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Review

Green Synthesis, Coordination Properties and Emerging Applications of Schiff Base Metal Complexes: Recent Advances and Future Perspectives

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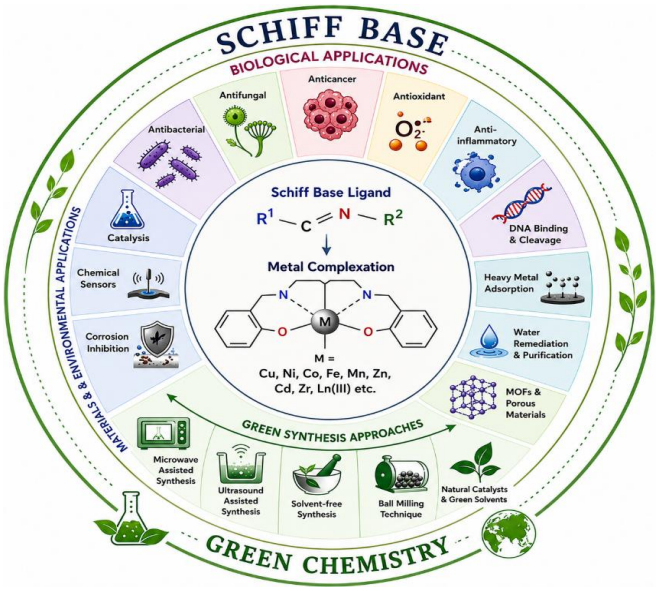
Abstract

Schiff base ligands are essential for a number of chemical reactions because of their adaptable coordination skills and adjustable characteristics. This paper examines the latest developments in the synthesis of Schiff base ligands, comparing conventional condensation methods with green synthetic approaches such as natural acid catalysis, aqueous media synthesis, mechanochemistry, microwave-assisted synthesis, and ultrasound irradiation. Their coordination chemistry is examined in terms of donor modes, coordination geometries, and spectroscopic/crystallographic characterization, with attention to how ligand structure and metal-ion selection govern structure–activity relationships, supported by recent computational and spectroscopic advances in understanding metal–ligand interactions. Biological activities, including antibacterial, antifungal, anticancer, antioxidant, and anti-inflammatory effects, and their mechanisms are discussed alongside applications in catalysis, chemical sensing, corrosion inhibition, metal–organic frameworks, and environmental remediation. Current limitations in scalability, reproducibility, and clinical translation are outlined, together with future directions emphasizing sustainable synthesis, advanced characterization, and rational ligand design.

Keywords Schiff bases, Green synthesis, Coordination chemistry, Biological activities Catalysis, Sustainable chemistry, Environmental applications.



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1. Introduction

The development of Schiff-base systems increasingly demands efficient control of ligand synthesis, coordination behavior, and functional properties alongside reduced environmental impact. The increasing demand for coordination compounds with tunable structural, electronic, and biological properties has stimulated considerable interest in Schiff bases because of their structural diversity, multiple potential donor atoms, and readily modifiable organic frameworks. Schiff base ligands are essential in coordination chemistry because of their adaptable coordination abilities and can function as L-type ligands through donor atoms such as nitrogen, oxygen, and sulfur. Multidentate Schiff-base ligands can donate electron pairs to metal centers without undergoing valence-shell redox changes, thereby providing control over the steric and electronic environment surrounding the coordinated metal ion [1]. This adaptability enables Schiff bases to interact with a broad range of metals, including early transition metals, d-block elements, and lanthanoid ions, while influencing oxidation-state stability, coordination geometry, and electronic properties [2]. Bidentate and tridentate Schiff bases containing donor sequences such as ON, NN, ONO, ONS, and NNS have consequently been reported to form chelated complexes with metal ions including Co(II), Ni(II), Cu(II), Pd(II), V(IV), Ti(IV), and uranium in several oxidation states [3]. Schiff bases are generally formed through the condensation of amines with carbonyl compounds involving the loss of water from amine–aldehyde or amine–ketone pairs [4]. Schiff first described these condensation products in 1864, establishing the class of organic bases now known as Schiff bases, while the structural class was subsequently formalized under IUPAC nomenclature as imines bearing a hydrocarbyl substituent on nitrogen, represented by the general fragment $R^1R^2C=NR^3$ [5]. This framework encompasses considerable structural diversity arising from alkyl and aryl groups, together with related compounds such as hydrazides, dihydrazides, hydrazones, and hydrazide–hydrazones discussed within related structural frameworks involving amide–iminol or imine–enamine tautomerism [6].

Conventional preparation generally relies on heating, organic solvents, and subsequent isolation and purification, and although such methods have enabled the synthesis of a wide variety of Schiff-base structures, prolonged reaction times, solvent consumption, energy requirements, and chemical-waste generation have encouraged the development of more sustainable alternatives. Consequently, recent research has increasingly focused on environmentally friendly synthetic strategies, including aqueous synthesis, natural-acid or bio-based catalysis, microwave-assisted synthesis, ultrasound-assisted synthesis, mechanochemistry, and solvent-free procedures, which can offer reductions in reaction time, solvent use, energy consumption, and waste generation; however, their sustainability benefits may depend on reaction conditions, substrate scope, reproducibility, isolation procedures, and scalability. Beyond synthetic advances, structural modification of Schiff-base frameworks has provided opportunities to control ligand stability, coordination behavior, and spectroscopic properties. For example, salicylaldimine-type Schiff bases containing an ortho-hydroxyl group can form intramolecular resonance-stabilized hydrogen bonds that influence ligand stability and spectroscopic behavior [7], while structural variations in N-arylsalicylaldimine nickel complexes have been associated with changes in geometry, magnetic behavior, and ligand-field splitting [8]. Criteria for correlating imine and phenolic functionalities with chelate-ring environments and assigning ON and ONO coordination modes have also been established through spectroscopic studies using infrared and proton NMR techniques [9].

Multidentate frameworks containing donor arrangements such as NNNN, ONNO, and NSNO can provide stabilizing environments for metal ions, including those in relatively high oxidation states, while ferrocene-based tetradentate Schiff bases have enabled stabilization of uranium and other metal centers over oxidation states ranging from +2 to +5 [1], [10]. Despite these advances, important research gaps remain concerning the reproducibility, substrate scope, isolation procedures, scalability, and overall sustainability of green synthetic approaches, as well as the systematic understanding of how ligand architecture, metal identity, coordination geometry, and electronic properties collectively govern chemical and biological behavior. Although metal coordination has frequently been associated with enhanced biological activity through changes in lipophilicity, cellular uptake, metal-ion delivery, and interactions with biological targets, free ligands may retain or even exceed the activity of their corresponding complexes in some systems [6], [11].

Schiff bases and their metal complexes have consequently attracted extensive attention for antibacterial, antifungal, antiviral, antitumor, anti-inflammatory, antipyretic, antimalarial, anticancer, anesthetic, and enzyme-inhibitory activities [11], with complexes of Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Au(I), and Pt(II) demonstrating diverse biological responses in selected studies [12]–[14]. Their applications extend beyond biomedicine to catalysis, crystal engineering, chemical and biological sensing, materials science, corrosion inhibition, metal–organic frameworks, and environmental

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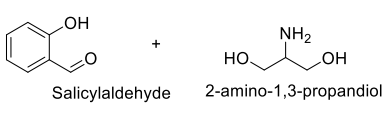
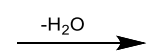
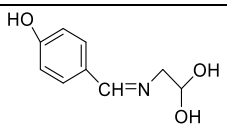
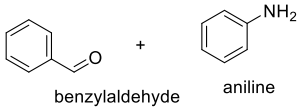
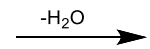
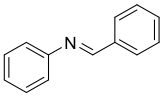
remediation [15], [16]. Against this background, the present review critically examines recent developments in the synthesis, coordination chemistry, characterization, and emerging applications of Schiff bases and their metal complexes, with particular emphasis on environmentally friendly synthetic approaches, their comparative advantages and limitations, and the relationships between ligand structure, metal coordination, and resulting chemical and biological properties. Current challenges, knowledge gaps, and future research opportunities are also highlighted to support the development of efficient, reproducible, and environmentally responsible Schiff-base systems.

2. Conventional synthesis of Schiff bases

The conventional preparation of Schiff bases is generally carried out by reacting equimolar amounts of a primary amine and an aldehyde or ketone in an organic solvent under reflux conditions. Ethanol and methanol are the most frequently employed reaction media because of their excellent solvating ability, ease of handling, and compatibility with a wide range of reactants. In most reported procedures, the reaction mixture is heated for several hours to facilitate condensation and promote complete conversion of the starting materials into the corresponding imine derivatives. The desired Schiff bases are subsequently isolated by cooling the reaction mixture, followed by filtration, washing, and recrystallization to obtain analytically pure products. Depending on the nature of the substrates, catalytic amounts of acids such as acetic acid, hydrochloric acid, or *p*-toluenesulfonic acid may be employed to accelerate the condensation process and improve product yields. According to Mir and Banik et al., the standard laboratory route to Schiff bases involves heating a carbonyl compound with a primary amine, which drives condensation and leads to efficient imine formation in solution [17]. Nagar et al. emphasized that, in typical protocols, the carbonyl compound and amine are dissolved in short-chain alcohols such as ethanol or methanol, the mixture is heated to reflux, and the applied heat simultaneously supplies the activation energy for bond formation and promotes removal of the byproduct water [18]. Raczuk et al. explained mechanistically that the lone pair on the amine nitrogen first attacks the electrophilic carbonyl carbon to generate a tetrahedral carbinolamine intermediate, and that this amino alcohol is intrinsically unstable and rapidly loses a water molecule to lock in the characteristic carbon–nitrogen double bond of the Schiff base [6]. Depending on the electronic and steric properties of the reactants, the reaction generally reaches completion within a few hours under reflux conditions, affording moderate to excellent yields [17], [18]. In many conventional protocols, catalytic amounts of acids such as acetic acid or hydrochloric acid are employed to activate the carbonyl group, thereby accelerating nucleophilic addition and facilitating dehydration of the intermediate [18]. Following completion of the reaction, the Schiff base product is typically isolated by cooling the reaction mixture, filtration of the precipitated solid, and purification by recrystallization from an appropriate solvent to achieve high purity. Conventional methodologies are applicable to a wide variety of aromatic and aliphatic aldehydes, ketones, and primary amines, enabling the synthesis of structurally diverse Schiff base ligands for coordination chemistry. However, these procedures often require prolonged heating and substantial volumes of volatile organic solvents, resulting in higher energy consumption and increased solvent waste. Consequently, although conventional synthesis remains reliable and widely adopted, its environmental limitations have encouraged the development of greener and more sustainable synthetic alternatives.

Table 1. Representative methods for the conventional synthesis of Schiff bases.

No.	Reactants	Reaction Equation	Product (Schiff Base)	Name of Product
1				Schiff base derived from halogenated salicylaldehyde and amino alcohol
2				Benzylideneaniline (N-benzylideneaniline)

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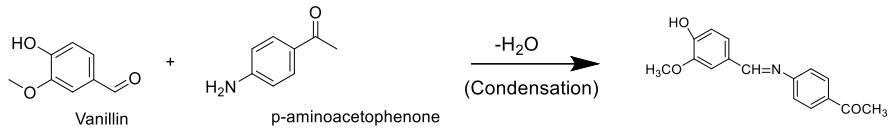
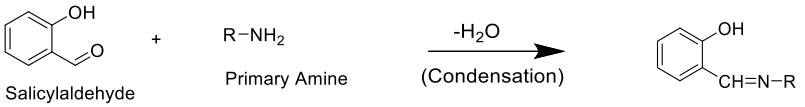
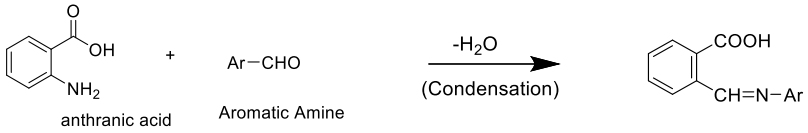
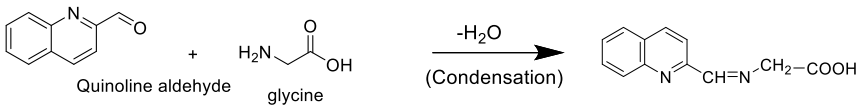
3			Vanillin–*p*-aminoacetophenone Schiff base
4	Ar−CHO Aromatic Aldehyde + Ar'—NH2 Aromatic Amine	-H2O (Condensation)	Ar−CH=N−Ar' Aromatic Schiff base (Ar–CH=N–Ar′)
5			Salicylideneimine (salicylaldehyde-derived Schiff base)
6			Anthranilic acid Schiff base
7			Quinoline–glycine Schiff base (quinoline–amino acid Schiff base)
8	Ar−CHO Aromatic Aldehyde + Ar'—NH2 Aromatic Amine	-H2O (Condensation)	Ar−CH=N−Ar' Aromatic Schiff base (Ar–CH=N–Ar′)

Mir and Banik stressed that this imine-forming condensation is fundamentally reversible, because water produced as a byproduct accumulates in the reaction medium and continuously drives the equilibrium back toward the starting carbonyl and amine [17]. Nagar et al. outlined several classical strategies used by synthetic chemists to overcome this limitation, including azeotropic distillation with toluene to continuously remove water, addition of activated molecular sieves that act as chemical sponges for the water formed, and use of a Dean–Stark apparatus to separate and collect the condensed aqueous phase before it can return to the reaction flask [18]. Raczuk et al. noted that, although these methods differ in practical implementation, they all rely on the same Le Chatelier-based principle that physical removal of water from the reaction system shifts the equilibrium toward the imine product and leads to higher yields and cleaner reactions [6]. Mir and Banik showed that the nature of the carbonyl partner has a dramatic influence on the ease of condensation, with aliphatic aldehydes occupying the most reactive end of the spectrum because their strongly electrophilic carbonyl carbon is flanked by only one substituent and is readily approached by the amine nucleophile [17]. Nagar et al. reported that ketones behave differently, since two substituents on the carbonyl carbon create additional steric congestion and donate electron density into the carbonyl, thereby decreasing electrophilicity and slowing imine formation relative to aldehydes [18]. Mir and Banik pointed out that aromatic ketones are often the most reluctant substrates, because conjugation between the aryl ring and the carbonyl group further reduces intrinsic reactivity while the bulk of the ring exacerbates steric hindrance, so that condensations with these substrates frequently require longer reaction times, higher temperatures or deliberate addition of acid or base catalysts [17]. Raczuk et al. observed that, despite these substrate-dependent challenges, the classical condensation route remains widely adopted in academic and industrial laboratories because it uses inexpensive and readily available reagents, tolerates a broad range of functional groups, and yields reproducible products with relatively simple experimental setups [6]. Nagar et al. nevertheless underlined that conventional protocols consume large volumes of organic solvent, rely on sustained heating and may involve catalysts or additives that are not environmentally benign, which makes their overall footprint incompatible with many principles of green chemistry [18]. Mir and Banik highlighted solvent-free procedures, mechanochemical grinding, microwave-assisted synthesis and aqueous-phase reactions as alternative methodologies that can furnish the same Schiff base products under milder, more sustainable conditions, and they systematically compared these approaches with the classical method in terms of reaction time, yield and environmental impact [17]. Nagar et al. reinforced this perspective by organizing green synthetic strategies into categories based on natural-acid catalysis, water as a green solvent, microwave irradiation, grinding, ball milling and other eco-

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friendly techniques, showing how each class can reduce solvent use, energy consumption or hazardous waste relative to traditional reflux-based condensations [18].

Malav and Ray discussed how the conventional route is equally capable of generating achiral Schiff bases when achiral aldehydes and amines are used, and they emphasized that such ligands form the structural core of many coordination complexes, materials and catalytic systems in which the imine framework simply serves as a robust scaffold around the metal center [20]. Mali et al. showed that, when the amine or carbonyl partner carries a built-in stereogenic element—for example, chiral amines, amino alcohols, diamines or amino acid derivatives—the resulting Schiff base inherits this chirality, and that coordination of these chiral ligands to metals creates asymmetric catalytic sites capable of steering enantioselective reactions [21]. Mir and Banik summarized that chiral Schiff bases have become privileged ligands in asymmetric catalysis, citing examples such as chiral Schiff base copper complexes used in Henry (nitroaldol) reactions and chiral metal–Schiff base systems applied in asymmetric cyclopropanation, where the chiral environment around the metal translates directly into high stereochemical control in the product [17]. Nagar et al. concluded that, taken together, these observations explain why the conventional condensation route, despite its environmental shortcomings, remains the foundational method for generating both achiral and chiral Schiff bases, and why ongoing development of greener variants continues to build upon its simple mechanistic logic and broad synthetic scope [18].

3 Green synthesis of Schiff bases

The increasing demand for more sustainable chemical processes has encouraged researchers to reconsider conventional approaches to Schiff-base synthesis. Traditional condensation methods are generally effective, but they may involve prolonged reflux, relatively large quantities of volatile organic solvents, and mineral-acid or metal-based catalysts. These requirements can increase energy consumption, solvent waste, and exposure to potentially hazardous reagents [17], [18], [26]. As a result, considerable attention has been directed toward synthetic procedures that reduce solvent use, shorten reaction times, decrease energy requirements, and simplify product isolation while maintaining satisfactory yields and product quality. For Schiff-base synthesis, the concept of green chemistry can be translated into several practical objectives. These include replacing hazardous or volatile solvents with safer media, reducing or eliminating toxic catalysts, lowering the temperature and duration of the reaction, and minimizing the amount of waste generated during synthesis and purification [17], [18]. The environmental performance of a reaction can also be assessed quantitatively using parameters such as atom economy, E-factor, process mass intensity (PMI), solvent consumption, energy requirement, and waste generated per unit mass of product. Such measurements are particularly useful because a reaction that is rapid or high-yielding is not necessarily the most sustainable if it requires excessive solvent, energy-intensive equipment, or extensive purification.

3.1. Aqueous and solvent-reduced synthesis

The use of water as a reaction medium is one of the simplest ways of reducing dependence on conventional organic solvents. Rao et al. demonstrated that Schiff bases can be prepared in aqueous media with good reaction rates and relatively simple product isolation procedures [24]. In suitable systems, the limited solubility of the resulting Schiff bases in water allows the products to separate from the reaction medium and be recovered by filtration, washing, and drying. This can substantially reduce the solvent requirements associated with extraction and recrystallization [17], [18], [24]. The suitability of water, however, depends strongly on the chemical nature of the substrates. Many aromatic aldehydes and amines have limited solubility in water, which can reduce contact between the reactants and consequently affect the rate of condensation. In addition, imine formation is reversible, and the presence of water can favor hydrolysis of the C=N bond under some conditions. Reaction pH, temperature, substrate concentration, and stoichiometry therefore need to be controlled carefully when aqueous procedures are developed [17], [18], [24]. Water should consequently be regarded as a useful green reaction medium rather than as a universally superior solvent for all Schiff-base systems.

The use of naturally derived acidic media provides another way of reducing reliance on conventional mineral-acid catalysts. Lemon juice, lime juice, tamarind extract, tomato extract, gooseberry extract, berry juice, and cashew nut shell liquid have been investigated as catalytic or reaction-promoting media for Schiff-base formation [17], [18] ,[25]–[35]. Their catalytic effects are generally associated with naturally occurring organic acids and other constituents capable of assisting carbonyl activation and dehydration during imine formation. Several of these systems have also been combined with microwave irradiation, ultrasound, or mechanical grinding, making it important to

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distinguish the contribution of the natural catalyst from that of the accompanying activation method. For example, lime juice has been used as an acidic medium during the grinding-assisted condensation of vanillin with *p*-aminoacetophenone. The reported procedure required approximately 50 min and afforded a 94% yield of the Schiff-base product [31]. The resulting compounds were subsequently investigated for corrosion inhibition, with reported efficiencies ranging from approximately 23.11% to 86.16%, demonstrating that compounds obtained through such green procedures can also have practical materials-related applications. Natural-acid catalysis has also been combined with ultrasound. In the synthesis of anthranilic-acid-derived Schiff bases, lemon juice was used together with ultrasonic irradiation, reducing the reported reaction time to approximately 10 min compared with about 1 h under conventional heating [28]. The shorter reaction time illustrates the potential advantage of combining a bio-derived catalyst with an external activation technique, although it would be inappropriate to attribute the entire improvement solely to the natural acid.

3.2. Solvent-free and mechanochemical approaches

Eliminating the reaction solvent altogether provides another means of reducing waste and simplifying the synthetic procedure. Mechanochemical methods generally use manual grinding or ball milling to bring the reactants into close contact and supply mechanical energy to the reaction mixture [17], [18]. Because little or no solvent is required, these procedures can reduce solvent waste and, in suitable cases, allow the product to be isolated with minimal work-up.

The grinding-assisted synthesis of vanillin-derived Schiff bases provides a representative example. Marufah et al. used lime juice during the grinding of vanillin and *p*-aminoacetophenone and obtained the corresponding Schiff bases in approximately 50 min with a 94% yield [31]. The same compounds displayed corrosion-inhibition efficiencies of approximately 23–86%, depending on the molecular structure and experimental conditions. Renewable waste-derived materials have also been incorporated into mechanochemical synthesis. Cashew nut shell liquid (CNSL), which contains a high proportion of anacardic acid, has been used as a sustainable catalytic material in the solvent-free grinding synthesis of a quinoline-based amino-acid Schiff base ligand [34]. The resulting ligand behaved as a dibasic tridentate ONO donor and formed octahedral complexes with divalent metal ions, demonstrating that a renewable catalytic medium can be used to access ligands that are subsequently useful in coordination chemistry. Other waste-derived catalytic systems have been investigated as well. Patil et al. reported calcined eggshell as a calcium-rich heterogeneous catalyst for Schiff-base synthesis under solvent-free conditions [18]. Such approaches have an additional sustainability advantage because they convert an otherwise discarded material into a useful component of the synthetic process. Nevertheless, the practical scalability of manual grinding and laboratory ball milling remains uncertain, and larger-scale studies are needed before these methods can be considered suitable replacements for conventional industrial processes.

3.3. Solvent-free and mechanochemical approaches

Among the different green approaches investigated for Schiff-base preparation, microwave irradiation provides some of the clearest quantitative evidence for reducing reaction time. Microwave energy interacts directly with microwave-absorbing species in the reaction mixture, allowing rapid heating under appropriate conditions [17], [18]. The resulting increase in heating rate can considerably shorten the time required for imine formation.

The comparative data compiled by Nagar et al. illustrate this effect clearly. In one reported system, microwave irradiation produced the Schiff base in 3 min with an 89% yield, whereas conventional heating required 30 min and gave 48%. A second example gave 97% in 3 min under microwave irradiation, compared with 92% after 180 min under conventional conditions. Other reported comparisons include 89% in 13 min versus 69% in 300 min, and 84% in 5 min versus 71% in 600 min, for microwave and conventional procedures, respectively. Further comparisons reinforce the reduction in reaction time. One Schiff-base synthesis gave 90.31% in 2–3 min under microwave irradiation, compared with 70.03% after 60–120 min using the conventional method. Another produced 79% in 4 min, whereas the conventional procedure required 1200–1260 min and afforded only 35%. Additional examples gave 93% in 6 min versus 69% in 120 min, and 89% in 15 min versus 61% in 60 min. The final examples in the reported comparison also demonstrate why both reaction time and yield should be considered. One reaction gave 94% after 10 min under microwave irradiation and 93% after 120 min conventionally, while another afforded 96% in only 1 min compared with 75% after 90 min using conventional heating. Thus, microwave irradiation does not necessarily increase the yield dramatically in every case. In some reactions, the principal advantage is the large reduction in reaction time, while in others both reaction rate and isolated yield improve.

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Microwave irradiation has been applied to a variety of Schiff-base systems, including salicylaldehyde derivatives, isatin-derived compounds, antibiotic-based ligands, chitosan-containing Schiff bases, and heterocyclic systems [18]–[23]. Bhagat et al. reported salicylaldehyde-derived Schiff bases in aqueous medium under microwave irradiation, with several products obtained in yields exceeding 90% and with substantially shorter reaction times than conventional procedures [18], [22]. Punitha et al. further combined microwave irradiation with sweet-lemon juice as a natural acid catalyst for the preparation of a cefotaxime–salicylaldehyde Schiff base and its Ni(II) and Cu(II) complexes [18], [27]. Other studies have extended microwave-assisted synthesis to piperonal–chitosan systems and pyrimidine-containing Schiff bases prepared using water as a reaction medium. These results make microwave irradiation one of the more extensively investigated alternatives to conventional heating. Nevertheless, the environmental benefit should not be inferred from reaction time alone. Microwave power, irradiation duration, reaction concentration, solvent volume, vessel type, and energy consumption should also be reported when possible. Such information would permit a more meaningful comparison between microwave and conventional heating from a sustainability perspective.

3.4. Ultrasound-assisted synthesis

Ultrasound irradiation offers another means of accelerating Schiff-base formation. The effect is generally attributed to acoustic cavitation, in which the formation and collapse of microscopic bubbles produces localized high-energy conditions that improve mixing and mass transfer [17], [18]. These effects can accelerate condensation while allowing the bulk reaction mixture to remain at a comparatively moderate temperature. A clear quantitative example was reported by Bakht for the synthesis of anthranilic-acid-derived Schiff bases. The ultrasonic procedure required approximately 10 min, whereas the corresponding conventional procedure took about 1 h [28]. The ultrasound-treated products also showed improved stability and crystallinity. Arafa and Shaker subsequently compared ultrasound, microwave irradiation, and conventional heating for the preparation of bis-Schiff bases under catalyst-free conditions, providing a direct comparison of the three activation approaches [40]. The use of ultrasound therefore offers a practical means of shortening reaction times without relying exclusively on prolonged thermal treatment. However, sonochemical performance depends on factors such as ultrasound frequency, power, reactor configuration, reaction volume, and the position of the reaction vessel within the ultrasonic field. These parameters can become particularly important during scale-up, where laboratory-bath conditions cannot necessarily be reproduced directly in larger reactors.

3.5. Comparative assessment of green synthetic approaches

The reported studies show that different green strategies address different limitations of conventional Schiff-base synthesis. Aqueous procedures primarily reduce dependence on organic solvents, whereas solvent-free and mechanochemical methods can eliminate the reaction medium altogether. Natural-acid catalysts provide renewable alternatives to mineral acids, while microwave and ultrasound irradiation primarily target reaction time and energy-transfer efficiency. In practice, these approaches are often combined; for example, natural acids have been used together with ultrasound or grinding, and water has been combined with microwave irradiation. The resulting improvement should therefore be evaluated in relation to the complete reaction system rather than assigned to one feature in isolation.

Quantitative comparisons are particularly useful in this regard. The microwave data reported by Nagar et al. show that reaction times of 30–1200 min under conventional conditions were reduced to approximately 1–15 min under microwave irradiation in the selected examples, while the corresponding reported yields ranged from 35–92% for conventional procedures and 79–97% for microwave procedures. These results indicate a substantial kinetic advantage for microwave processing, although the yield improvement varies from one substrate to another. In the 10 min/94% example, for instance, the conventional method already gave 93%, meaning that microwave irradiation provided a major time saving rather than a major increase in yield. Other green approaches show similar benefits in selected systems. Lime-juice-assisted grinding produced the vanillin-derived Schiff base in approximately 50 min with a 94% yield, while ultrasonic treatment of the anthranilic-acid system reduced the reaction time from approximately 60 min to 10 min. These examples provide stronger evidence for the efficiency of green methods than general statements that they are “rapid” or “high-yielding.”

Despite these advances, direct comparisons between different green methods remain difficult because experimental reporting is not standardized. Studies frequently provide reaction time and isolated yield but omit information on energy consumption, catalyst loading, solvent volume, concentration, work-up requirements, or process mass intensity. In addition, reaction performance can vary considerably with the structure and solubility of the aldehyde and amine, making it difficult to

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compare yields from unrelated substrate systems directly. Reproducibility is another important issue. Microwave reactions can be affected by power and vessel geometry, while sonochemical reactions depend on equipment configuration and operating parameters. Mechanochemical reactions may vary with grinding time, milling frequency, ball-to-material ratio, and scale. Natural catalysts introduce an additional source of variation because their composition can depend on biological origin and preparation. These factors should be reported in sufficient detail if green Schiff-base procedures are to be reproduced and compared across laboratories. Future studies should therefore move beyond reporting only isolated yield and reaction time. Wherever practical, authors should provide the reaction temperature, solvent volume, catalyst identity and loading, substrate concentration, reaction scale, energy input, and purification procedure together with the isolated yield. Reporting metrics such as PMI and E-factor would also strengthen comparisons between conventional and green protocols. Such information would allow the sustainability of Schiff-base synthesis to be evaluated on the basis of measurable process performance rather than on the use of a particular technique alone.

4. Natural acid catalysts and bio-based media

Naturally derived acidic materials have attracted attention as alternatives to conventional mineral-acid catalysts in Schiff-base synthesis. Nagar et al. highlighted fruit juices, plant extracts, and other bio-based materials as potential green catalytic media, while Anastas and Warner placed their use within the broader principles of green chemistry, particularly the reduction of hazardous reagents and waste generation [18]–[37]. Yadav and Mani reported several renewable sources, including lemon juice, tamarind extract, lime juice, gooseberry extract, berry juice, tomato extract, and cashew nut shell liquid (CNSL), which contain naturally occurring organic acids and other bioactive constituents that can promote condensation reactions [18], [38].

4.1. Natural acids as catalytic media: method and reaction trend

The catalytic effect of these materials follows the general acid-assisted pathway of Schiff-base formation. Protonation of the carbonyl group increases its electrophilicity and facilitates attack by the primary amine. The resulting carbinolamine intermediate subsequently undergoes dehydration to form the C=N linkage [18], [38]. Thus, the main role of the natural acid is to facilitate carbonyl activation and dehydration, allowing the condensation to proceed under comparatively mild conditions. The reported reaction conditions show a general trend toward lower temperatures, shorter reaction times, and reduced dependence on corrosive mineral acids. For example, Sobhi Daniel prepared 2-hydroxybenzaldehyde-based Schiff bases using lemon juice at room temperature for 30 min, while Alikhani et al. employed lemon juice at 55 °C for condensation involving 4,6-diamino-2-thiolpyrimidine [29], [49]. These examples indicate that natural-acid systems can operate without the prolonged reflux commonly associated with conventional synthesis. Elemike et al. used a few drops of lemon juice in the condensation of 3,4-dimethoxybenzaldehyde with 2-aminoethanesulfonic acid. The lemon juice markedly accelerated crystallization compared with the uncatalyzed system. The same study also used sugarcane sap in preparing a silver nanocomplex, which showed enhanced antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, and *Staphylococcus aubeus* compared with the parent ligand and nanoparticles alone [18], [25].

4.2. Combination with microwave and ultrasound methods

Natural-acid catalysis has also been combined with alternative energy sources. Punitha et al. reported microwave-assisted synthesis of a cefotaxime–salicylaldehyde Schiff base using sweet lemon (Citrus limetta) juice as the natural catalyst. The corresponding Ni(II) and Cu(II) complexes exhibited antimicrobial activity against E. coli and S. aureus [18], [27]. Bakht combined lemon juice with ultrasonic irradiation for the condensation of anthranilic acid and 4-hydroxy-3-methoxybenzaldehyde. The reaction time was reduced to approximately 10 min, compared with about 1 h for the conventional procedure, while improvements in product yield and crystallinity were also reported [18], [27], [28]. This comparison suggests that the benefit arises from the combination of natural-acid catalysis and enhanced mass transfer produced by ultrasound rather than from the catalyst alone. The same principle is evident in other bio-based catalytic systems. Bentoumi et al. used a lemon-derived acidic medium to prepare benzoxazole-containing Schiff bases and reported moderate yields, shorter reaction times, antioxidant activity, and favorable predicted ADMET properties [30]. Adesina showed that benzylideneaniline formation from benzaldehyde and aniline did not occur without tamarind extract, whereas lemon-juice-catalyzed condensation of benzaldehyde with urea produced benzylideneurea derivatives with biological activity [26].

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4.3. Natural acids in solvent-free and mechanochemical synthesis

A further development is the combination of natural acids with solvent-free grinding. Marufah et al. used lime juice (Citrus aurantifolia) as a natural acid catalyst in the grinding-assisted synthesis of Schiff bases from vanillin and p-aminoacetophenone. The reaction required approximately 50 min and gave a 94% yield [18], [31]. The resulting compounds showed corrosion-inhibition efficiencies ranging from approximately 23% to 86%, depending on the compound and experimental conditions [31]. This result compares favorably with the general aim of solvent-free synthesis because mechanical grinding eliminates the need for a conventional reaction solvent while the lime juice provides the acidic environment required for condensation. However, the reported advantage should be interpreted in terms of the complete process, including catalyst preparation and product purification, rather than reaction yield alone. Manjula et al. used Solanum lycopersicum extract as a natural acid catalyst for Schiff bases derived from L-histidine and o-hydroxybenzaldehyde. The products showed anti-inflammatory, larvicidal, antibacterial, and antifungal activities [18], [31], [32]. Subathra Sheeba Daniel similarly used gooseberry extract for the condensation of benzaldehyde and p-toluidine, and the resulting Schiff base exhibited moderate antimicrobial activity against S. aureus, K. pneumoniae, E. coli, P. aeruginosa, and A. flavus [33]. CNSL provides another example in which a bio-based material also contributes to waste valorization. Vidyavathi et al. used CNSL, which is rich in anacardic acid, as a catalyst for the solvent-free grinding synthesis of a quinoline-based amino-acid Schiff base ligand. The ligand behaved as a dibasic tridentate ONO donor and formed octahedral complexes with divalent metal ions [18], [33], [34]. The method therefore combines renewable catalytic material, solvent reduction, and preparation of a ligand useful for coordination chemistry.

4.4. Comparison and interpretation of natural-acid systems

Comparison of the reported examples shows that natural-acid catalysts can be used under several different reaction formats. Lemon juice has been applied under room-temperature conditions, at 55 °C, and in combination with ultrasound or microwave irradiation [27]–[29], [49]. Lime juice has been successfully combined with grinding, giving a 94% yield in approximately 50 min [31]. CNSL has similarly been used under solvent-free grinding conditions [34]. These examples indicate that the natural catalyst is compatible with both conventional mild heating and non-conventional activation techniques. The main advantage is therefore not simply that a fruit juice or plant extract replaces a mineral acid. Rather, these materials can be integrated with reaction conditions that reduce solvent consumption, shorten reaction time, or lower the severity of the process. The ultrasound example is particularly illustrative: reducing the reaction time from approximately 60 to 10 min represents a substantial improvement in processing time [28]. Likewise, the 94% yield obtained in 50 min using lime juice and grinding demonstrates that a solvent-free natural-acid system can provide an efficient product-forming route [31]. The reported biological and functional applications also show that natural-acid-catalyzed synthesis is not limited to obtaining the Schiff-base product. Products prepared using these approaches have been investigated as antimicrobial agents, antioxidant compounds, corrosion inhibitors, colorimetric receptors, and ligands for metal complexes [18], [25]–[35], [49]. However, these applications primarily demonstrate the usefulness of the synthesized compounds and should not automatically be interpreted as evidence that the natural catalyst itself improves biological performance.

4.5. Limitations and future requirements

Despite these advantages, natural-acid catalysis has several limitations. Fruit juices and plant extracts are chemically variable, and their acid content can depend on plant source, maturity, season, extraction procedure, and storage conditions. Such variation can affect reaction reproducibility when compared with standardized mineral acids. In addition, many studies have been performed at laboratory scale, and the availability, preparation, storage, and standardization of natural catalytic materials at larger scale remain insufficiently established. A second limitation is incomplete quantitative reporting. Some studies provide exact reaction times or yields, whereas others describe the outcome only as “good,” “high,” or “moderate.” This makes direct comparison difficult. Future studies should therefore report catalyst amount or concentration, substrate ratio, temperature, reaction time, isolated yield, solvent volume, and purification requirements wherever possible. Energy consumption and green metrics such as E-factor or process mass intensity would further strengthen comparisons with conventional methods. Finally, biological activity should be evaluated using appropriate controls. The same Schiff base prepared through conventional and natural-acid routes should ideally be compared under identical biological-testing conditions. Such experiments would clarify whether differences in activity arise from

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the synthetic route or simply from the molecular structure of the Schiff base. Overall, natural acids and bio-based media provide promising alternatives for Schiff-base synthesis, particularly when combined with ultrasound, microwave irradiation, or solvent-free grinding. The available evidence supports their potential to reduce reaction time, solvent use, and reliance on conventional mineral acids [18], [27]–[35]. Nevertheless, standardization, reproducibility, scale-up, complete quantitative reporting, and direct comparison with conventional methods remain necessary before these approaches can be considered universally applicable replacements for established catalytic systems.

Table 2. Representative natural-acid catalysts used for green Schiff-base synthesis.

Natural catalyst	Model reaction	Conditions	Reaction time	Yield (%)	Reported feature	Application	Ref.
Lemon juice	2-Hydroxybenzaldehyde + amine derivatives	Room temperature; stirring	30 min	NR	Mild reaction conditions	Colorimetric sensing of acetate and fluoride ions	[49]
Lime juice	Vanillin + p-aminoacetophenone	Grinding (solvent-free)	50 min	94.45	Solvent-free mechanochemical synthesis	Corrosion inhibition	[31]
Tamarind extract	Benzaldehyde + aniline	Natural-acid catalysis	NR	NR	Reaction did not proceed without catalyst	Schiff-base synthesis / bioactive compounds	[26]
Cashew nut shell liquid (CNSL)	2-Hydroxyquinoline-3-carbaldehyde + L-tryptophan	Solvent-free physical grinding	NR	NR	Renewable catalyst; waste valorisation	Schiff-base ligand and metal complexes	[34]
Berry fruit juice	Anisaldehyde / salicylaldehyde / benzaldehyde + aniline	Freeze-dried berry-juice extract	NR	NR	Bio-based natural-acid catalyst	Antioxidant applications	[35]

Note: NR = not reported. CNSL = cashew nut shell liquid. Numerical reaction times and yields are given only where explicitly reported in the cited literature.

5. Water as a green solvent

Water is widely utilized as a green reaction medium due to its safety, low cost, and environmental compatibility, offering a sustainable alternative to volatile organic solvents employed in conventional synthesis. The utilization of aqueous media is consistent with the principles of green chemistry, as it reduces hazardous waste generation, minimizes solvent-related environmental impacts, and enhances the sustainability of chemical processes. In many cases, aqueous reaction systems exhibit improved chemoselectivity and suppress competing side reactions, resulting in higher product purity and enhanced reaction efficiency. Furthermore, the limited solubility of the synthesized Schiff base products in water often promotes direct precipitation from the reaction medium, facilitating product isolation by simple filtration and washing while reducing the need for solvent-intensive purification techniques. The condensation reaction may also be accelerated by naturally derived acidic or basic catalysts, such as citric acid, lemon juice, or other bio-based additives, which provide a mild and environmentally compatible catalytic environment. Despite these advantages, aqueous synthesis remains associated with certain challenges, including the poor aqueous solubility of hydrophobic reactants and the reversible nature of imine (C=N) bond formation, which renders Schiff bases susceptible to hydrolytic degradation under aqueous conditions. These limitations may affect reaction yields and present challenges for process optimization and industrial-scale implementation. Nevertheless, aqueous synthesis represents a sustainable and efficient alternative to conventional solvent-based methods for Schiff base synthesis by integrating environmental compatibility with operational simplicity and improved process efficiency. The use of water also facilitates compliance with several principles of green chemistry, particularly those related to safer solvents, waste prevention, and reduced environmental impact. Recent studies have demonstrated that aqueous synthetic protocols are compatible with a broad range of aldehydes and primary amines, enabling the efficient preparation of structurally diverse Schiff bases under relatively mild reaction conditions. Moreover, the integration of aqueous media with one-pot synthesis and naturally derived catalysts further simplifies experimental procedures while reducing reaction time and purification requirements. These advantages improve the economic feasibility and scalability of Schiff base synthesis, making aqueous methodologies attractive for both laboratory-scale and industrial applications. Consequently, water-based synthetic strategies have emerged as an important component of sustainable organic synthesis, offering an effective balance between reaction efficiency, operational simplicity, and environmental responsibility.

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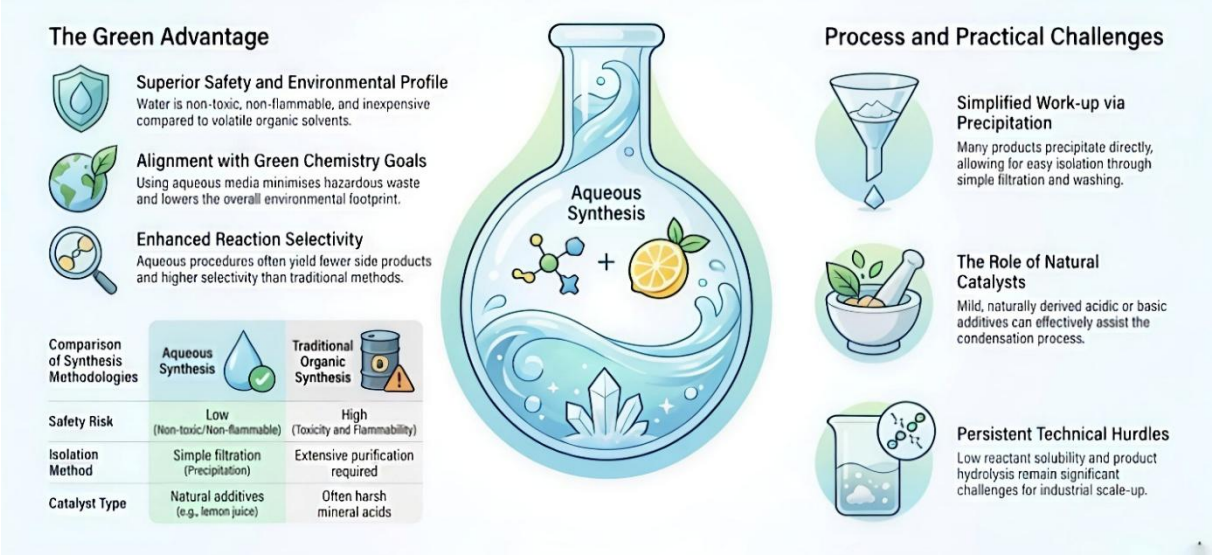

Fig 2. Sustainable synthesis: the aqueous path for Schiff base ligands.

5.1. Water as an environmentally benign reaction medium

Mir and Banik and Nagar et al. have both highlighted water as one of the most attractive green solvents for Schiff base synthesis, emphasizing that it is inexpensive, non-toxic, non-flammable, and readily available on a scale unmatched by conventional organic solvents [17], [18]. In line with the broader principles of green chemistry articulated by Mir and Banik, replacing volatile organic solvents with water directly addresses several of the core goals of sustainable synthesis: minimizing hazardous waste, reducing flammability and toxicity risks, and lowering the overall environmental footprint of the reaction [17]. Compared with conventional organic solvents, water presents markedly fewer environmental and safety concerns, a point stressed by Nagar et al. in their systematic review of green methods for Schiff base preparation, which makes aqueous media especially suitable for sustainable synthetic protocols [18]. The increasing reliance on aqueous reaction media documented by both review groups reflects a broader shift in synthetic organic chemistry toward cleaner and safer alternatives to solvent-intensive traditional methods [17], [18]. Rao et al., as reviewed by Mir and Banik, reported the successful aqueous-phase synthesis of various Schiff base ligands via direct condensation of aromatic aldehydes with amines and diamines, including the room-temperature reaction of 1,2-diaminobenzene with aromatic aldehydes in water without acid catalysts or organic co-solvents [3], [17]. In most cases described by Nagar et al. and by Mir and Banik, the reactants are simply stirred in aqueous medium at room temperature or under mild heating, sometimes with a small amount of a naturally derived acidic or basic additive to assist condensation, echoing the natural-acid-catalyzed protocols reported elsewhere by Elemike et al. and Punitha et al. [4], [6], [17], [18]. Because many Schiff base products are only sparingly soluble in water, Rao et al. observed that the compounds often precipitate directly from the reaction mixture, allowing easy isolation by simple filtration, washing, and drying without the need for extensive purification [3].

5.2. Advantages and limitations of water-based methodologies

Water-based synthesis offers several practical and environmental advantages for Schiff-base preparation. Rao et al. and Nagar et al. reported that aqueous procedures can provide good selectivity and relatively simple product isolation, particularly when the resulting Schiff bases have limited solubility in water and precipitate directly from the reaction mixture [3], [18]. Such precipitation can reduce the need for extensive solvent-based purification. Water is also inexpensive, non-flammable, and readily available, while its use can reduce dependence on volatile organic solvents [17], [18]. The reported scope, however, is not universal. Poor aqueous solubility of many aromatic aldehydes and amines can limit contact between the reactants and consequently affect conversion [17], [18]. In addition, imine formation is reversible, and the presence of water can promote hydrolysis of the C=N bond under conditions where the equilibrium is unfavorable [17], [18]. Reaction performance may therefore depend on substrate structure, pH, temperature, and the use of additional catalysts or additives. These factors mean that an aqueous procedure that performs well for one substrate

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combination may not necessarily provide the same outcome for another. Water-based synthesis has also been applied to more complex systems. Ariyaeifar et al. prepared chiral Schiff bases under ambient aqueous conditions, while Sachdeva et al. employed an aqueous multicomponent procedure using lemon juice as a natural catalyst [19], [20]. Gharagozlou et al. further demonstrated the use of water in the preparation of an amino-acid-based Zn(II) Schiff-base complex and its subsequent conversion to ZnO nanoparticles [21]. These examples demonstrate the versatility of aqueous systems, but they do not by themselves establish that water is universally superior to conventional organic solvents. Overall, the principal advantage of water-based Schiff-base synthesis lies in its potential to reduce solvent-related hazards and simplify isolation, whereas its main limitations are substrate solubility, competing hydrolysis, sensitivity to reaction conditions, and challenges associated with reproducibility and scale-up [17], [18]. Therefore, the suitability of water should be assessed on a substrate- and process-specific basis rather than assumed solely from its green-solvent classification.

5.3. Current challenges and future perspectives

Despite these advantages, Mir and Banik and Nagar et al. both acknowledge that aqueous Schiff base synthesis faces practical limitations, including the poor solubility of many aromatic aldehydes and amines in water, the reversible and equilibrium-controlled nature of imine formation that can be complicated by competing hydrolysis of the product back to the parent carbonyl and amine, and the sensitivity of certain aqueous protocols to reaction pH and temperature [17], [18]. Nagar et al. further note that, while water-based methods perform well at laboratory scale, questions remain about reproducibility across different reaction setups and about the engineering challenges of translating these mild aqueous conditions into industrially scalable processes [18]. Looking ahead, both review groups suggest that combining water as a green solvent with complementary green techniques—such as microwave or ultrasound activation, as illustrated by Bhagat et al.—and with naturally derived catalysts offers a promising direction for overcoming these solubility and scale-up challenges while preserving the environmental benefits that make water such an appealing medium for sustainable Schiff base synthesis [15], [17], [18].

6. Solvent-free grinding and mechanochemical methods

Mechanochemical synthesis has emerged as an appealing green strategy for preparing Schiff bases and their coordination compounds, and both Nagar et al. and Mir and Banik identify grinding and ball milling among the most practical eco-friendly alternatives to solution-phase synthesis [17], [18]. In contrast to conventional solution-phase routes, this approach depends on mechanical energy delivered through techniques such as mortar-and-pestle grinding or ball milling to initiate and sustain the reaction [17], [18]. Because these methods require little or no solvent, they generate less waste, reduce environmental burden, and simplify work-up, while often providing shorter reaction times and better synthetic efficiency than thermal procedures, a conclusion echoed throughout Nagar et al.'s survey of green Schiff base chemistry [17], [18]. A major advantage of grinding-assisted synthesis is its ability to promote condensation reactions under mild and environmentally benign conditions [17], [18]. Marufah et al. demonstrated this by grinding vanillin with p-aminoacetophenone in the presence of a small amount of lime juice as a naturally derived acidic catalyst; the mechanical mixing drove the condensation to completion in under an hour and delivered the corresponding Schiff base in excellent yield [18], [31]. According to Nagar et al., the resulting compound also displayed noteworthy inhibitory and biological activity in follow-up studies, reinforcing the practical value of fruit-derived catalysts under grinding conditions [18], [31]. The scope of mechanochemical synthesis can be further expanded by incorporating heterogeneous catalysts [18]. Patil et al. showed that calcined eggshell, a waste-derived material rich in calcium oxide, can serve as a reusable basic catalyst for Schiff base formation [18]. As reported by Nagar et al., under solvent-free grinding conditions this catalyst promotes condensation between a wide range of aromatic aldehydes and amines, giving rapid reactions, high conversions, and excellent isolated yields, while also converting an agricultural waste product into a genuinely useful catalytic material [18]. Mechanochemical approaches are not limited to simple imines and can also be applied to more complex ligand systems [17], [18]. Vidyavathi et al. employed Cashew Nut Shell Liquid (CNSL) as an environmentally benign catalyst in a solvent-free mechanochemical grinding approach to synthesize a quinoline-derived amino acid Schiff base through the condensation of 17-hydroxyquinoline-31-carbaldehyde with L-tryptophan [18], [34]. As described by both Nagar et al. and Mir and Banik, this ligand possesses multiple donor sites and behaves as a tridentate ONO donor, and its reactions with divalent metal ions readily produce octahedral complexes with good structural stability and interesting physicochemical properties [17], [18], [34]. Beyond reducing solvent use,

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mechanochemical protocols championed across these studies also offer practical advantages such as lower energy demand, shorter reaction times, improved atom economy, and reduced hazardous waste generation [17], [18]. Taken together, the use of solvent-free conditions demonstrated by Marufah et al., naturally sourced catalysts employed in several of the studies reviewed by Nagar et al., waste-derived catalytic materials introduced by Patil et al., and the structurally diverse substrates explored by Vidyavathi et al. have established grinding and ball-milling methods as valuable tools in sustainable synthesis [18], [31], [34]. Consequently, mechanochemical synthesis is gaining widespread recognition as an efficient, cost-effective, and environmentally sustainable strategy for the preparation of Schiff bases and their metal complexes, as highlighted by Mir and Banik [17], [18].

7. Microwave- and ultrasound-assisted synthesis

Microwave-assisted synthesis has become an effective and sustainable strategy for the preparation of Schiff bases, and according to Mir and Banik, it represents a significant advancement in green synthetic chemistry, providing distinct advantages over traditional heating techniques [17], [18]. Mir and Banik reported that, in microwave-mediated processes, energy is absorbed directly by polar molecules and ionic species through dipole rotation and ionic conduction mechanisms, enabling fast and uniform heating throughout the reaction system [18]. This efficient energy delivery reduces heat loss, shortens reaction times, and often improves product yields, making microwave technology an important tool that both Mir and Banik and Nagar et al. highlight repeatedly across their reviews of green Schiff base chemistry [17], [18]. The advantages of microwave irradiation are especially evident in salicylaldehyde-derived Schiff bases. Bhagat et al. showed that under microwave conditions, reactions of salicylaldehyde with various aromatic amines in water can reach completion in seconds or minutes and often provide excellent yields, including several examples above 90% [18], [22]. In contrast, Bhagat et al. found that the same transformations under conventional reflux generally required several hours and gave lower yields, higher solvent use, and a more difficult work-up [18], [22]. As reported by both Nagar et al. and Mir and Banik, these salicylaldehyde-based Schiff bases synthesized in water under microwave irradiation showed markedly shorter reaction times and better yields than the corresponding conventional methods [17], [18], [22]. Microwave-assisted synthesis has also been successfully applied to a broad range of Schiff base systems. Microwave-assisted synthesis has been widely employed for the efficient preparation of Schiff bases and their metal complexes. For instance, chem et al. synthesized a series of isatin-derived Schiff bases using both microwave and ultrasound irradiation techniques, whereas Punitha et al. prepared a Schiff base derived from cefotaxime and salicylaldehyde under microwave irradiation in the presence of sweet lemon juice as a natural acid catalyst [18], [19], [21]. Similarly, Chauhan et al. reported the microwave-assisted synthesis of a piperonal–chitosan Schiff base and investigated its corrosion inhibition properties, while Karati et al. developed a series of pyrimidine-based Schiff base congeners under microwave conditions using water as a green solvent [18], [22], [23]. In another study, Srivastava et al. employed microwave irradiation for the synthesis of Schiff base metal complexes derived from salicylaldehyde and antibiotic ligands, including amoxicillin and cephalexin, demonstrating the versatility of this technique in coordination chemistry [18], [39]. Many of these compounds and their complexes, as documented by Nagar et al., exhibit useful properties such as antimicrobial activity, anticancer potential, and corrosion inhibition [18].

Ultrasound-assisted synthesis provides another environmentally friendly route for Schiff base preparation. Mir and Banik reported that the effectiveness of this method arises from acoustic cavitation, whereby the generation and subsequent collapse of microbubbles produce transient high-energy microenvironments that enhance reaction rates and promote chemical conversion [17]. Although these extreme conditions occur only in microscopic regions, the bulk reaction can still proceed under relatively mild conditions, which helps lower overall energy demand and reduce thermal degradation of sensitive substrates [17]. Sonochemical methods have been used effectively for the synthesis of Schiff base derivatives. Bakht demonstrated that anthranilic acid-derived Schiff bases could be prepared under ultrasonic irradiation in around ten minutes, considerably faster than the one hour required under conventional heating, while also yielding a more stable and crystalline product [18], [28]. Arafa and Shaker employed a sonochemical approach to synthesize a series of bis-Schiff bases under catalyst-free conditions and systematically compared the reaction yields and completion times obtained through conventional heating, microwave irradiation, and ultrasonic treatment [40]. Similarly, Mermer et al. conducted a comparative investigation of conventional, microwave-assisted, and ultrasound-sonication methods, revealing that ultrasonic irradiation provided significant advantages over the conventional approach by reducing reaction times and improving the stability of the resulting products [18], [41]. Overall, microwave- and ultrasound-assisted approaches support the broader shift toward sustainable Schiff base synthesis by reducing reaction time, energy use, solvent consumption,

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and waste generation, as emphasized throughout the reviews by Nagar et al. and Mir and Banik [17], [18]. Their successful use in salicylaldehyde-based systems demonstrated by Bhagat et al., isatin derivatives reported by Chemchem et al., cefotaxime-based ligands prepared by Punitha et al., chitosan-functionalized Schiff bases developed by Chauhan et al., and bis-Schiff bases synthesized by Arafa and Shaker together demonstrate the versatility and effectiveness of these techniques [18], [19], [21], [22], [40]. These methods therefore remain important green strategies for the preparation of Schiff bases and their metal complexes [17], [18].

Table 3. Comparison of sustainable synthetic strategies for Schiff bases and their metal complexes.

Green strategy	Reaction conditions	Green catalyst/solvent	Typical time	Typical yield (%)	Major advantages	Representative applications	Ref.
Conventional reflux	Alcoholic solvent, reflux	None/mineral acid	1–12 h	60–95	Broad substrate scope	General Schiff base ligands	[3], [17], [18]
Natural-acid catalysis	Ambient–70 °C	Lemon, tamarind, lime, CNSL	5–180 min	80–98	Renewable, biodegradable	Bioactive ligands	[18], [26], [31], [34], [35]
Water as solvent	Water, mild heating	Water ± natural acid	30–180 min	75–95	VOC-free, easy isolation	Amino acid Schiff bases	[17]–[21]
Mechanochemistry	Grinding/ball milling	Solid catalysts	5–60 min	85–99	Solvent-free, scalable	Metal complexes	[17], [18], [31], [34]
Microwave	MW irradiation	Water/natural acid	1–20 min	85–98	Rapid heating	Antibiotic Schiff bases	[17], [18], [22], [23], [39]
Ultrasound	Ultrasonic bath	Natural acid/none	10–60 min	80–96	Low energy	Anthranilic derivatives	[17]–[21]

8. Coordination properties of Schiff base complexes

Schiff bases occupy a prominent position in coordination chemistry due to their strong affinity for metal ions, which originates from the azomethine nitrogen and additional coordinating atoms, including oxygen, nitrogen, and sulfur [17], [43], [44]. The coordination behavior of these ligands varies according to the number and disposition of donor sites, enabling them to act as bidentate, tridentate, tetradentate, or polydentate chelating agents [43], [44], [48]. Typical examples include bidentate ON donor systems such as salicylideneamines, tridentate ONO donor ligands, and tetradentate N_2O_2 ligands obtained through the condensation of diamines with dialdehydes [43], [48]. These coordination modes enable Schiff bases to accommodate a wide range of metal ions and coordination geometries [43], [44], [48].

8.1. Donor modes and coordination flexibility

Schiff base ligands exhibit exceptional versatility in their coordination behavior owing to the tunable nature of their donor atom sets [43], [44], [48]. Bidentate ON systems, typified by salicylideneamine derivatives, represent the simplest chelating framework and readily form five-membered chelate rings with most transition metal ions [43], [48]. Tridentate ONO ligands, which bear an additional phenolic or alkoxide oxygen, impose greater geometric constraints and are frequently employed in the preparation of mononuclear complexes with square-pyramidal or octahedral environments [43], [48]. The most architecturally versatile class comprises tetradentate N_2O_2 ligands, commonly derived from the double condensation of salicylaldehydes with ethylenediamine or related diamines; these salen-type frameworks provide a planar binding pocket well-suited to accommodating square-planar d8 metal ions as well as larger metal centers in octahedral or distorted geometries [43], [48]. Beyond these well-established types, Schiff base ligands incorporating pyridyl, thioether, or imidazolyl pendant arms can function as pentadentate or hexadentate donors, enabling access to higher coordination numbers and more elaborate coordination polyhedra [43], [44].

8.2. Transition Metal Complexes

Numerous transition metals are capable of forming stable complexes with Schiff base ligands owing to their versatile coordination behavior [11], [43], [44]. Among these, Cu(II), Ni(II), Co(II), Fe(III), Mn(II/III), Zn(II), and Cd(II) have been extensively investigated, producing coordination compounds characterized by a broad range of structural and physicochemical features [11], [17], [18]. Depending on the ligand design and synthetic conditions, both mononuclear and polynuclear complexes can be obtained [43], [44], [48]. In addition to first-row transition metals, Schiff bases have also been successfully utilized for the coordination of Zr(IV) and various lanthanide ions, demonstrating their adaptability toward both transition and f-block metal centers [18], [50].

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Ahmad et al. synthesized a series of mononuclear mixed-ligand complexes of Fe(III), Co(II), Cu(II), and Cd(II) using a furfural-derived Schiff base ligand that functioned as a neutral ONNO tetradentate donor in combination with 2,2′-bipyridine as a secondary ligand [18], [46]. Related studies published in the same year further demonstrated the extensive coordination potential of Schiff bases toward Fe(III), Co(II), Cu(II), Cd(II), and other transition metals, yielding complexes that predominantly adopted octahedral or closely related geometries. The structures of these complexes were established through comprehensive spectroscopic and thermal characterization, complemented in several cases by single-crystal X-ray diffraction analysis [18], [46]. Nanosized V(III), Fe(III), and Ni(II) mixed-ligand complexes bearing a naphthalene-derived Schiff base and 2-amino-4-methylpyrimidine were synthesized and characterized by thermogravimetric analysis and XRD, with particle size calculations confirming nanoscale dimensions of the resulting complexes, illustrating how variation in the metal ion identity, auxiliary ligands, and synthetic conditions can be used systematically to tune the structural and physical properties of Schiff base coordination compounds [17], [18].

8.3. Coordination chemistry and structural features of Schiff base complexes

The coordination chemistry of Schiff base ligands is governed by the nature, number, and spatial arrangement of their donor atoms. The presence of imine nitrogen and additional donor groups such as phenolic, alcoholic, carboxylate, or ether oxygen atoms enables Schiff bases to coordinate with metal ions through different denticities and coordination modes. Depending on the ligand architecture and metal-ion preferences, Schiff bases can act as mono-, bi-, tri-, tetra-, and higher-dentate ligands and may also exhibit bridging coordination. These variations in coordination behaviour strongly influence the coordination number, geometry, electronic environment, and consequently the physicochemical and functional properties of the resulting metal complexes.

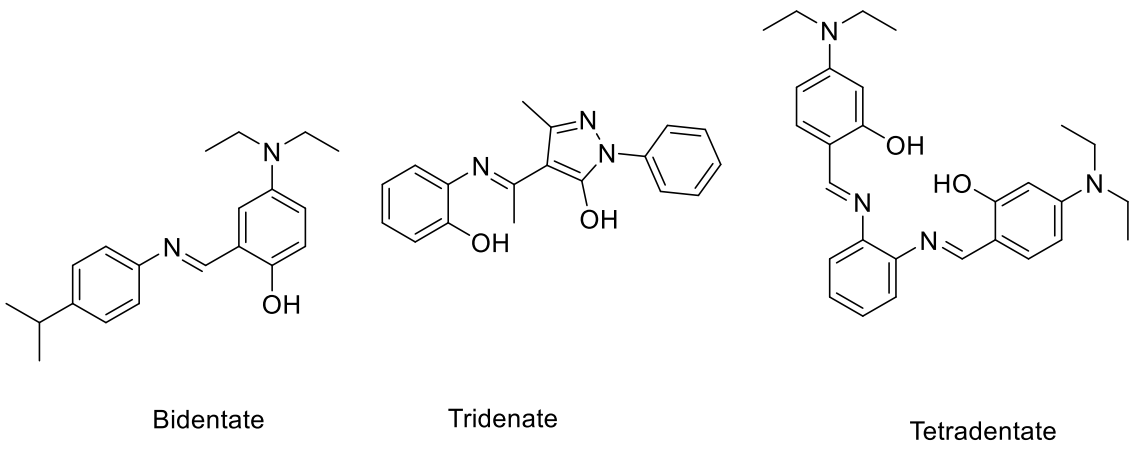

Fig 3. Representative coordination modes of Schiff base ligands.

Tetradentate N_2O_2 coordination

N_2O_2-type Schiff bases represent an important class of tetradentate ligands containing two nitrogen and two oxygen donor atoms. These ligands can simultaneously coordinate to a metal centre through the imine nitrogen and oxygen donor atoms, generally producing stable chelate rings. The N_2O_2 donor arrangement can support different coordination geometries depending on the metal ion and the presence of additional ligands. Structural investigations by single-crystal X-ray diffraction are particularly valuable for establishing the coordination mode and determining metal–nitrogen and metal–oxygen bond distances, bond angles, and the overall geometry around the metal centre. Tetradentate N_2O_2 Schiff base ligands derived from ethylenediamine and dihydroxybenzaldehydes represent one of the most extensively studied classes of coordination ligands due to their strong chelating ability and structural rigidity [17], [43], [48]. A notable example was reported by Tahereh Hosseinzadeh Sanatkar et al., who synthesized a tetradentate N_2O_2 Schiff base ligand through the condensation of ethylenediamine with 2,4-dihydroxybenzaldehyde in methanol at room temperature, followed by refluxing the reaction mixture for three hours under continuous stirring [18], [45]. The resulting ligand was subsequently coordinated with Cu(II) and Ni(II) ions to form metal complexes that were employed as modifiers of a glassy carbon electrode (GCE) for the development of an electrochemical sensor capable of detecting hydrazine in real samples [18], [45]. The rigid N_2O_2 donor

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framework of these ligands provides a well-defined chelating environment that efficiently stabilizes metal ions in preferred coordination geometries, thereby contributing to their widespread application in coordination chemistry and sensor development [43], [45], [48]. Complexes formed with such ligands commonly adopt square-planar arrangements in suitable d8 metal systems or octahedral geometries when additional donor molecules participate in coordination [43], [45], [48]. The well-defined ligand framework often contributes to enhanced thermal stability, electronic properties, and catalytic performance of the resulting complexes [43], [42], [51].

Abdel-Rahman et al. described a new tetradentate N2O2 Schiff base ligand prepared by condensation with 5-bromosalicylaldehyde and examined its Co(II), Ni(II), Cu(II), and Zn(II) complexes for enzymatic and biological activities; related crystallographic and spectroscopic studies on symmetrical tetradentate Schiff base complexes likewise confirm geometries consistent with the planar N2O2 coordination pocket provided by the ligand [42], [47], [51]. A Zn(II)/Na(I) dinuclear complex assembled from an N2O2O′2 Schiff base metalloligand was crystallographically characterized, highlighting the capacity of tetradentate Schiff base metalloligands to serve as building blocks for heterometallic architectures [42], [43] ,[51].

Pentadentate N_3O_2 coordination

N_3O_2 Schiff base ligands contain three nitrogen and two oxygen r atoms and can therefore provide five donor sites for metal coordination. Their multidentate nature promotes extensive chelation and can generate well-defined coordination environments around the metal centre. The arrangement and flexibility of the donor atoms may result in different coordination geometries and degrees of distortion, depending on the metal ion and the coordination requirements of the complex.

Hexadentate N_4O_2 coordination

N_4O_2 Schiff bases provide six donor atoms, comprising four nitrogen and two oxygen atoms, and can act as hexadentate ligands toward suitable metal centres. The high denticity enables extensive metal–ligand interactions and can favour six-coordinate environments, frequently associated with octahedral or distorted-octahedral geometries. The specific coordination geometry is determined by the donor-atom arrangement, ligand conformation, metal-ion preference, and the presence of additional coordinating species.

Heptadentate N_2O_5 coordination

N_2O_5 Schiff bases represent highly dentate ligand systems containing two nitrogen and five oxygen donor atoms. Their high number of donor sites provides multiple points of interaction with metal ions and allows the formation of highly chelated and structurally complex coordination environments. Such ligands can impose distinctive geometrical and conformational requirements on the metal centre, while variations in donor-atom arrangement and ligand flexibility can influence the structural and functional characteristics of the resulting complexes.

Single-crystal X-ray diffraction (SCXRD)

Single-crystal X-ray diffraction (SCXRD) provides definitive structural information for Schiff base metal complexes by establishing the coordination mode, coordination number, metal-centre geometry, and molecular conformation. Representative crystal structures of N_2O_2, N_3O_2, N_4O_2, and N_2O_5 Schiff base complexes demonstrate how increasing ligand denticity and variation in donor-atom composition influence the coordination environment of the metal centre. Important crystallographic parameters, including metal–nitrogen and metal–oxygen bond distances and selected bond angles, should be considered when comparing these complexes. Such structural parameters provide a direct basis for understanding differences in coordination geometry and ligand–metal interactions.

Structure–property relationship

The coordination behaviour of Schiff base ligands is closely associated with the properties of their metal complexes. Increasing ligand denticity from N_2O_2 to N_3O_2, N_4O_2, and N_2O_5 increases the number of donor atoms available for metal coordination and can substantially modify the coordination environment and geometry of the metal centre. Changes in donor-atom composition, metal–donor bond distances, bond angles, chelate-ring formation, and ligand conformation can alter the electronic structure and reactivity of the complexes. Consequently, these structural factors may influence their magnetic, catalytic, electrochemical, optical, and biological properties [72]-[74].

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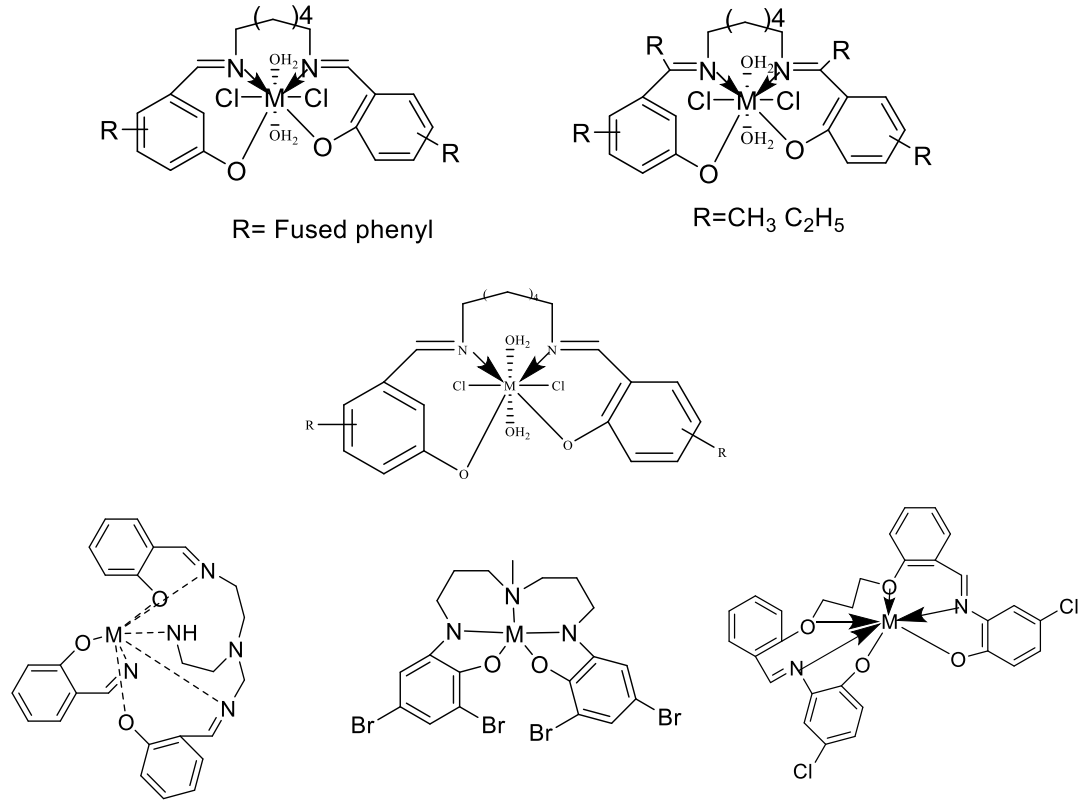

Fig. 4. Selected complexes of Schiff bases.

8.4. Dinuclear and polynuclear assemblies

Schiff bases containing phenoxide donor groups frequently display bridging behavior during complex formation [17], [43], [48]. In such cases, a phenoxide oxygen atom can coordinate simultaneously to two metal centers, resulting in the formation of dinuclear complexes featuring phenoxo-bridged cores [17], [43]. These bridged structures are of considerable interest because they often exhibit distinctive magnetic properties, electronic communication between metal centers, and catalytic activity [42], [43], [51]. Consequently, Schiff base ligands are capable of supporting a wide spectrum of molecular architectures ranging from simple mononuclear species to more elaborate multinuclear assemblies [17], [43], [48]. A recent crystallographic study documented a Ni(II) dimer, [Ni2L2(OH)(OH2)]ClO4·CH2Cl2, derived from a tridentate NNO Schiff base ligand obtained from salicylaldehyde and N,N-dimethylethane-1,2-diamine, in which the two nickel atoms are bridged by a phenoxo oxygen from the ligand and a hydroxo group, with one Ni adopting square-planar and the other octahedral geometry within the same complex; more broadly, current literature shows that dinuclear and higher-nuclearity Schiff base assemblies are accessible through phenoxo, alkoxo, and related bridging modes [17], [43], [42], [51]. Cadmium(II) coordination polymers incorporating bis-imine Schiff base ligands with nitrite end-stop groups have also been structurally characterized, affording 2D sheet architectures and further demonstrating the structural diversity attainable through Schiff base coordination chemistry [17], [43].

Table 4. Representative Schiff base coordination systems: ligands, metal centre and applications.

Aspect	Representative system	Metal(s)	Key feature
Donor mode	ON, ONO, N_2O_2 ligands	Cu, Ni, Co, Fe, Zn	Bi-/tri-/tetradentate coordination
Transition complexes	Mixed-ligand Schiff bases	Fe, Co, Cu, Cd, V, Ni	Mono- & polynuclear complexes
Tetradentate systems	Salen-type ligands	Cu, Ni, Co, Zn	High stability; square-planar/octahedral
Dinuclear assemblies	Phenoxo-bridged complexes	Ni, Cd	Magnetic & catalytic properties
Characterization	FT-IR, UV–Vis, NMR, EPR, XRD	NA	Geometry confirmation
Chiral complexes	Salen & amino acid ligands	Mn, Cu, Co, Zr	Asymmetric catalysis
Applications	Catalysis, sensing, bioactivity	Various	Versatile coordination platform

8.5. Structural elucidation and spectroscopic characterization

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Structural characterization of Schiff base complexes relies on a combination of spectroscopic and analytical techniques [17], [43], [48]. Infrared spectroscopy is commonly used to monitor coordination through changes in the characteristic C=N stretching frequency, which generally shifts to lower wavenumbers upon metal binding due to the reduction in electron density at the azomethine bond [43], [48]. UV-Visible spectroscopy provides information regarding electronic transitions and ligand-field effects, while NMR spectroscopy is particularly useful for diamagnetic ligands and complexes [43], [48]. EPR spectroscopy offers valuable insight into the electronic environment of paramagnetic metal ions such as Cu(II), and additional confirmation of molecular composition and stoichiometry can be obtained through mass spectrometry [42], [45]. Nevertheless, single-crystal X-ray diffraction remains the most reliable technique for establishing coordination geometry, bonding parameters, and the overall molecular structure of Schiff base complexes [42], [45], [47].

Recent studies illustrate the increasingly multidisciplinary and computationally augmented character of modern structural investigations of Schiff base coordination compounds [42], [51]. Reports combining FT-IR, UV-Vis, EPR, TGA, powder XRD, single-crystal X-ray diffraction, Hirshfeld surface analysis, and DFT calculations have confirmed square-planar or distorted square-planar geometries in several Cu(II) and Ni(II) Schiff base systems while also quantifying supramolecular packing interactions and noncovalent contacts in the solid state [42], [45], [47], [51].

8.6. Chiral Schiff base ligands in coordination chemistry

Chiral Schiff base ligands derived from optically active amino alcohols, amino acids, and other stereochemically defined building blocks constitute an important class of ligands in coordination chemistry [17], [43]. Through coordination to metal ions, these ligands establish well-defined chiral environments around the metal center, thereby enhancing their utility in asymmetric catalytic transformations [17], [43]. Such metal complexes are widely employed in enantioselective transformations, where control over product stereochemistry is essential [17], [43]. The ability of chiral Schiff bases to induce and transfer chirality has made them indispensable components in numerous catalytic processes used in modern synthetic chemistry [17], [43]. Chiral salen-type Mn(III) complexes continue to serve as benchmark catalysts for asymmetric epoxidation of unfunctionalized alkenes, while chiral Cu(II)-Schiff base systems remain widely applied in asymmetric Henry (nitro-aldol) and cyclopropanation reactions [17], [43]. The structural integrity of these chiral environments has been examined in solution and in the solid state by spectroscopic and crystallographic methods, and the degree of enantioselectivity is strongly influenced by the steric and electronic properties of substituents flanking the imine bond [17], [43]. Recent work has further broadened the substrate scope of chiral Schiff base catalysis, including asymmetric Diels-Alder and aldol-type transformations, establishing these platforms as versatile tools in modern asymmetric synthesis [17], [43].

9. Biological applications of Schiff base metal complexes

Schiff base ligands and their corresponding metal complexes are widely studied owing to their broad spectrum of biological and pharmacological effects. Nagar et al. reported that such complexes exhibit antifungal, antibacterial, antitubercular, antiviral, anticancer, anti-inflammatory, antioxidant, cytotoxic, DNA-binding, DNA-cleavage and antidiabetic activities, highlighting their importance in medicinal chemistry [44]. Mir and Banik emphasized that the versatility of these ligands, including chiral and achiral systems, underpins numerous applications in catalysis and bioactive molecule design under green synthetic conditions [57].

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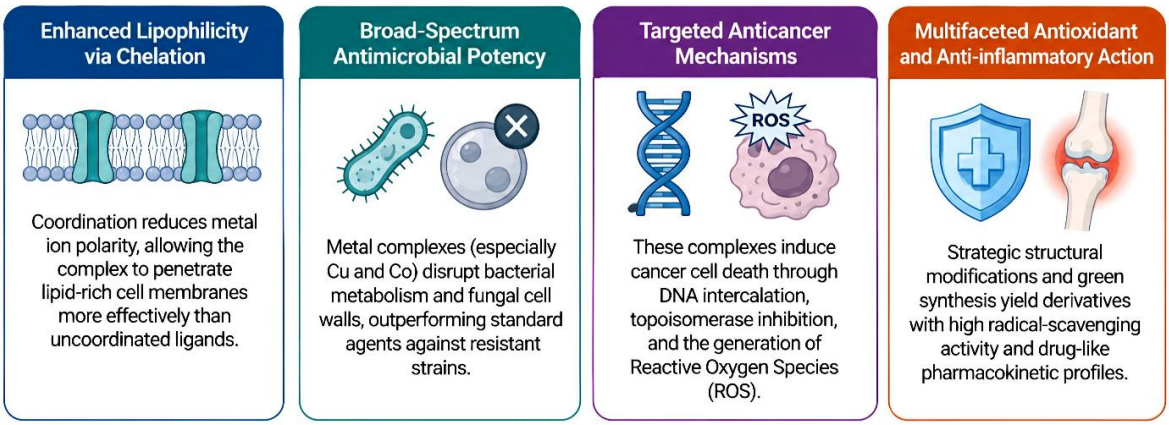

Fig. 5. Versatility of Schiff base metal complexes.

9.1. Antibacterial activity

Schiff base metal complexes have attracted considerable attention as promising antibacterial agents because metal coordination frequently enhances the biological activity of the parent ligands. According to the chelation theory proposed by Tweedy, coordination reduces the polarity of the central metal ion through partial sharing of its positive charge with the donor atoms of the Schiff base ligand. This increase in lipophilicity facilitates the penetration of the complex through the lipid-rich bacterial cell membrane, thereby improving intracellular accumulation and interaction with vital biomolecular targets. Furthermore, transition metal ions can interfere with bacterial metabolism by disrupting enzyme function, damaging nucleic acids, generating reactive oxygen species (ROS), and altering membrane permeability, ultimately leading to inhibition of bacterial growth and cell death.

Rangaswamy et al. reported that transition-metal Schiff base complexes exhibited significantly greater antibacterial activity than the corresponding free ligand against both Gram-positive and Gram-negative bacterial strains, including *Escherichia coli*, *Proteus mirabilis*, *Streptococcus pneumoniae*, and *Bacillus subtilis*, underscoring the positive influence of metal coordination on antimicrobial efficacy [59]. Similarly, Ahmed et al. synthesized Cd(II), Ni(II), and Mn(II) complexes of a novel imidazole-based Schiff base and observed superior antimicrobial performance of the metal complexes against a range of bacterial pathogens as well as fungal species such as *Aspergillus flavus* and *Candida albicans* [44]. The enhanced biological activity was attributed to the increased membrane permeability of the complexes and their stronger interactions with intracellular biomolecular targets, which facilitate more effective microbial inhibition compared with the uncoordinated ligand and, in certain cases, even established antimicrobial agents [44]. Zayed et al. and Mahmoud et al. reported that Schiff base complexes incorporating Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) exhibit notable antibacterial activity against both Gram-positive and Gram-negative bacterial strains [62]–[64]. These complexes showed inhibitory effects against clinically important Gram-positive bacteria, including *Staphylococcus aureus* and *Bacillus subtilis*, as well as Gram-negative species such as *Escherichia coli*, *Neisseria gonorrhoeae*, and *Pseudomonas aeruginosa* [62]–[64]. Their findings further revealed that antimicrobial performance is strongly influenced by the coordinated metal ion and the electronic nature of the Schiff base framework. Among the investigated complexes, copper- and cobalt-containing derivatives often displayed the highest antibacterial activity, a behavior commonly associated with their redox properties and their ability to generate reactive oxygen species that disrupt essential cellular processes in microbial pathogens. [62]–[64]. In addition to conventionally synthesized compounds, green synthetic methodologies have also produced biologically active Schiff bases with excellent antibacterial properties. Mermer et al. reported that Schiff bases prepared through environmentally benign synthetic routes exhibited promising antibacterial activity together with significant antiurease effects, demonstrating that sustainable synthesis can yield compounds with biological activities comparable to or exceeding those prepared by conventional methods [41]. This finding highlights that green chemistry principles can be successfully integrated into medicinal chemistry without compromising biological efficacy.

9.2. Antifungal Activity

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Schiff base ligands, particularly their transition-metal complexes, have attracted significant attention as promising antifungal agents due to their effectiveness against a wide range of pathogenic fungal species. Numerous investigations have demonstrated that metal coordination enhances the antifungal activity of Schiff bases by increasing their lipophilicity, facilitating membrane penetration, and strengthening interactions with intracellular biological targets. Furthermore, metal complexation can promote fungal growth inhibition through disruption of cell membrane integrity, interference with key enzymes involved in cell wall synthesis, and the generation of reactive oxygen species (ROS), which induce oxidative stress and ultimately result in fungal cell death. Consequently, Schiff base metal complexes have emerged as promising candidates for overcoming fungal resistance associated with conventional antifungal drugs.

Joseyphus and Nair demonstrated that Zn(II) complexes derived from Schiff base ligands possess significant antifungal activity against *Candida albicans* and other pathogenic fungal species, exhibiting substantially greater inhibitory effects than the corresponding uncoordinated ligands [53]. The superior biological activity of these zinc complexes was attributed to the synergistic influence of the Zn(II) center and the Schiff base framework, which enhanced cellular penetration and promoted stronger interactions with fungal biomolecular targets [53]. These findings demonstrate that metal coordination can substantially enhance the therapeutic potential of Schiff base derivatives. Similarly, Gangani and Parsania synthesized a series of symmetrical double Schiff bases using environmentally benign synthetic protocols and evaluated their antifungal properties against *Aspergillus niger* using the cup-plate diffusion method [66]. The synthesized compounds exhibited significant inhibition of fungal growth together with moderate antibacterial activity, and minimum inhibitory concentration (MIC) studies confirmed their effectiveness against the tested microorganisms. Their work further demonstrated that green synthetic methodologies can successfully produce biologically active Schiff bases without compromising antifungal efficacy, highlighting the compatibility of sustainable chemistry with pharmaceutical research. Lima et al. investigated dimeric Cu(II) dithiocarbazate Schiff base complexes and demonstrated that these compounds possessed superior antifungal and antibacterial activities compared with the corresponding free dithiocarbazate ligands, particularly against multidrug-resistant fungal species [61]. The enhanced activity of the Cu(II) complexes was associated with their greater ability to penetrate fungal cells and induce oxidative damage through redox-mediated processes. Copper-mediated generation of reactive oxygen species, together with the strong chelating ability of the Schiff base ligand, was proposed to play a significant role in the observed fungicidal activity.

9.3. Anticancer activity

Schiff base ligands and their metal complexes have emerged as an important class of compounds in anticancer research because of their structural versatility, tunable coordination environments, and ability to interact with multiple intracellular targets. Coordination of Schiff bases with transition metal ions generally enhances their cytotoxic activity by increasing lipophilicity, facilitating cellular uptake, and promoting selective accumulation within cancer cells. The anticancer mechanisms of these complexes are multifaceted and include DNA intercalation or cleavage, inhibition of topoisomerases and other essential enzymes, induction of reactive oxygen species (ROS), mitochondrial dysfunction, cell-cycle arrest, and activation of apoptotic pathways. The nature of the coordinated metal ion, ligand architecture, and coordination geometry collectively influence the biological activity and selectivity of Schiff base metal complexes. Mahmoud et al. reported that Cu(II) complexes derived from a symmetric Schiff base displayed markedly enhanced cytotoxic activity against MCF-7 human breast cancer cells compared with the corresponding free ligand, as reflected by significantly lower IC_{50} values [62]. This increased anticancer efficacy was attributed to the redox properties of the Cu(II) ion, which promote the generation of intracellular reactive oxygen species (ROS) and subsequent oxidative damage to vital cellular components, leading to apoptosis. These results underscore the positive impact of copper coordination on the therapeutic potential of Schiff base ligands [62].

Similarly, Abd El-Razek et al. synthesized guanidine-containing Schiff base complexes of Cu(II) and Co(II) and reported pronounced antiproliferative activity against HepG-2 human liver carcinoma cells while exhibiting comparatively low cytotoxicity toward normal cells [60]. This selective cytotoxic profile suggests that appropriate ligand design and metal coordination can improve the therapeutic index of Schiff base complexes, making them attractive candidates for further preclinical investigation. The incorporation of guanidine functionality was also considered to enhance hydrogen-bonding interactions with biological targets, thereby contributing to the observed anticancer activity. Hassan et al. investigated a series of tridentate Schiff base complexes containing Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Zr(IV) ions and reported notable cytotoxic activity against HCT-116 human colon carcinoma and MCF-7 breast carcinoma cell lines [67]. The study revealed that anticancer activity was strongly

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influenced by the nature of the coordinated metal ion, highlighting the significant roles of the metal center's electronic characteristics and coordination geometry in modulating biological efficacy. These findings emphasize the importance of strategic metal-ion selection in the development of Schiff base-based anticancer agents [67]. Chang et al. investigated chiral Mn(II) and Cu(II) Schiff base complexes synthesized from optically active ligands and reported cytotoxic activities against HepG-2, MDA-MB-231, and A549 cancer cell lines that exceeded those of cisplatin under comparable *in vitro* conditions [58]. The superior performance of these chiral complexes was attributed to their enhanced interactions with biological macromolecules and improved stereochemical recognition within cancer cells. These findings demonstrate that ligand chirality, in combination with appropriate metal coordination, can substantially influence anticancer potency and may provide opportunities for developing more selective antitumor agents.

9.4. Antioxidant and anti-inflammatory activity

The synthesis of Schiff base derivatives using sustainable and environmentally benign methodologies has gained significant interest owing to their notable antioxidant and anti-inflammatory potential. Sonmez et al. synthesized a series of spiro-isatin-based Schiff bases and reported pronounced free-radical scavenging activity. Their study demonstrated that the antioxidant performance of these compounds was highly dependent on the type and position of substituents present on the aromatic ring, with hydroxyl groups particularly enhancing electron-donating ability and facilitating effective radical stabilization. The study established a clear structure–activity relationship, indicating that appropriate structural modifications can significantly improve the antioxidant potential of Schiff base scaffolds [52]. Bentoumi et al. employed an environmentally friendly synthetic approach to prepare benzoxazolinone-derived Schiff bases under green reaction conditions. Biological evaluation showed that several synthesized compounds possessed significant antioxidant activity, while computational ADMET analyses predicted favourable pharmacokinetic and drug-likeness characteristics. The combined experimental and theoretical findings suggested that these derivatives not only exhibit effective radical-scavenging properties but also possess the potential for further pharmaceutical development as safe and efficient antioxidant agents [30]. Green chemistry strategies have increasingly been employed in the development of Schiff base derivatives with anti-inflammatory potential. Sahoo et al. utilized a microwave-assisted synthetic approach to prepare a series of 1,3,4-oxadiazole-based Schiff bases, offering an efficient and environmentally benign route to biologically active compounds. Pharmacological evaluation revealed that several of the synthesized derivatives exhibited moderate to significant anti-inflammatory activity when compared with the standard drug indomethacin. The results highlighted the beneficial role of the oxadiazole moiety in enhancing biological activity and suggested that these compounds could serve as valuable templates for the design of new anti-inflammatory therapeutics [65]. Similarly, Manjula et al. utilized natural acid catalysts to synthesize histidine-based Schiff bases through a sustainable and environmentally benign process. The resulting compounds exhibited a broad spectrum of biological activities, including antioxidant, anti-inflammatory, antibacterial, and antifungal effects. The study emphasized that green synthetic protocols can successfully generate multifunctional Schiff base derivatives with enhanced pharmacological properties while reducing environmental impact. These findings collectively demonstrate that the integration of green chemistry strategies with rational molecular design offers an effective pathway for the development of Schiff base-based therapeutics with diverse biomedical applications [32].

9.5. Structure-activity relationships and mechanisms

Coordination of Schiff base ligands with metal ions has emerged as a powerful approach for simproving their biological performance. Mahmoud et al. demonstrated that complexation with transition metals significantly enhances both the antimicrobial and anticancer activities of Schiff base derivatives [62], [63]. Among the investigated complexes, those containing Cu(II), Cr(III), and Cd(II) exhibited superior cytotoxic effects against MCF-7 human breast cancer cells, displaying lower IC_{50} values than the corresponding free ligands [62], [63]. In addition to their anticancer potential, these metal complexes showed pronounced antibacterial activity against a variety of pathogenic microorganisms. The enhanced biological efficacy was primarily attributed to the chelation effect, whereby coordination reduces the polarity of the metal ion while increasing the overall lipophilic character of the complex. This increase in lipophilicity facilitates permeation through lipid-rich cellular membranes, enabling more effective interaction with intracellular biomolecular targets and ultimately leading to improved therapeutic activity [62], [63]. The interaction of Schiff base metal complexes with nucleic acids is considered a key mechanism underlying their diverse biological activities. Studies by Ghorai et al. and Samuel and Raman demonstrated that Cu(II) and Zn(II) complexes derived from N,O-donor and

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diketimine Schiff base ligands exhibit strong DNA-binding affinity along with significant DNA-cleavage capabilities [54], [55]. Comprehensive investigations employing spectroscopic techniques, molecular docking analyses, and density functional theory (DFT) calculations revealed that these complexes predominantly associate with DNA through groove-binding interactions [54], [55]. In addition, the coordinated metal ions promote oxidative DNA cleavage via redox-mediated pathways involving the generation of reactive oxygen species (ROS), leading to DNA strand breakage and structural degradation. Such DNA-targeted interactions can interfere with critical cellular processes, thereby contributing to the antimicrobial and cytotoxic properties of the complexes and highlighting their potential as candidates for DNA-directed therapeutic applications [54], [55]. Similarly, El-Gammal et al. and Vidyavathi et al. demonstrated that Schiff base complexes exhibit strong affinity toward biologically important macromolecules, including DNA and proteins. These interactions play a crucial role in determining their pharmacological properties. Binding to DNA may interfere with replication and transcription processes, while interactions with proteins can alter enzyme function and cellular signaling pathways. In addition, many Schiff base complexes are capable of generating reactive oxygen species (ROS), which induce oxidative stress within microbial or cancer cells. The combined effects of biomolecular interactions, ROS production, and enzyme inhibition contribute significantly to their antimicrobial and anticancer activities. These multifaceted mechanisms highlight the versatility of Schiff base complexes as biologically active compounds capable of targeting multiple cellular pathways simultaneously [34], [56]. Further insights into the structure–activity relationships of Schiff base systems have been provided by Mir and Banik, who emphasized the importance of ligand design in controlling biological and catalytic behaviour. Their studies revealed that modifications such as changing donor atom sets, introducing chiral centers, and employing green synthetic methodologies can substantially alter the electronic distribution, coordination environment, and redox properties of Schiff base compounds. Such changes influence metal–ligand interactions, stability, reactivity, and biological performance. The authors concluded that rational structural modifications offer an effective approach for tailoring Schiff base complexes with enhanced biological responses, improved selectivity, and superior catalytic efficiency. These findings underscore the significance of molecular engineering in the development of next-generation Schiff base-based materials and therapeutic agents [57].

9.6. Future perspectives

Mir and Banik identified research gaps including inconsistent reporting standards in green synthesis, limited industrial-scale trials, and insufficient long-term sustainability metrics, and recommended life-cycle assessment and scalability studies for promising ligand families [57]. Nagar et al. emphasised that newer green approaches such as ball-milling, use of industrial waste or egg white, and plastic-waste-derived precursors are still under-explored, yet could provide more sustainable access to bioactive Schiff base ligands and complexes [44]. Hassan et al. and Chang et al. suggested that the combination of chiral or macrocyclic Schiff bases with transition metals and green synthesis could yield next-generation anticancer and antimicrobial agents, but that systematic *in vivo* validation and clinical translation are required before therapeutic applications can be realised [58], [67].

Table 5. Representative Schiff base metal complexes and their biological applications.

Ligand system	Metal ion(s)	Application	Key outcome
Salen (N_2O_2)	Cu(II), Ni(II)	Hydrazine sensor	Stable electrode modifier
Imidazole–ONNO	Fe(III), Co(II), Cu(II), Cd(II)	Antimicrobial, anticancer	Cu complex: lowest IC_{50}
Dithiocarbazate	Cu(II)	Antimicrobial	Dimer > free ligand
Chitosan–Schiff base	Cu(II)	Corrosion inhibition	Excellent protection in 15% HCl
Quinoline hydrazone	Cu(II), Ni(II), Co(II)	Broad-spectrum antimicrobial	Good activity
Thiazole Schiff base	Ni(II), Zn(II)	Antibacterial	Ni: lowest MIC
Surfactant Schiff base	Ni(II), Zn(II)	Antibacterial	Very low MIC
Pyridine–Ru Schiff base	Ru(II)	Transfer hydrogenation	70–100% conversion

Abbreviations: IC_{50} = half-maximal inhibitory concentration; MIC = minimum inhibitory concentration.

10. Materials and environmental applications

Beyond their biological significance, Schiff base ligands and their metal complexes have attracted considerable interest as multifunctional materials in the fields of materials science and environmental technology. As emphasized by Mir and Banik, the widespread applicability of Schiff bases arises from

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their distinctive structural features, including the presence of multiple donor sites, straightforward synthetic accessibility, and a high degree of structural versatility [17], [57]. The ability to modify the aldehyde, ketone, and amine precursors enables precise tuning of the electronic, steric, and coordination characteristics of the resulting ligand framework, allowing the rational design of materials with tailored properties [17], [57]. Owing to this exceptional adaptability, Schiff base-based systems have been successfully employed in diverse applications such as chemical sensing, porous and functional materials, heterogeneous catalysis, and environmental remediation, demonstrating their value as versatile platforms for advanced technological developments [17], [57]. One of the most significant applications of Schiff base complexes is in chemical sensing, where their strong metal-binding abilities and tunable electronic properties enable the selective detection of metal ions, anions, and organic pollutants. Changes in optical, electrochemical, or fluorescent properties upon analyte binding allow Schiff base-based sensors to function as efficient and highly sensitive detection systems. Furthermore, Schiff base ligands have been incorporated into porous coordination networks and metal–organic frameworks (MOFs), where their well-defined coordination sites contribute to enhanced adsorption, molecular recognition, and gas-storage capabilities. Such materials have attracted considerable interest for applications in environmental monitoring, gas separation, and pollutant capture [17], [57]. Schiff base metal complexes also serve as effective catalysts in numerous organic transformations owing to their ability to stabilize metal ions in different oxidation states and provide well-defined coordination environments. Their catalytic applications include oxidation, reduction, condensation, and carbon–carbon bond-forming reactions, where high selectivity and efficiency are often achieved. In environmental remediation, these complexes have demonstrated the ability to adsorb, detect, or degrade toxic contaminants, including heavy metal ions and industrial pollutants, thereby contributing to sustainable environmental management strategies. The combination of catalytic activity and environmental compatibility further enhances their practical significance in green chemistry and pollution-control technologies [17], [57]. Similarly, Nagar et al. emphasized that the utility of Schiff base metal complexes extends far beyond biological applications. Their review highlighted the growing importance of these complexes in catalysis, corrosion protection, and ion-extraction processes. As catalysts, Schiff base complexes offer excellent activity and selectivity due to the tunable coordination environment around the metal center. In anticorrosion applications, the adsorption of Schiff base molecules onto metal surfaces forms protective films that inhibit oxidation and corrosion, thereby improving the durability of industrial materials. Additionally, their strong chelating ability enables selective extraction and separation of metal ions from complex mixtures, making them valuable in hydrometallurgy, wastewater treatment, and resource recovery processes. These diverse applications demonstrate the broad functional versatility of Schiff base systems and underscore their increasing importance in modern applied chemistry and materials science [18].

10.1. Metal-organic frameworks and sensors

Schiff base ligands have emerged as valuable components in the design and synthesis of metal–organic frameworks (MOFs) due to their rich coordination chemistry and structural versatility. The presence of azomethine nitrogen atoms, together with additional donor groups such as hydroxyl and carboxyl functionalities, enables Schiff base ligands to readily coordinate with metal ions and form highly ordered porous networks. Mir and Banik noted that a wide range of transition metals, including Cu(II), Co(II), Ni(II), Fe(III), and Zn(II), can be incorporated into Schiff base-based MOFs, yielding materials characterized by high surface areas, adjustable pore structures, and extensive structural diversity [17]. These features have contributed to the growing use of such frameworks in gas storage and separation, heterogeneous catalysis, and selective adsorption applications. Furthermore, recent advances in MOF chemistry have highlighted the utility of salen-type Schiff base ligands as versatile linkers for constructing functional porous materials. In particular, Cu- and Zn-based MOFs derived from salen frameworks have demonstrated promising adsorption capacities and luminescent properties, expanding the scope of Schiff base-based materials for advanced technological applications [68], [69].The incorporation of Schiff base moieties into MOF structures not only enhances framework stability but also provides opportunities for tailoring physicochemical properties through rational ligand and metal-ion selection. Consequently, Schiff base-based MOFs continue to receive significant attention for applications in environmental remediation, molecular recognition, and advanced functional materials.In addition to their role in porous materials, Schiff base complexes have found important applications in chemical sensing. Nagar et al. summarized several examples in which Cu(II) and Ni(II) Schiff base complexes were employed as modifiers of glassy carbon electrodes for the sensitive electrochemical detection of hydrazine [18]. Furthermore, Schiff base receptors have been developed for the selective colorimetric sensing of anions such as acetate and fluoride, exploiting

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analyte-induced changes in optical properties. These findings demonstrate that the tunable coordination behavior and electronic characteristics of Schiff base systems make them promising candidates for the development of efficient sensing platforms and advanced functional materials [18].

10.2. Corrosion inhibition

Schiff base compounds have been extensively investigated as corrosion inhibitors because of their excellent adsorption properties, structural versatility, and relatively environmentally benign nature. Their corrosion-inhibiting action is primarily associated with the presence of donor atoms such as nitrogen, oxygen, and sulfur, together with conjugated π-electron systems that promote strong adsorption onto metal surfaces. Upon adsorption, these molecules form protective films that isolate the metallic substrate from aggressive corrosive species, thereby reducing the rate of metal degradation. Owing to these favorable characteristics, Schiff base derivatives have emerged as promising alternatives to traditional corrosion inhibitors, particularly for the protection of metals exposed to acidic environments frequently encountered in industrial operations and chemical processing systems. Chauhan et al., as cited by Nagar et al., synthesized a piperonal–chitosan Schiff base using a microwave-assisted approach and investigated its corrosion inhibition performance for carbon steel in 15% HCl solution [18]. The modified chitosan derivative exhibited significant inhibition efficiency due to its enhanced adsorption on the steel surface, which reduced the rate of metal dissolution and minimized corrosive attack. The study demonstrated that Schiff base formation can improve the physicochemical properties of chitosan, thereby enhancing its effectiveness as a corrosion-protective material. Chitosan-based Schiff bases have been extensively reviewed as environmentally benign corrosion inhibitors for steel in acidic environments [70]. The introduction of Schiff base functionalities into the chitosan backbone improves solubility, coordination ability, and surface adsorption characteristics, leading to stronger interactions with metallic substrates. These modified polymers can chelate metal ions and form compact protective films that act as barriers against the diffusion of corrosive species such as hydrogen ions and chloride ions. Consequently, Schiff base modification significantly enhances the corrosion resistance performance of chitosan compared with the parent polymer. Several experimental investigations have confirmed the effectiveness of chitosan Schiff base derivatives in corrosion protection. These compounds readily adsorb onto mild steel surfaces through donor atoms and π-electron systems, producing stable protective layers that inhibit anodic and cathodic corrosion reactions. High inhibition efficiencies have been reported in acidic media, with one representative study achieving approximately 92% corrosion inhibition for mild steel in hydrochloric acid solution [71]. The excellent performance of these materials has been attributed to the synergistic effects of surface coverage, metal–ligand interactions, and film-forming capabilities.

10.3. Remediation catalysis

Schiff base metal complexes have attracted significant attention as versatile catalysts due to their excellent coordination capabilities, structural adaptability, and tunable redox behavior. The nitrogen- and oxygen-containing donor sites of Schiff base ligands facilitate the formation of stable transition-metal complexes, while systematic ligand modification enables precise regulation of the electronic and steric environment surrounding the metal center. Consequently, these complexes have been successfully employed in a broad range of catalytic processes, including oxidation, reduction, hydrogenation, and carbon–carbon bond-forming reactions [17]. Mir and Banik highlighted that Schiff base ligands play a crucial role in catalysis by tuning the redox characteristics of the coordinated metal ion and enhancing substrate activation during chemical transformations [17]. As a result, Fe-, Cu-, Mn-, Ni-, Co-, and Pd-based Schiff base complexes have been widely reported as highly efficient catalysts for environmentally significant oxidation and hydrogenation processes. In particular, the use of green oxidants such as hydrogen peroxide and molecular oxygen has attracted considerable attention because these oxidants are inexpensive, readily available, and generate fewer harmful by-products. The combination of Schiff base ligands with redox-active metal ions therefore provides versatile catalytic systems for sustainable chemical transformations [17]. In addition to homogeneous catalysis, Schiff base-based materials have shown significant potential in environmental remediation. Their strong chelating ability enables effective interaction with pollutants and metal ions, making them useful for contaminant removal and wastewater treatment applications. Recent studies have focused on the incorporation of Schiff base functionalities into porous materials to improve adsorption capacity and selectivity toward environmentally hazardous species. Among these materials, Schiff base-functionalized metal–organic frameworks (MOFs) have gained considerable attention as advanced materials for water treatment and heavy-metal removal. Incorporation of Schiff base coordination sites into MOF structures effectively combines the large surface area and porous nature of MOFs with the selective metal-chelating

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capabilities of Schiff base ligands. Consequently, these materials exhibit enhanced adsorption efficiency toward toxic heavy metal ions in aqueous media and have been explored for the selective removal of contaminants from water systems [69].The combination of catalytic activity, metal-ion binding capability, and structural versatility has established Schiff base-based systems as important materials for both catalysis and environmental remediation. Continued advances in ligand design and framework engineering are expected to further expand their applications in sustainable chemistry and environmental protection [17], [69].

10.4. Green materials outlook

The future of Schiff base materials chemistry is expected to be strongly influenced by the growing demand for sustainable and environmentally responsible technologies. Mir and Banik emphasized that further progress in this field will require the integration of green synthetic methodologies, scalable production processes, and application-driven material design to develop functional materials with reduced environmental impact [17]. In particular, Schiff base-based porous materials, catalytic systems, sensors, and adsorbents are increasingly being designed with an emphasis on resource efficiency, waste minimization, and energy conservation. The inherent structural versatility of Schiff base ligands, combined with their ability to coordinate a wide range of metal ions, provides significant opportunities for tailoring material properties to meet specific industrial and environmental requirements. As a result, Schiff base-derived materials are emerging as promising candidates for sustainable applications in catalysis, pollutant removal, gas separation, sensing, and advanced functional materials. In addition to application-oriented design, considerable attention has been directed toward the development of greener synthetic routes for Schiff base preparation. Nagar et al. highlighted several underexplored yet promising approaches, including mechanochemical synthesis through ball milling, industrial-waste-assisted synthesis, egg-white-mediated methods, and the use of plastic-waste-derived precursors [18]. Ball milling offers a solvent-free and energy-efficient alternative to conventional synthesis, reducing chemical waste and reaction times while maintaining high product yields. Similarly, the utilization of industrial by-products and waste materials as raw materials or reaction media supports circular economy principles by transforming waste streams into valuable chemical resources. Biological approaches, such as egg-white-mediated synthesis, provide renewable and biodegradable alternatives to traditional reagents, while the conversion of plastic waste into Schiff base precursors presents an innovative strategy for waste valorization and environmental protection. Collectively, these developments reflect a broader shift toward sustainable materials chemistry, where environmental considerations are integrated into every stage of material design and production. The continued adoption of green synthetic technologies, renewable feedstocks, and scalable manufacturing processes is therefore expected to expand the applicability of Schiff base-based materials and contribute significantly to the advancement of sustainable chemistry and environmental stewardship [17], [18].

Table 6. Materials and environmental applications of Schiff base metal complexes.

Application	Representative system	Metal(s)	Key function
MOFs	Schiff base linkers	Cu(II), Zn(II)	Gas storage, separation, catalysis
Corrosion inhibitor	Chitosan–Schiff base	Cu(II)	Protective film on steel
Dye degradation	Schiff base catalysts	Cu, Fe, Co, Mn	Oxidation of organic dyes
Advanced oxidation	Metal complexes/H_2O_2	Cu, Fe, Co	Pollutant degradation
Photocatalysis	Schiff base photocatalysts	Ti, Zn, Cu	Visible-light degradation
Gas adsorption	Schiff base MOFs	Cu(II), Zn(II)	CO_2/gas capture
Heterogeneous catalysis	Supported complexes	Pd, Ru, Cu, Ni	Recyclable catalysts
Chemical sensing	Schiff base complexes	Cu(II), Ni(II), Zn(II)	Detection of ions & molecules

11. Challenges and future directions

Mir and Banik emphasized that, despite substantial progress in Schiff base synthesis and application, important challenges remain in sustainability, scalability, and the transfer of laboratory methods to practical use [17]. They noted that green synthetic approaches based on natural acid catalysts, benign solvents, microwave or ultrasound irradiation, and other low-waste methods are promising, but their wider adoption depends on better reproducibility, industrial scalability, and clearer reporting of sustainability-related parameters such as atom economy, energy efficiency, and waste minimization [17]. Nagar et al. similarly highlighted that newer green routes such as ball milling, industrial-waste-assisted synthesis, egg-white-mediated methods, and plastic-waste-derived precursors remain comparatively underexplored, even though they may offer more sustainable access to Schiff base ligands

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and complexes [18]. Mir and Banik also pointed out that future work should place greater emphasis on ligand and metal selection from a sustainability perspective, especially by moving away from systems that depend heavily on costly or less sustainable metals and toward complexes of earth-abundant metals that can deliver useful activity with lower environmental burden [17]. Across catalysis and materials chemistry, they further stressed that practical deployment will require stronger links between mechanistic understanding and real operating conditions, including catalyst stability, recyclability, and performance in chemically complex media [17]. In medicinal and biological applications, recent reviews indicate that a major gap still separates promising *in vitro* results from clinically relevant Schiff-base-derived agents. This gap is largely associated with issues such as solubility, off-target toxicity, pharmacokinetic behavior, and long-term safety. More systematic *in vivo* validation, mechanistic investigation, and integrated ADMET assessment are therefore needed, together with ligand design strategies that balance potency, selectivity, biocompatibility, and controlled metal release [21], [72]. Another important direction is the increasing use of advanced spectroscopy, computational chemistry, and data-driven modelling to guide the design of Schiff base systems. When experimental studies are combined with theory, docking, electronic-structure analysis, and predictive modelling, ligand and complex design can become more rational and target-specific [21], [72]. If these developments are paired with standardised sustainability metrics and more transparent reporting, the field is likely to move from isolated demonstrations toward broader, optimized, and practically useful strategies for green and functional Schiff base chemistry [17], [18].

12. Conclusion

Schiff base ligands and their metal complexes constitute a versatile and extensively studied family of coordination compounds, valued for their ease of synthesis, structural flexibility, tunable electronic features, and wide-ranging applications. Systematic variation of donor atoms, functional groups, and stereochemistry allows precise control over coordination modes, metal-binding affinity, and redox behavior, making these ligands adaptable platforms for catalysis, medicinal chemistry, sensing, and materials applications. Green and sustainable synthetic methodologies—solvent-free reactions, microwave and ultrasonic irradiation, mechanochemistry, aqueous media, and naturally derived catalysts—have reduced energy consumption and hazardous waste without compromising yield, while advances in spectroscopic, crystallographic, electrochemical, and computational characterization continue to deepen understanding of metal–ligand interactions and structure–property relationships. Schiff base complexes exhibit well-documented antibacterial, antifungal, antiviral, antioxidant, anti-inflammatory, and anticancer activities, often enhanced by metal coordination through increased lipophilicity, membrane permeability, and macromolecular interactions, with DNA binding/cleavage, enzyme inhibition, and reactive-oxygen-species generation identified as key mechanisms. Beyond biomedicine, these systems support catalysis, sensing, corrosion inhibition, and metal–organic framework construction. Realizing this potential fully will require standardized green-synthesis protocols, scalable production, long-term stability and toxicological data, and *in vivo* validation, alongside computational modeling and AI-assisted design to accelerate discovery. The convergence of sustainable synthesis, rational ligand engineering, and multidisciplinary application positions Schiff base chemistry as a dynamic field with continued relevance to coordination chemistry, medicinal chemistry, catalysis, and environmental science.

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