

Importance of Schiff base Complexes with transition metals : A Review

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Abstract : Schiff's bases are commonly used for industrial purpose and also exhibit a wide range of biological activities. These are the most widely used organic compounds which are used as intermediates in organic synthesis, catalysts, pigments and dyes, polymer stabilizers, etc. Complexes of Schiff base with transition metals, the largest group of elements on the periodic table, have been used as medicine, pharmacy, coordination chemistry, biological activities, food packages, dyes and polymer and also used as an O₂ detector. Recent studied about Schiff bases and their metal complexes show numerous applications in pharmacology such as antiviral, antifungal, antimicrobial, antimalarial, antituberculosis, anticancer, anti- HIV, catalytic application in oxidation of organic compounds and nanotechnology. Due to the interaction of metal chelates with the DNA helix, they can be used in the design of new design of new models in diagnosis and therapy. Due to their photochromism feature, they can be used in different fields, such as controlling and measuring radiation intensity, image systems and optical computers. They are also used as pigment dyestuffs in the dye industry, especially in textile dyeing. Moreover, they are widely used in the perfume. They can be used in aircraft construction, television and computer screens, digital clock displays by taking advantages of the liquid crystal feature that occurs in some metal complexes.

(Keywords : Schiff's base ligands, transition metal complexes).

Introduction

German chemist Hugo Schiff first reported Schiff bases in 1864¹. Schiff bases are organic compounds that result from the

condensation reaction of carbonyl compounds with primary amines². Their structure may be represented generally as R'-CR=N-R'', in which R, R', and R'' may vary. R and R' can be alkyl, aryl, or heterocyclic substituents. The carbonyl fragment may come from an aldehyde or a ketone (>C=O). Because of the azomethine (>C=N-) group present in them, Schiff bases are also known as azomethines or imines. Those formed from aldehydes and ketones are termed as aldimines and ketimines, respectively.

A general representation of Schiff base formation by condensation of an amine with a carbonyl group is shown in Figure 1. In the formation of Schiff bases, nucleophilic amines attack electrophilic carbonyl compounds by nucleophilic addition to form a hemiaminal intermediate, which then dehydrates to provide the imine product. Initially, the amine attacks the aldehyde or ketone to form the unstable carbinolamine adduct. The carbinolamine dehydrates under acid- or base-catalysis. Since carbinolamine is an alcohol, it dehydrates in the presence of an acid catalyst (Figure 2). The reaction often proceeds under reversible acid or base catalysis or heating during Schiff base formation from aldehydes or ketones. When the product is isolated or water is removed (or both), the reaction proceeds to completion. Hydrolysis of a number of Schiff bases with aqueous acid or base gives corresponding aldehydes, ketones, and amines.

Schiff bases with aryl substituents are more stable and can be prepared easily, while the ones with alkyl substituents are comparatively less stable^{3,4}. Aliphatic aldehyde Schiff bases are labile and tend to polymerize, whereas aromatic aldehyde Schiff bases enjoy effective conjugation and show increased stability. Considering that aldehydes have less steric hindrance than ketones, the former react faster; moreover, higher carbon content reduces the electrophilicity of a ketone compared to aldehyde. Due to simple preparation, ready availability, and electronic properties, Schiff bases have received much attention, and there is immense interest in exploring wide-ranging applications in organic⁵, inorganic^{6,7}, coordination⁸⁻¹⁰, bioinorganic^{11,12}, and environmental chemistry¹³⁻¹⁶. Schiff base derivatives have been used in medical, pharmaceutical, metal refining, metallurgy, catalysis, food, sensing, filtration, environmental, photography, and diagnostic areas. The discovery of Schiff bases marked an important development in coordination chemistry. In association with a wide range of transition metal ions, the Schiff base ligand forms stable metal complexes that find applications in various fields. Schiff bases are noted for their chelating properties; hydroxyl and thiol groups in azomethine systems could form five- or six-membered chelate rings with metal ions. Bidentate, tridentate, tetradentate, and polydentate Schiff bases are possible. The azomethine nitrogen is sp^2 -hybridized, and its lone pair is highly significant biologically and chemically. In heterocyclic rings containing Schiff bases, the abundance of donor atoms enriches their role in coordination chemistry¹⁷⁻¹⁹. The Schiff bases show a wide range of biological activity, such as nematicidal²⁰, insecticidal, antibacterial, antifungal, antileukemic, anti-inflammatory, anti-HIV activity, antimycobacterial activity, antioxidant, anticancer, and plant growth regulatory effects.

Besides biological areas, Schiff bases and their metal complexes have great potential in analytical chemistry, dye industry, and corrosion

inhibition. The compounds have received much attention from both experimentalists and theorists owing to their interesting photoluminescent properties in the visible region at room temperature, and thus, can be applied to microelectronics, optoelectronics, and biological sensing. Schiff bases show excellent catalytic activity for many reactions, such as polymerization, reduction of thionyl chloride, reductions of ketones, oxidation of organic substrates, aldol reactions, epoxidation of alkenes, hydrosilylation of ketones etc.

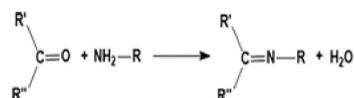


Figure - 1 General scheme of formation of Schiff base

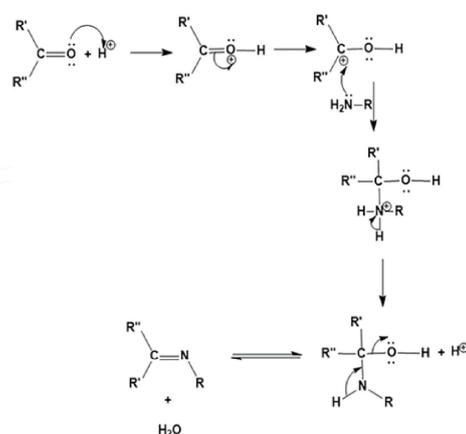


Figure - 2 Mechanistic explanation of the formation of Schiff base

Chemists have applied Schiff bases and the related metal complexes in numerous processes, including the oxidation of alkene and catalytic transformation of hydrocarbons to useful oxygenated products like alcohols, aldehydes, and epoxides. A closely related field of interest

involves the catalysis of alkene oxidation by soluble transition metal complexes. Diverse donor sites present in Schiff bases support a wide range of transition metal complexes. The metal complexes of Schiff bases have resulted in several biological applications, as well as significant advances in a variety of chemical fields. In consideration of their unique property profiles and ease of synthesis, metal-containing Schiff bases are considered ideal candidates for new antibiotic drug molecules inhibiting the growth of bacteria. The properties of the metal complexes of Schiff bases are directly influenced by the nature of the ligands and the central metal ion. On the whole, considerable attention has been paid to Schiff bases due to their diverse chemical and physical properties and simple preparation procedure.

2. Synthesis of Schiff Bases and Their Metal Complexes

The synthesis of Schiff bases is straight forward and highly tunable, allowing for the incorporation of diverse functional groups to tailor properties²¹. The general reaction involves the condensation of a primary amine ($R-NH_2$) with an aldehyde or ketone ($R'-CHO$ or $R'-C(=O)-R''$), yielding the imine ($R-N=CH-R'$ or $R-N=CR'-R''$) along with water as a byproduct²². This reaction is typically catalyzed by acids or bases and proceeds efficiently in solvents like ethanol or methanol under reflux conditions.

Aromatic aldehydes, such as salicylaldehyde or 2-hydroxybenzaldehyde, are preferred due to the resulting stability of the Schiff base, attributed to conjugation and intramolecular hydrogen bonding²³. Aliphatic counterparts, while reactive, often lead to less stable products prone to hydrolysis or polymerization. Examples include the formation of N-(2-thiophenecarboxaldene)-2-aminobenzoic acid (HL) from 2-thiophene carboxaldehyde and 2-aminobenzoic acid, or indole-3-carboxaldehyde with m-aminobenzoic acid. Amino acids like L-alanine or L-phenylalanine react with 5-

bromosalicylaldehyde to yield biologically relevant ligands.

Once synthesized, these ligands are complexed with transition metal salts. The metal precursor—often chlorides, nitrates, or acetates of Fe(III), Co(II), Ni(II), Cu(II), or Zn(II)—is added in a 1:1 or 1:2 (metal: ligand) stoichiometric ratio, and the mixture is refluxed in a polar solvent²⁴. For instance, Fe(III)-HL complexes are prepared by reacting $FeCl_3 \cdot 6H_2O$ with the deprotonated ligand, yielding octahedral geometries. Microwave-assisted synthesis has gained traction for its speed and energy efficiency; for example, Pd(II) complexes from salicylaldehyde derivatives can be obtained in minutes with yields exceeding 90%.

Green chemistry approaches, such as solvent-free grinding or use of ionic liquids, are increasingly employed to minimize environmental impact²⁵. Chiral Schiff bases, derived from chlorides, nitrates, or acetates of Fe(III), Co(II), Ni(II), Cu(II), or Zn(II)—is added in a 1:1 or 1:2 (metal: ligand) stoichiometric ratio, and the mixture is refluxed in a enantiopure amines, enable asymmetric catalysis when complexed with metals like Ru or Rh²⁶. Overall, synthetic flexibility allows for the design of mono-, bi-, or polydentate ligands, dictating the coordination sphere and reactivity of the resulting complexes.

3. Transition Metal Complexes of Schiff Bases

3.1 Coordination Behavior: Transition metals readily coordinate with Schiff bases, forming complexes with diverse geometries. The imine nitrogen is the primary donor site, but additional donor atoms (e.g., hydroxyl, carboxyl, or thiol groups) enhance chelation^{27,28}.

3.2 Electronic Properties: Metal–ligand interactions alter the electronic spectra of complexes, often leading to intense coloration. These properties are exploited in dye manufacture and optical devices.

3.3 Structural Diversity: Complexes may adopt octahedral, square planar, tetrahedral, or distorted geometries depending on the metal ion and ligand denticity²⁹. X ray crystallography has revealed intricate supramolecular architectures in many Schiff base complexes.

3.4 Spectroscopic Characterization: Techniques such as UV-Vis, IR, NMR, ESR, and mass spectrometry are employed to characterize these complexes³⁰. Spectroscopic data provide insights into bonding modes, electronic transitions, and stability.

4. Industrial Applications

Schiff base complexes have found extensive industrial utility:

4.1 Catalysis: Transition metal–Schiff base complexes catalyze oxidation, polymerization, and hydrolysis reactions. For example, Mn(III)–Schiff base complexes are efficient in epoxidation of olefins^{31,32}.

4.2 Pigments and Dyes: Their intense coloration and stability make them valuable in textile dyeing and pigment production³³.

4.3 Polymer Stabilizers: Schiff base complexes act as antioxidants, preventing degradation of polymers under heat or UV exposure.

4.4 Nanotechnology: Metal–Schiff base complexes are incorporated into nanomaterials for enhanced catalytic and electronic properties.

5. Biological Applications

Schiff base transition metal complexes have garnered significant attention for their pharmacological potential, often surpassing the activity of free ligands due to chelation-enhanced liposolubility and targeted interactions with biomolecules like DNA and enzymes.

5.1 Antimicrobial Activity: Antibacterial efficacy is a hallmark of these complexes, attributed to

Tweedy's chelation theory, which posits that coordination reduces polarity and increases delocalization of π -electrons, facilitating lipid solubility and bacterial membrane disruption. Gram-positive bacteria (e.g., *Staphylococcus aureus*, *Bacillus subtilis*) are generally more susceptible than Gram-negative ones due to thicker peptidoglycan layers in the former.

Zn(II) complexes of 5-amino-4H-1,2,4-triazole-3-thiol-derived Schiff bases exhibit superior inhibition against *E. coli*, *Klebsiella pneumoniae*, and *Pseudomonas aeruginosa*, with minimum inhibitory concentrations (MICs) as low as 10 $\mu\text{g/mL}$, outperforming ligands by 2–4 fold. Cu(II) mixed-ligand complexes with unsymmetrical tridentate Schiff bases and 1,10-phenanthroline show potent activity against *S. aureus* and *Salmonella typhi*, linked to intercalative DNA binding. Activity trends often follow Cu(II) > Ni(II) > Co(II) > Zn(II), as seen in indole-3-carboxaldehyde-m-aminobenzoic acid complexes³⁴.

Chitosan-based Schiff bases complexed with Ru(II) enhance activity against *Bacillus subtilis* and *E. coli* through oxidative stress induction. Recent 2025 studies on Er(III), Pr(III) complexes with anthracene-9-carbaldehyde ligands report broad-spectrum efficacy, with Pr(III) showing 95% inhibition of *P. aeruginosa* at 50 μM .

5.2 Antifungal Activity: Fungal infections pose a growing threat, and Schiff base complexes offer viable alternatives to azoles. Cu(II) and Ni(II) o-phthalaldehyde-amino acid complexes inhibit *Aspergillus niger* and *Rhizoctonia solani* with zones of inhibition up to 20 mm, attributed to enzyme disruption. Cr(III), Mn(III), Fe(III) macrocyclics from hydrazones excel against *Aspergillus* spp., with Cr(III) > Fe(III) > Mn(III) potency.

Thiazole-Schiff base Cu(II) complexes, bearing methoxy or halogen substituents, combat

Candida albicans and *Fusarium oxysporum* via ROS generation, with MICs 5-10 $\mu\text{g/mL}$ lower than fluconazole in resistant strains. Oxovanadium (IV) triazoles show 80% inhibition of *Alternaria alternata* at low doses. Chitosan-pyrazole Schiff bases with Ru(II) are particularly effective against *A. fumigatus*, leveraging the pyridyl moiety for enhanced binding.

5.3 Anticancer Activity: The anticancer potential stems from DNA intercalation, proteasome inhibition, and apoptosis induction. Cu(II), Zn(II), Cd(II) complexes from 2-acetylpyridine-L-tryptophan target MDA-MB-231 breast cancer cells, with Cd(II) achieving $\text{IC}_{50} = 15 \mu\text{M}$ via caspase activation. Water-soluble Pt(II) reduced-Schiff bases outperform cisplatin against HL-60 leukemia ($\text{IC}_{50} = 8 \mu\text{M}$ vs. $20 \mu\text{M}$), minimizing nephrotoxicity.

Tetradentate N_2O_2 Cu(II) complexes inhibit MCF-7 breast cancer proliferation by 70% at $50 \mu\text{M}$, altering hydrophilicity for better cellular uptake³⁵. Ni(II) dinuclear complexes from 6,6'-dimethoxy-diphenolato ligands show selectivity for HCT116 colon cancer, inducing G2/M phase arrest. Halogenated R-enantiomers of salicylaldehyde-3-amino-1,2-propanediol complexes exhibit higher cytotoxicity against HeLa cells than S-forms, due to stronger DNA groove binding. Cu(II)-6-aminobenzothiazole complexes bind DNA intercalatively, reducing A549 lung cancer viability by 85%.

5.4 Antioxidant Activity: These complexes scavenge free radicals like DPPH(2,2-diphenyl-1-picrylhydrazyl)(figure4) and ABTS[2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid)] (figure5), protecting against oxidative stress³⁶. Chitosan-Schiff bases with carboxymethyl groups inhibit superoxide by 90% at 1 mg/mL. Ferrocenyl-Schiff bases (e.g., OFP) trap ABTS radicals with 95% efficiency, outperforming ascorbic acid, thanks to the ferrocene redox shuttle. Ru(II/III) complexes with 4-

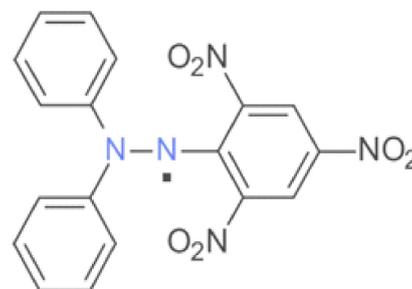


Figure.4 DPPH(2,2-diphenyl-1-picrylhydrazyl)

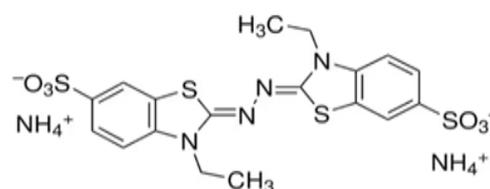


Figure.- 5 ABTS[2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid)]

5.5 Anti-inflammatory and Antiviral Activity: Anti-inflammatory effects mimic NSAIDs (Nonsteroidal anti-inflammatory drugs); Cu(II)-dien complexes reduce carrageenan-induced edema by 60%, comparable to indomethacin. 3-Benzylideneamino-phenylimino indolinones inhibit COX-2 with $\text{IC}_{50} = 25 \mu\text{M}$.

Antivirally, salicylaldehyde-1-amino-3-hydroxyguanidine Schiff bases suppress mouse hepatitis virus replication by 70%³⁷. Silver(I)-glycine salicylaldehyde complexes regulate cucumber mosaic virus in plants. Gossypol-derived bases inhibit HIV reverse transcriptase.

6. Catalytic Applications

Schiff base complexes excel as catalysts due to their tunable redox potentials and steric control, enabling efficient mediation of organic reactions under ambient conditions.

6.1 Polymerization Reactions: Fe(III) and Co(II) pyridine bis(imine) complexes polymerize ethylene with activities up to $10 \text{v g/mol}\cdot\text{h}\cdot\text{bar}$, producing high-molecular-weight polyethylenes.

Salen-Co(II) initiates epoxide ring-opening, yielding polycarbonates with >99% selectivity³⁸. Organocobalt tridentate complexes drive vinyl emulsion polymerization.

6.2 Oxidation Reactions: Ru(II) ONS complexes oxidize alcohols to aldehydes using NMO, with turnover numbers (TONs) >500. Cu(II) salen derivatives epoxidize styrene (91% yield) with TBHP, mimicking cytochrome P450. Mo(VI) complexes selectively oxidize olefins to epoxides, reusable up to 5 cycles³⁹. Hydroxybenzaldehyde-Co(II)/Fe(II) oxidize cyclohexane to cyclohexanol quantitatively.

6.3 Reduction Reactions: Chiral Rh-Schiff bases reduce ketones asymmetrically with ee >95%. Pd(II)-chitosan supports hydrogenate 1-tetralone to tetralin (99% conversion). Co(II) cyanohydrins reduce alkenes via oxygenation.

6.4 Other Reactions: Al(III) salen catalyzes enantioselective aldol additions (ee 90%). Cu(II)-cinchona Henry reactions yield nitroalcohols with 98% ee. Zn(II) hydrosilylates ketones quantitatively

7. Environmental and Technological Uses

7.1 Oxygen Detection: Schiff base complexes, particularly those involving transition metals like cobalt (Co(II)), are indeed effective as optical or electrochemical sensors for molecular oxygen (O₂) due to their ability to undergo reversible binding with O₂⁴⁰. This property mimics natural oxygen carriers like hemoglobin, allowing the complexes to detect O₂ concentrations in real-time without permanent alteration, which is crucial for sensor applications in environmental monitoring, biomedical devices, or gas analysis.

7.2 Photochromism: Photochromism refers to the reversible transformation of a chemical species between two forms with different absorption spectra, typically induced by light exposure, resulting in a visible color change⁴¹. In

coordination complexes—molecules where a central metal atom or ion is bound to ligands—this phenomenon is particularly intriguing because the metal-ligand interactions can modulate the photochromic behavior, enabling tunability and enhanced properties compared to purely organic photochromes. These complexes often incorporate photochromic ligands (e.g., diarylethenes, spiropyrans, or azobenzenes) that undergo isomerization, electron transfer, or other photochemical reactions upon irradiation.

7.3 Liquid Crystals: Metal–Schiff base complexes exhibit liquid crystal behavior, useful in display technologies such as televisions, computer screens, and digital clocks.

7.4 Food Packaging and Perfumes: Their stability and antimicrobial properties make them suitable for food preservation and fragrance industries.

8. Case Studies and Recent Advances

Recent literature highlights innovative applications:

8.1 Nanotechnology Integration: Schiff base complexes embedded in nanoparticles enhance drug delivery and catalytic efficiency⁴².

8.2 Comparative Analysis: Studies comparing Cu(II) and Ni(II) complexes reveal differences in biological activity and stability.

8.3 Smart Materials: Photoresponsive Schiff base complexes are being developed for sensors and adaptive materials.

9. Challenges and Future Perspectives

Despite their promise, Schiff base complexes face challenges:

9.1 Synthetic Limitations: Coordination complexes, which consist of a central metal ion or atom bonded to surrounding ligands, often face significant synthetic challenges. These arise

primarily from thermodynamic instability (e.g., unfavorable equilibrium favoring decomposition), kinetic lability (rapid ligand exchange or dissociation), sensitivity to external conditions (e.g., air, moisture, or light), and practical issues like volatility, toxicity, or similarity in solubility to impurities, making purification difficult. As a result, many complexes cannot be prepared via standard solution-based methods or require specialized techniques like inert atmospheres, low temperatures, or non-traditional approaches⁴³ (e.g., mechanochemistry or microwave-assisted synthesis)

9.2 Stability Issues: Hydrolysis of imine bonds can reduce long term stability⁴⁴. While this limits their long-term use in aqueous or humid conditions, careful ligand design, metal coordination, and encapsulation strategies can significantly improve durability.

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9.3 Toxicity Concerns: Biocompatibility must be thoroughly evaluated before clinical use

9.4 Future Directions: Research is focusing on green synthesis, biocompatible complexes, and integration into smart materials for medicine and technology.

10. Conclusion

Schiff base complexes with transition metals represent a versatile class of compounds, pivotal in coordination chemistry due to their facile synthesis, chelating properties, and tunable structures. They exhibit profound applications in catalysis, industrial dyes, polymer stabilization, and nanotechnology, while showcasing potent biological activities including antimicrobial, anticancer, and antioxidant effects. Despite challenges like stability and toxicity, ongoing advances in green synthesis and smart materials integration herald their expanded role in medicine, environmental sensing, and optoelectronics, promising innovative solutions for global challenges.

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