, heterocyclic ligands such as 2,20-bipyridine, 4,40-di-t-butyl-2,20-bipyridine, or 1,10-phenanthroline, were used to create ternary complexes of Cu (II).

Ligand. Condensation of 2-aminophenol with benzaldehyde (L1), 2-aminopyridine with salicylaldehyde (L2), and pyridine-2-aldehyde (L3) using 2-phenylpyridine (ppy) as a secondary ligand produced iridium (III) heteroleptic complexes of $[\text{Ir}(\text{ppy})_2(\text{L})]^{0/}$ with Schiff base ligands. Transition metal mixed-ligand complexes with Schiff base ligand (NNO) have been created by condensing 2-aminophenol, 1,10-phenanthroline, and quinolone-2-carboxaldehyde. The reactions of benzo-hydrazide with 5-fluoro-2-hydroxybenzaldehyde, 5-chloro-2-hydroxybenzaldehyde, and 5-bromo-2-hydroxybenzaldehyde resulted in the synthesis of homo-binuclear copper (II) complexes of Schiff bases. Schiff base hetero-binuclear cobalt (II) and copper (II) complexes were created. N, N'-phenyl-ene-bis-(3-methoxysalicylideneimine), a Schiff base ligand, was used to create a trinuclear (Zn-Y-Zn) complex. A virtually linear, dinuclear trinuclear structure is formed from the Schiff base N1, N3-bis(3-methoxysalicylidene) diethylene triamine. Both Zn(II) and Cd(II) are acceptable.

APPROACHES FOR CHARACTERIZATION

Physical (melting point, color, yields, solubility), elemental (CHN) analysis, thermal analysis, magnetic susceptibility, electrochemical (conductance measurements and cyclic voltammetry), and spectral (UV-visible, FTIR, ^1H NMR, ^{13}C NMR, and mass analysis) analytical techniques are used to determine the structures of the ligands and their complexes. The coordination of several functional groups of Schiff bases, such as OH, NH, CO, HC 14 N, and azomethine nitrogens, was discovered using FT-IR spectral analyses. The presence of the azomethine group (m-HC 14 N) is confirmed by a prominent absorption at 1608 cm^{-1} in the FT-IR spectra of the Schiff bases and metal complexes. The band areas are moved to higher wavenumbers by the development of the metal complexes. The presence of the OH proton or the absence of the aromatic carboxylic proton on the ligands was confirmed by ^1H NMR spectra. The SBL complex's ^1H NMR spectrum shows a signal at 12 ppm caused by NH protons and a signal at 8.0 ppm caused by azomethine protons. A signal caused by aromatic protons is also seen between 6.0 and 8.0 ppm. A distinct signal from azomethine carbon can be seen in ^{13}C NMR spectra around 165.00 ppm. The Schiff's UV-vis spectrum.

Strong intra-ligand charge transfer transition absorptions at 400 nm and broadband absorptions at 500 nm from d-d transitions were seen in base complexes. Electronic absorption spectra and magnetic susceptibility tests reveal the electronic structure of the metal ion in the complexes. Cyclic voltammetry is used to examine the metal complexes' electrochemical (redox) behavior. Data on conductance show that metal complexes are electro-lytic. The coordination behavior of ligands and the shape of metal complexes are suggested in light of all the experimental findings. Thermogravimetric experiments examine the Schiff base's thermal stability, breakdown, and complexes in an inert atmosphere. This means that the presence of metal ions modifies the appropriate breakdown steps. The molecular formula is consistent with the m/z values derived from mass spectra, and elemental analysis findings support this. According to an X-ray crystallographic study, complexes of Schiff bases were found to have comparable molecular structures with bond lengths and angles. The findings from SEM-EDS offer morphological details on Schiff bases and their complexes. The crystalline nature of the complexes is reflected in the X-ray diffraction of the powder. Complex geometry is optimized through computational chemistry investigations. Theoretical examinations were carried out to assess the structural specifics of the synthesized compounds. The complexes' structure, as proposed by the experimental study, is backed up by computations in quantum mechanics employing density functional theory (DFT) techniques. The exceptional stability of the compounds was validated by computer study using frontier molecular orbitals (FMOs) and natural bonding orbitals (NBOs). Data from theoretical spectroscopy agreed with those from experiments. Data from spectroscopy (FTIR et al.). Schiff bases and their complexes' molecular docking can help forecast how they interact with particular proteins.

Applications in biomedicine

The nitrogen of the azomethine group has a single pair of electrons on it, which has chemical and biological significance. By creating a hydrogen link between the active centers of several cell components, sp^2 hybridized nitrogens disrupt typical cellular functions.

Analgesic, antibacterial, anticonvulsant, antitubercular, anticancer, antioxidant, anthelmintic, antiglycation, and antidepressant are only a few biological functions that Schiff bases demonstrated. Figure 2 displays a pie graph comparing several biomedical uses. Table 1 lists chosen Schiff bases and their metal complexes' biological applications.

Antimicrobial

Multiple antibiotic resistances in bacteria lead to infectious illnesses with rising fatality rates. There is a critical medical need for the creation of novel antibacterial medications. Schiff bases are effective antibacterial compounds. Systemic fungal infections, which have the potential to be fatal, have increased recently. There has been a significant rise in overall fungal infections, making the research and development of more potent antifungal medications attractive antifungal therapies.

Methoxy, halogen, and naphthyl groups increase the ligands' capacity to kill fungus. Effective antifungal action is present in sulfur-containing Schiff bases generated from thiazole and benzothiazole derivatives.

Chelation might make it easier for a complex to pass through a cell membrane, increasing antibacterial activity. Due to the partial sharing of the metal ion's positive charge with donor groups and electron delocalization over the chelate ring, chelation diminishes the polarity of the metal ion. OCH₃, CH₃CH₂CH, and C₆H₅ are lipophilic groups that make the Schiff base and its metal complexes hazardous to some bacterial strains. The delocalization of p-electrons in the chelate ring increases the complexes' lipophilicity, facilitating their penetration through the lipid layer of the cell membrane. Most metal chelates are suited for penetration into cells and tissues because they have polar and nonpolar characteristics. N and O donors in the metal chelates of the ligand inhibit the synthesis of enzymes. The metal ion of polychelates is especially capable of deactivating enzymes that need a free hydroxyl group. Each of the metal polychelates is more hazardous than its corresponding ligand.

Bacillus megaterium and other organisms were examined for their antibacterial and antifungal properties in vitro. Candida tropicalis for 4-[(4-bromo-phenylamino)- Schiff bases complexed with Cd (II) and Cu (II) p-tolyl iminomethyl]-benzene-1,2,3-triol, 3-[(4-bromo-phenylamino)-methyl]-benzene-1,2,3-triol, and 4-[(3,5-di-tert-butyl-4-hydroxy-phenylimino)-methyl]-benzene-1,3-diol were highly effective against the tested bacteria.

Schiff bases of bis(ethan-1-yl-1-ylidene) and bis(azan-1-yl-1-ylidene) bis(1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one and (E)-1,5-dimethyl-2-phenyl-4-(1-(pyridine-2-yl) ethylidene amino)-1Hpyrazol-3(2H)-one derived from P. aeruginosa, Enterobacter cloacae, E. coli, Staphylococcus aureus, Klebsiella pneumoniae, Mycobacterium smegmatis, and Micrococcus letters. According to a report, the antibacterial activity of the Zn (II) complex of the Schiff base 4-chloro-2-(2morpholinoethylimino) methyl phenolate methanolchloro against Bacillus subtilis, S. aureus, E. Fluorescence of E. coli and Pseudomonas. According to research, the free salicylidene ligands show lower antibacterial activity toward gram-negative and gram-positive bacteria than the Cu (II), Co (II), and Mn (II) complexes.

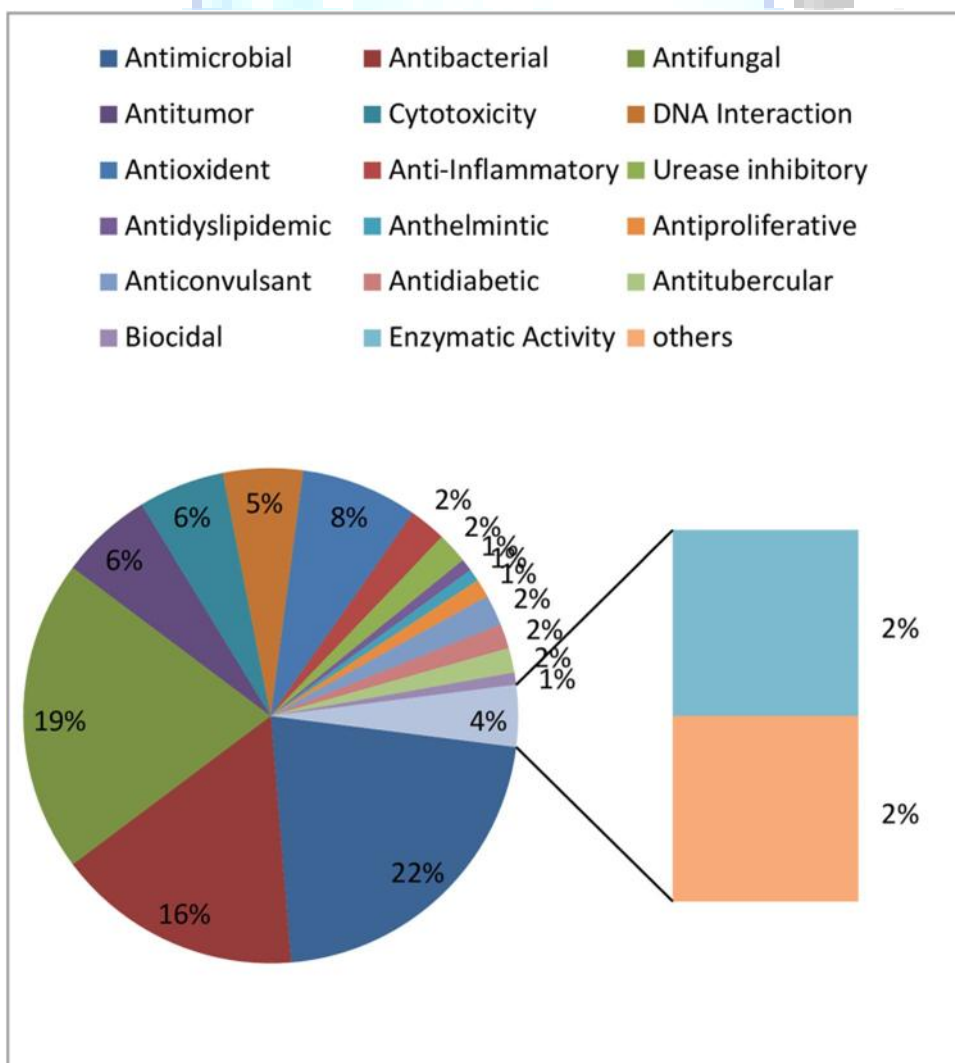


Figure 2. Comparison of articles on various biological processes.

Complexes containing nitro group showed better activity than complexes with halogen Schiff base 3-[40(4'-chloro phenyl)-60-(4'-methyl phenyl)pyrimidin-20-yl]iminoisatin obtained from substituted Isatin and 4-(40-chlorophenyl)-6-(4'-methyl phenyl)-2-aminopyrimidine were more active when tested for in vitro antibacterial activity against *Salmonella typhimurium*, *S.aureus*, *Enterococcus faecalis*, *P. aeruginosa*, *K. Aeromonas hydrophila*, *B. pneumonia*, *Staphylococcus albus*, *Vibrio cholera-01*, and *B. both Providencia rettgeri* and *S. subtilis*.

Cu (II), Ni (II), Zn (II), Co (II), and VO(II) complexes of the Schiff bases 1-phenyl-2,3-dimethyl-4(4-iminopentane-2-one)-pyrazole-5-one and 1-phenyl-2,3-dimethyl-4(4-imino pentane-2-one)-pyrazole-5-one were produced by the reaction of the former with the latter.

Phenol demonstrated more antibacterial action against *Salmonella typhi*, *S. Niger*, *S. aureus*, and *Pseudomonas aeruginosa*. Thiophene carboxaldehyde and aminobenzoic acid benzimidazole are the sources of Schiff bases.

CONCLUSION

Due to their straightforward synthesis and ease of complex formation with various metal ions possessing diverse denticity, Schiff bases are intriguing ligands. Due to the bioactive azomethine core of many Schiff bases, these compounds have become more important in medicine. The versatile uses of Schiff bases and their metal complexes in treating ailments ushered in a new age in medical science. The human body uses Schiff base metal complexes to replenish trace and ultra-trace levels of transition metal ions. The antibacterial efficacy of metal complexes was higher than that of the comparable Schiff base ligands.

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