Synthesis and Some Versatile Applications of N_2O_2 Schiff base Metal complexes- Review

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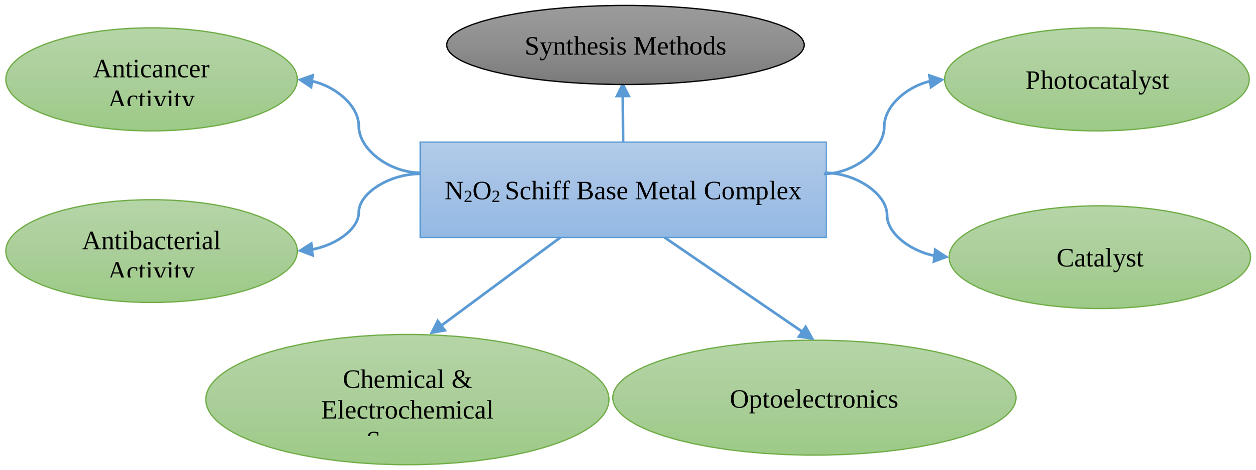
Abstract:

Schiff bases are versatile ligands, synthesized by the condensation of carbonyl groups with primary amines. These ligands have sigma donor ability towards the metal cations and also have π acceptor properties in their imine nitrogen atom, which makes it a good donor ligand in coordination chemistry. So, they can easily form metal complexes with most of the metals. Metal complexes with Schiff base due to their unique properties, are applicable in various fields including biology and industry. The complexes have also been found to display interesting biological activities, including antibacterial, antifungal, and anticancer properties. Overall, the Salen-type Schiff base metal complexes have emerged as a promising class of compounds with significant potential in various fields, and their further development is expected to lead to innovative solutions for real-world challenges. This review presents an outline of the synthesis pathways of N_2O_2 Schiff base metal complexes and some of their versatile applications in various fields.

Graphical Abstract



Key words: Schiff Base, Metal Complex. Anticancer, Antibacterial, Catalyst, Optoelectronics, Photocatalyst, Sensor

INTRODUCTION

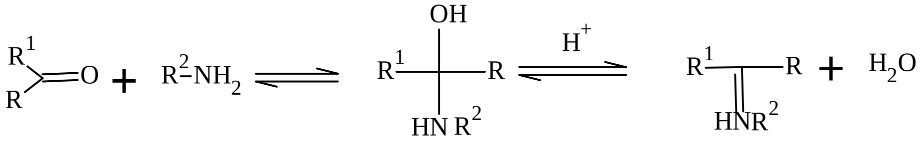
Schiff bases, characterized by the azomethine group (–CH=N–), class of compounds due to their anti-inflammatory, antifungal, antiproliferative, antibacterial, antitubercular, anticonvulsant and antiviral properties are applicable in medicinal and pharmaceutical chemistry[1,2]. It is considered as a versatile ligand since they undergo complexation effectively with most of the transition metals owing to their facile approach, readily adjustable ancillary ligands and tunable stereo-electronic structures[3-5]. Salen-type Schiff base metal complexes have been a fascinating area of research in recent years, with numerous studies showcasing their exceptional properties and potential applications. The complexes exhibit a remarkable ability to stabilize high-oxidation-state metal centres, which enables their use as efficient catalysts for various reactions, such as epoxidations, hydrocarbon oxidations, and alkene polymerizations. Additionally, their redox-active nature and tunable electronic properties make them attractive candidates for electrochemical applications, including energy storage devices and sensors.

Usually N, O heterodentate Schiff bases is prepared by condensing aldehydes/ketones with various amines or amino acids. N_2O_2 Schiff bases are derived from aldehydes and diamines and also by treating dialdehydes or diketones with diamines or amino acids. Various methods were adopted for the synthesis of metal- Schiff base complexes; conventional heating method and green method of synthesis. Conventional method of synthesis involves either heating or stirring different aldehydes or ketones with different types of primary amines. Green method involves an ecofriendly method of synthesizing which reduces the usage of harmful or toxic organic solvents. Most of the methods have financial benefit over conventional synthetic routes[6].

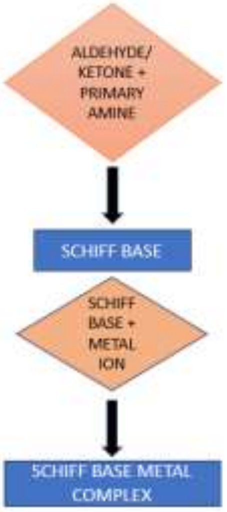
Conventional method of synthesis:

Reflux method:

In this method, a carbonyl compound and amine/ amino acid are condensed using various solvents and at varied processing parameters to prepare Schiff bases.



The metallic salt is then complexed with Schiff base to produce the appropriate metal- Schiff base complex.



N_2O_2 Schiff bases are prepared by the reaction between carbonyl compounds(ketone/aldehyde) and amines, which on complexation with metal produces Metal-Salen complexes.

N_2O_2 Schiff base is synthesised by treating dicarbonyl compound(diketone/dialdehyde) with amine/amino acid. It involves the condensation of two molecules of amino acid/amine with one molecule of dicarbonyl compound, resulting in the formation of a tetradentate ligand. The Schiff base was then refluxed with metal salts to form the corresponding metal-salen complex. It can also be prepared by the condensation between carbonyl compound and diamine. Here, two carbonyl components are treated with one molecule of the amine.

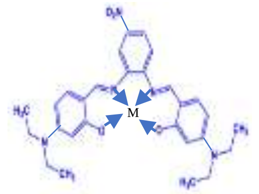
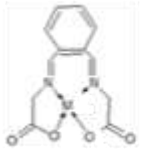
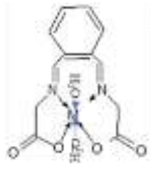
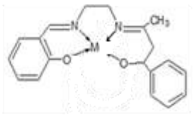
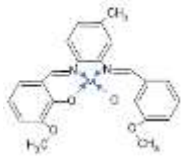
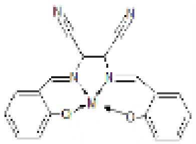
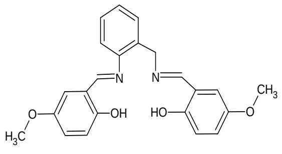
Carbonyl Component	**Amine/Amino Acid**	**Metal Ion (Mn+)**	**Resulting Complex**	**Reference**
3-hydroxybenzaldehyde	4-nitrobenzene-1,2-diamine	**Co(II), Cu(II) and Zn(II)**		[7]
o-phthalaldehyde	L-tryptophan or Histidine	**Co(II), Ni(II), Pd(II), Cu(II)**		[8]
o-phthalaldehyde	L-tryptophan	**M = Co(II), Ni(II), Zn(II)] and [CuL]**		[9]
DFMPM	L-Alanine	Zr(IV) And Th(IV)	**N2O2 Schiff Base complex**	[10]
2′,4′-dihydroxyacetophenone and 1-phenylbutane-1,3-dione	ethylenediamine	Zn(II), Cu(II), Ni(II) & Co(II) acetate		[11]
3-methoxysalicylaldehyde	4-methylbenzene-1,2-diamine	Ni(II) and Pd(II)		[12]
5-Methy1 salicylaldehyde, salicylaldehyde	diaminomaleonitrile	Ni(II), Cu(II)		[13]
2-aminobenzylamine	5-methoxysalicylaldehyde	Mn(II),Co(II), Cu(II), Zn(II)	 Schiff base ligand	[14]

Table 1: Examples of N_2O_2 Schiff base

Metal Complexes formed with dicarbonyl and amine compounds

Green method of synthesis:

Numerous strategies were considered for the green synthesis of Schiff base ligands and their metal complexes, including the use of natural acids as catalyst, water as a green solvent, microwave irradiation, grinding etc. Nowadays green synthesis was mostly considered in the synthesis of Schiff base as it minimises or eliminates the use and generation of waste as well as hazardous substances. Of the 12 principles of green chemistry, the first principle was primarily focussed on the prevention and minimisation of waste at every step of process rather than treating the waste after it was formed. Most of complexation reaction were synthesised by microwave method and currently ultrasonic method of syntheses were preferred due their advantages over conventional method.

Microwave synthesis is considered as an alternative method for conventional synthesis due to low reaction time, economically beneficial, carried out under free or less solvents, reduces pollution and have high productivity together with ease in processing and handling. Microwave synthesis uses microwave radiation for generating heat for conducting the chemical reaction. Here, the target molecule in polar solvents and reactant molecules are heated by microwave radiation, thus forcing them to vibrate and rotate in resonance with the applied field. This frequent collision and vibration results in the generation of heat. Thus, the reaction rate increases and the time for conducting the reaction reduces. A wide variety of Schiff bases and metal complexes are synthesised using this method [15-17.]

Sonication method uses higher power to excite particles to higher levels for various purpose. Here sound energy is applied to agitate particles in a sample. In this method sound waves propagate into the liquid media and results in alternating high pressure (compression) and ow pressure (rarefaction) cycles. During the compression, the average distance between the molecules is get decreased and during rarefaction, the average distance between the molecules is increased. In the rarefaction, under appropriate conditions, bubbles are be formed by overcoming the attractive forces and if the internal forces are sufficiently large, the collapse of these bubbles may generate very high local temperatures (approximately 5000 °C) and pressures (over 1000 bar). Due to the very high temperatures and pressures, chemical reactions occur. When sonication uses frequencies greater than 20KHz, the process is known as ultrasonication. An ultrasonic bath or probe named as sonicator is typically used for the laboratory purpose. Ultrasound method, due to its uniqueness in accelerating many organic reactions through cavitation, it provides shorter reaction times and have greater yields when compared to other methods of synthesis such as conventional heating, use of catalysts etc. The cavitation purpose involves the formation, growth and collapse of bubbles irradiated with sound, produces a large amount of energy and it converts kinetic energy into heating spots [18-21].

Microwave synthesis of Metal Complex:

The method of synthesis involves the reaction of aldehyde with diamino compounds or diketones with amino compounds and the desired metal salts. Mostly green solvents like water or alcohols are preferred, also some reactions are conducted in solvent free conditions The reaction can be conducted with/ without a catalyst. Microwave irradiation was performed by placing the reaction mixture on a microwave oven or reactor. Some researchers incorporated both conventional and microwave method of preparation to demonstrate the advantage of microwave method over the other one. One example is mentioned here.

The conventional method of synthesis involves the reaction of an amine with aldehyde to form a form the Schiff base ligand. Then metal complexes are prepared by refluxing the ligand with metal salts in ethanol for 6 to 10 hours. The Microwave method applies microwave irradiation to facilitate internal heating through molecular rotation and ionic conduction. The reactants, (carbonyl compounds, amines and metal salts) are mixed in a small amount of solvent and irradiated in a microwave oven for only 2 to 5 minutes. As the energy is transferred directly to the molecules, the reaction reaches the activation energy near instantaneously.

Replacing classical method with microwave irradiation offers a more convenient and eco-friendly heating alternative. This method mostly optimizes productivity, providing yields above 75% and reducing reaction time from 2–10 hours to a mere 2-5 minutes.[22]

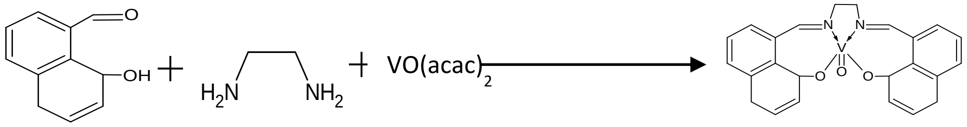
Microwave-assisted synthesis has become a popular choice in many fields of chemistry due to its advantages over traditional methods. They have faster reaction time, higher yields, more convenience, good energy efficiency and have greater selectivity. As a result, microwave-assisted synthesis has become a popular choice in many fields, including organic synthesis, polymer chemistry, materials science, and biotechnology. Many researchers and industries are now adopting microwave synthesis as a reliable and efficient method for synthesizing a wide range of compounds and materials.

Ultrasonic method of synthesis:

Nowadays most of the organic reactions were conducted using Ultrasound method, since it provides shorter reaction times and have greater yields when compared to other methods of synthesis like conventional heating, use of catalysts etc.

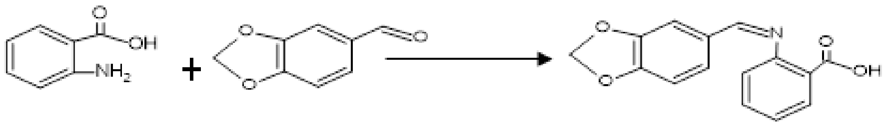
All the reagents (the aldehyde or ketone, the diamine or amino acid, and the metal salt) were mixed together without the aid of any catalyst, and the reaction was carried out in an ultrasonic bath. Employing ultrasound boosts the reaction by creating tiny bubbles that may collapse and generate very high temperatures and pressures, which speeds up the reaction, enhances their mixing, and increases the product yield. As a result, this method, provides higher yields and requires much shorter reaction time compared to the traditional method.

Oxovanadium(IV) complex with a tetradentate Schiff base ligand was synthesised by ultrasound irradiation. All reactants are mixed and exposed to ultrasonic waves, that generate cavitation bubbles that collapse and create localized high temperatures and pressures in the reacting mixture. This enhances the interaction between reactants and speeds up the formation of the Schiff base complex without support of any catalyst.



By reducing the reaction time from 3 hours in case of conventional method of synthesis, to just 40 minutes, ultrasonic irradiation has achieved a significant reduction in reaction time and affords the desired product in a higher yield and purity. Additionally, the higher yield and purity of the desired product obtained through ultrasonic irradiation are likely due to the more efficient mixing and reaction conditions achieved with this technique. The use of free solvent, which means no need for a solvent other than water, is also an eco-friendly approach, reducing waste and minimizing the environmental impact of the reaction [23].

Schiff base was prepared by the condensation of piperonal and anthranilic acid in the presence of acetic acid in methanol (solvent) and the mixture is sonicated at 37 kHz at 25^0C in ultrasonic bath for 10 minutes.



The synthesised Schiff base and metal salts are mixed in 2:1 ratio in methanol and then sonicated with 37 kHz in ultrasonic bath for 25-30 minutes at 60 °C.

When compared to conventional methods of synthesis, the reaction time was greatly reduced and also the product yield was very high [24].

Application of Schiff Base Metal complexes:

Schiff base metal complexes have a wide variety of applications in many fields including analytical, biological, inorganic chemistry and organic chemistry. They gained importance in medicinal and pharmaceutical fields due to a broad spectrum of biological applications such as anti-inflammatory, antifungal, antibacterial, anticancer, analgesic, antioxidant and so on. In addition to biological activities, they are used as catalysts, intermediates in organic syntheses, dyes, pigments, polymer stabilisers and corrosion inhibitors [25].

Biological activities of Schiff base metal complexes:

Anticancer activities:

N_2O_2 Schiff base complexes have been investigated for their potential anticancer activities, and several studies have shown promising results. Ligands and metal complexes exhibited antiproliferative activity, cytotoxicity, antioxidant activity etc. Their capability to form stable, square-planar or octahedral complexes with most of the transition metals like Copper (Cu), Zinc (Zn), Nickel (Ni), and Cobalt (Co), Palladium(Pd), Ruthenium(Ru) greatly enhances their biological activity. The transition from a free Schiff base ligand to a metal complex mostly increases lipophilicity (according to Overtone's concept and Tweedy's chelation theory), allowing greater penetration through the lipid bilayer of cell membranes Here, the anticancer activities of some salen – metal complexes and their mode of action were demonstrated.

One of the studies reported that the ligand and its metal complexes exhibited anticancer screening against colon cancer cell lines (HCT116). Copper (II) complexes show significant cytotoxicity and DNA-cleaving ability because of their ability to generate ROS through oxidative and hydrolytic pathways, leading to DNA damage and cell apoptosis. The intrinsic mitochondrial pathway is also activated by excessive ROS production, thus amplifying the apoptotic signal [26].

Another study was done to compare the anticancer property of salen and salophen complexes of Cobalt(III)ion, where, both the complexes showed anticancer activity. The cytotoxic property of ligands, metal ions and complexes against A549 lung cancer cells and vero normal kidney cells were explored. In tests against A549 human lung carcinoma cells, complex 1 and complex 2 exhibited IC50 values of 80 µM and 65 µM, respectively, explaining that complex 2 has superior cytotoxic activity. Here, the complexes interact with DNA through intercalation as well as hydrophobic modes, expected that aromatic moiety is involved in the intercalation. Also, the studies pointed out that, the presence of additional aromatic phenyl ring in salophen caused increased binding, due to the enhanced stacking interaction between aromatic moiety and DNA bases. The hydrophobic interaction with DNA occurred due to the presence of long aliphatic chain in the complexes. Both the complexes bind with protein- BSA through hydrophobic modes. It is vital to study the Protein - Drug interaction in medicinal chemistry, as it is closely related to drug efficacy in the treatment of diseases. Cell cycle analysis also showed that both the complexes cause death of A549 cells through apoptosis. Additionally, both the complexes act as anti-angiogenic agents, productively inhibiting the formation of new blood vessels, with complex 2 showing the highest level of activity.[27]

A manganese-salen complex prepared from (R)-1,2-Diaminobicyclo[2.2.2]octane showed 16 times more potent than cisplatin against the Human Colon cancer HCT116 cell lines, with an IC50 of 336 (±10) nM. The complex is acting as a mimetic of enzyme such as Superoxide Dismutase or catalase. Consequently, the increased biological activity of the complex is likely due to its involvement in an oxidation-reduction reaction, generating activated oxygen and triggering apoptosis of the cells [28].

Palladium- Picolinic acid complex is reported as a promising potent anticancer agent against human colorectal adenocarcinoma and breast cancer with IC50 values of 27.6 and 47 mg/mL, respectively[29]. Another study on metal complex also showed the cytotoxic effect MDA-MB-231 (a highly aggressive, triple-negative human breast cancer cell line) might be due to strong stacking mode of interaction between the DNA bases of the cancer cells as well as extended ROS production efficacy. They work by producing reactive oxygen species (ROS) that trigger mitochondrial dysfunction and induce the activation of caspases (3/7 and 9). It was also reported that antitumour activities of these complexes were induced due to apoptosis on the cancer cells [30].

Synthesizing the reported data, we can conclude that the complexes exhibit multifaceted mode of action, which may include generating ROS through oxidative and hydrolytic pathways, leading to DNA damage and cell apoptosis. Furthermore, the intrinsic mitochondrial pathway is activated by excessive ROS production, which amplifies the apoptotic signal. Notably, some complexes mimic like Superoxide Dismutase or catalase and generate activated oxygen and triggering apoptosis of the cells. Recent investigation revealed that reactive oxygen species (ROS) production may trigger mitochondrial dysfunction ultimately instigating the activation of caspases.

Antibacterial activities:

Several studies on Schiff base metal complexes have reported the antibacterial activities against various bacterial species, including Gram-positive and Gram-negative bacteria. The antibacterial activities of these complexes are mostly attributed to their ability to interact with bacterial membranes and thus leading to disruption of membrane function and cell death. Some studies suggested their capability to bind to DNA and inhibiting its replication and transcription. They also inhibit bacterial enzymes, such as protein synthesis and metabolic pathways.[31-34] Some of the ligands and metal complexes with anti-bacterial activities were reviewed in this work.

Bacteria Type	Metal Complex	Mode of Action	Study Result	Reference
Gram-negative (e.g., *E. coli E. asburiae*) Gram-positive (S. aureus)	dimer of Pd(II), [(bpy)Pd(μ-OH)2Pd(bpy)]2+	Decrease of formal charge on the Pd metal of complex due to chelation, which in turn decreases the hydrophilic nature and increases the lipophilic nature of the complex. An increase in the lipophilic nature allows to permeate through the membrane lipid layer of the bacterial cell	Complexes show higher inhibition zones compared to free ligands(bpy); Pd(II) complexes often show highest potency.	*35*
S. aureus, P. aeroginosa, K. pneumonia, B. cearus, and E. coli.	nickel(II) and copper(II)	activity of the metal complexes and their corresponding ligands due to their lipophilic nature across the various bacteria	Complexes containing electron-withdrawing group show higher activity	13
Gram-positive: S. aureus and B. subtilis. Gram-negative: E. coli and K. pneumoniae	Co(II) Ni(II), Cu(II), and Zn(II)	Reduced Polarity- polarity of the metal ion is reduced due to chelation. Lipophilicity- polarity reduction increases the lipophilicity of the metal ion, which in turn increases the cell permeation	Copper(II) complex mostly showed the highest activity as it has the ability to disturb the respiratory process of the cell /interact more efficiently with DNA/proteins.	36
Gram-positive (*S. aureus* and *B. cereus*) and Gram-negative (*E. coli* and *P. aeruginosa*)	nickel(II)	Tweedy's chelation theory: chelation reduces the polarity, increases the lipophilicity and the penetration through the cel membrane. After entering the cell, it disrupts cellular homeostasis by intervening with protein synthesis, impeding respiratory enzymes, and forming hydrogen bonds with cellular components, finally leading to the death of the microorganism.	The complex is more active than the free ligand. Structural geometry (square planar -Ni complex) and the presence of the metal ion plays a critical factor in improving the biocidal profile of these types of Schiff base derivatives	37
Gram-Positive Bacteria:(S.aureus, B.subtilis) Gram-Negative Bacteria: (E. coli, P. aeruginosa)	Iron(III) and cobalt(II)	Chelation increases the lipophilicity and thus improves the permeation through cell membrane. The complexes interfere with normal cellular processes by binding to the active sites of enzymes—thereby inhibiting respiration and protein synthesis, which	The metal complexes showed higher activity than the ligands. The report suggests that the combination of a Co(III) center and a salophen-type ligand exhibited a potent antimicrobial agent.	*38*

Bacteria Type	Metal Complex	Mode of Action	Study Result	Reference
		ultimately leads to the death of the bacterial cell.		
Gram-Positive Bacteria:(S.aureus, B.subtilis) Gram-Negative Bacteria: (E. coli, P. aeruginosa	Fe (III), Co (II), Ni (II), Cu (II), Y (III), Zr (IV), La (III), and U (VI)	The complex can easily permeate through the cell membrane, then interfere with normal cellular processes by binding to the active sites of cellular enzymes, thereby inhibiting respiration and protein synthesis, which ultimately leads to the death of the bacterial cell.	The metal complexes were found to be more potent than the free ligand. The Copper(II) complex showed the most potent antibacterial effect, especially against *S. aureus*, often performing comparably to standard reference antibiotics (like Ciprofloxacin)	*39*

Table 2: metal complexes with their mode of action

Rather than anticancer and antibacterial activities, metal complexes display antifungal, antioxidant, antitubercular and antiviral properties. Metal complexes have various applications in industrial purposes such as catalysts, sensors, optoelectronics and industrial protectives and additives.

Metal complexes in industrial applications

Photocatalyst:

The complexation of Schiff base ligand to metal ion often leads to ligand-to-metal charge transfer (LMCT) transitions, this reduce the bandgap compared to the free ligand and causes extension of light absorption into the visible region which is considered as a key requirement for photocatalysis.

Mechanism of photocatalytic activity:

The photocatalytic mechanism of N_2O_2 Schiff base metal complexes involves a multi-step process, initiated by photoexcitation, here visible-light irradiation excites electrons from the HOMO to the LUMO, thus creating essential electron-hole (e^-/h^+) pairs. To become effective, the complex must sustain a low recombination rate and allowing these charge carriers to migrate to the surface. At the surface, these carriers allow the generation of reactive species: electrons reduce molecular oxygen (O_2) to superoxide radicals ($\bullet O_2^-$), while holes oxidize water into highly reactive hydroxyl radicals ($\bullet OH$). These radicals subsequently attack target pollutants, such as organic substrates, pollutant dyes, or environmental contaminants, bringing their oxidative degradation into harmless byproducts. The overall efficiency of the complex is eventually determined by its surface area and its ability of the radicals to interact with the substrate[40,41]. The following section adds an extensive review of the photocatalytic applications associated with various N_2O_2 Schiff base metal complexes.

Dye degradation:

The catalytic activity of N_2O_2 Cu(II) complex was demonstrated in the photodegradation of organic dyes – methylene blue and methyl violet under UV-Visible light. The photocatalytic decay of organic dye contaminants in the presence of Cu (II) complexes was initiated by the generation of electrons and holes, which eventually produced free radicals such as $^{\bullet}OH$ and $O_2^{\bullet}$. The photodegradation rate is directly proportional to the capability for the generation of these radicals on the surface of the photocatalyst and their reaction with the dye molecules.[40]

$$\mathbf{Cu(II)\ complex + h\upsilon \longrightarrow e^- + H^+}$$

$$\mathbf{H_2O + H^+ \longrightarrow {}^{\cdot}OH + H^+}$$

$$\mathbf{O_2 + e^- \longrightarrow O_2^{\cdot -}}$$

$$\mathbf{O2^{\cdot -} + H^+ \longrightarrow HO_2^{\cdot}}$$

$$\mathbf{2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2}$$

$$\mathbf{H_2O_2 \longrightarrow 2{\cdot}OH}$$

$$\mathbf{HO_2^{\cdot}\ Or\ O2^{\cdot -}\ or\ .OH + Dye \longrightarrow byproducts}$$

Hydrogen production: binuclear Ruthenium(II) complex with bis-bidentate N_2O_2 Schiff base ligand acts as a photocatalyst for the production of hydrogen from water splitting. The complex may enhance the light absorption and improve the production of hydrogen from splitting of the water molecules.[41]

Polymer synthesis: Ni(II) complex acts as a highly potent, visible-light-responsive initiators for polymer synthesis. The complex acts as a photosensitizer, interacting with various additives (such as amines or iodonium salts) to produce reactive radicals. These radicals initiate the Free Radical Photopolymerization of acrylates and also the Cationic Photopolymerization of epoxides. As the Ni(II) complex due to its tunable electronic structure perform as an efficient charge transfer, ensures high polymerization rates and deep curing, which are crucial for high-resolution 3D printing, even under low-intensity LED light sources.[42]

Chemical and electrochemical sensors

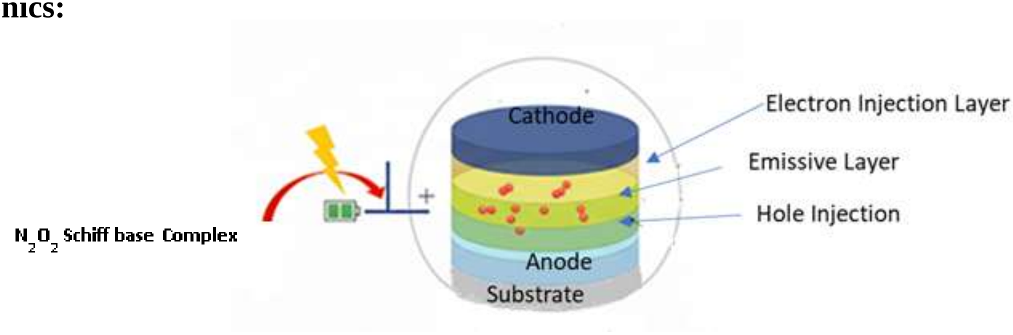
Chemical sensors are devices that translates chemical interactions into a measurable signal (electrical, optical etc.), while electrochemical sensors specifically use reduction-oxidation reaction (redox) at surface of the electrode to generate electrical signals (current, voltage or conductivity. Electrochemical sensors quantitatively detect specific chemical species as an oxidation or reduction current. They convert electrochemical information in to analytical signal.[43]

Metal complexes of N_2O_2 tetradentate Schiff base ligands represent a pillar in the development of multifunctional sensing platforms, serving as a pivotal focus for modern review articles on molecular recognition. These complexes act as a powerful chemical and electrochemical sensor due to their electronic structure and coordination environment. They can be used for modifying electrodes so that the ligand/metal centre acts as a recognition element which can interacts selectively with an analyte (e.g., metal ions or small molecules). Upon binding the target, these interactions may alter the local chemical environment at the surface of the electrode, which changes measurable electrical signals and allows sensitive detection with improved selectivity.[44] Some works are reviewed here.

Copper (II) and Nickel (II) complexes of tetradentate N_2O_2 Schiff base ligand (N,N'-bis-(4-hydroxysalicylidene)-ethylenediamine) can be used as a high-performance electrochemical sensor by modifying a Glassy Carbon Electrode (GCE) to specifically detect a toxic industrial pollutant, Hydrazine (N_2H_4). Of these two, the Nickel (II) complex act as a superior nano-modifier because of its excellent electrocatalytic activity, that permitted the oxidation of hydrazine to occur at a substantially lower potential of 0.55 V. On application level, the sensor was utilised for the detection of hydrazine levels in water samples taken from the Jajrood River, it was able to select hydrazine even in the presence of common interfering chemical species.[44]

In chemical sensing, the N_2O_2 coordination environment allows the dramatic colorimetric and fluorometric transitions through mechanisms like Internal Charge Transfer (ICT) or Photoinduced Electron Transfer (PET), enabling for the high-sensitivity naked-eye detection of environmentally hazardous metal ions. Concurrently, their electrochemical activity is due their ability to stabilize various oxidation states of the central metal atom (typically Cu, Ni, Mn or Co).[45]

Optoelectronics:



Optoelectronics, deals with the interaction of light and electricity that focuses on devices that can either convert electrical signals into light (like an LED) or convert light into electrical energy (like a solar cell).

The purpose of N_2O_2 Schiff base complexes in optoelectronics is to create efficient, low-cost, and tunable organic electronic materials that can be used in Luminescent Materials (OLEDs), Photovoltaic (Solar) Materials (complexes act as light-harvesting dyes), Nonlinear Optics (NLO) and Optical Sensors.[46] Some research activities were reviewed here to support this application.

Binuclear metal carbonyl complexes of N_2O_2 Schiff base ligand prepared with Chromium, Molybdenum, and Tungsten shows significant optoelectronic activity, that makes them v candidates for photoactive materials. They retain distinct fluorescence properties and direct electronic transitions. The optical band gap which was estimated to range between 2.91 eV and 3.52 eV, serves as the key aspect of their optoelectronic profile. These energy values reveal the semi conductivity properties of the compounds, proposing their potential application in the development of optoelectronic devices.[47]

The study done by Juliet Gradinaru et al. [48] serves as a substantial proof for the potency of N_2O_2 Schiff base complexes in the field of optoelectronics by pointing their superior Second-Order Nonlinear Optical (NLO) performance, determined both by measurements of solution-phase direct current electric-field-induced second harmonic generation and by theoretical time-dependent density functional theory (TDDFT) calculations. The critical influence of metal ion in NLO activity was validated by Ultra-Violet spectroscopy that identified the presence of metal-to-ligand in closed-shell complexes and ligand-to-metal in open-shell configurations charge-transfer bands which operate along with intrinsic charge-transfer transitions. They have large thermal stability up to 310^0C, which are essential for optoelectronics applications as optical switching.

In the field of advanced optoelectronics, N_2O_2 donor Schiff base complexes, have gained significant prominence as a blue-light-emitting materials in Organic Light-Emitting Diodes (OLEDs). OLED consists of functionally distinct semi-conducting layers arranged in a p-n junction configuration that produce electroluminescence. Recent investigation on pyrazolone-based azomethine ligands demonstrated that rigid N_2O_2 coordination environment suppresses the non-radiative vibrational relaxation, thereby enhancing photoluminescence efficiency. The dehydration of complex resulted in brilliant blue luminescence and amplified their photoluminescence quantum yield to 55.5%. Furthermore, due to the high thermal stability and high efficiency of brilliant blue luminescence the complex is ideal for developing blue electroluminescent material. From the study of the electroluminescent properties, the material exhibits blue emission with brightness up to 5300 Cd/A, choosing it as a viable candidate for next generation full-color displays and lighting technologies.[49,50]

Catalysis:

N_2O_2 Schiff base metal complexes are the most versatile catalyst in Modern Chemistry. Their catalytic power emerged from the privileged nature of the ligand (mostly salen type ligand) which can be easily regulated to stabilise the metal oxidation states. There are many fields where these complexes can be used as a catalyst.

Oxidation reaction: This is the most prominent application.

N_2O_2 Schiff base metal complex can be used as a catalyst for the conversion of alcohol into carbonyl compounds (aldehyde and ketone).[51] The nanoparticles produced form Zinc and cobalt metal complexes can be used as a catalyst for the selective oxidation of benzyl alcohol in to benzaldehyde using hydrogen peroxide at room temperature.[52]

The conversion of alkenes to epoxides is a critical catalytic process in organic synthesis. The N_2O_2 Schiff base complexes play a key role as a tunable and efficient catalyst in this transformation, supporting the use of green and milder oxidants like H_2O_2 instead of toxic peracids. For example, the mono oxovanadium(IV) complexes of the N_2O_2 ligands can selectively catalyse the epoxidation of cyclooctene using molecular oxygen in polar solvents. Due to the availability of strong donor ligands vanadium complex are extremely stable during the course of reaction.[53]

Corrosion inhibitor: they are compounds that are used to slow down or prevent corrosion process. Metal complexes inhibit corrosion by forming a protective layer on the metal surfaces, blocks the active sites and shield it from oxygen and water. These complexes use the ligands that binds to the metal surface and makes them less reactive.[54] In the context of protecting mild steel from degradation in 1M HCl, The Co(II), Ni(II), Cu(II) complex of unsymmetrical tetradentate N_2O_2 Schiff base complex acts a robust inhibitor by forming a cohesive molecular barrier on the surface of the metal. They act as a mixed inhibitor reducing both the anodic dissolution of iron and cathodic evolution of hydrogen, where the inhibition mechanism is driven due to the adsorption of complex onto the steel surface and facilitated by the donation of pi electrons and lone pair of electrons from azomethine Nitrogen and phenolic oxygen atoms to the metal's vacant d-orbital. As the concentration of complex increases, the inhibition efficiency increases and also higher electron density of the chelated structure provide more surface coverage compared to free ligands.[55]

C- C Coupling reactions: these reactions are the corner stone of modern organic chemistry which enables the formation of complex framework by linking two carbon containing fragments. Due to high stability, tunability and recyclability N_2O_2 Schiff base metal complexes are highly considered as a heterogenous catalyst in such reactions. The multi-walled carbon nanotubes anchored Pd(II) Schiff base complex acts as a heterogenous catalyst in the C-C coupling reaction (Suzuki- Miyuara cross coupling and Sonagashira-Hagihara coupling reaction) in aqueous media under aerobic condition. Rather than high catalytic activity, the complex has good thermal stability, oxygen insensitivity and recyclability. The complex offers a promising outlook due to their facile synthesis and easy recyclability.[56]

Hydrogenation and reduction reaction: The N_2O_2 Schiff base metal complexes are good catalyst because of their aptitude to stabilise the active metal centers and also influence the electronic environment that assist hydride formation and hydrogen transfer, which are fundamental steps in hydrogenation and transfer hydrogenation. This can be demonstrated by considering a ruthenium Schiff base complex which serves as catalyst that mediates the reductive transfer of hydrogen from isopropanol to the organic substrates. This reaction involves the formation of metal hydride intermediates that allows hydrogen transfer and thus reduction of carbonyl compounds.[57]

Future Outlook and Conclusion

The synthesis and application of the metal complexes with N_2O_2 Schiff base ligands function as a pillar for modern coordination chemistry. As highlighted throughout the review, the tetradentate nature of these ligands establishes a stable and versatile framework that are capable of stabilizing a wide range of metal ions in various oxidation states. Due to the structural stability and tunable electronic properties of the ligands, the complexes are indispensable in both biological and catalytic frontiers.

N_2O_2 Schiff base complex has emerged as a promising candidate in medicinal chemistry, showing significant characteristics as anticancer and antimicrobial agents. Because of the geometry of the metal complex and also due to their lipophilic nature, they are able to interact with DNA and also inhibit the enzyme activity. The metal complexes exhibit significant catalytic activities across wide variety of organic transformations such as oxidation, reduction and C-C Coupling reactions. Their structural tunability permits for the design of green chemistry pathways that reduce waste and energy consumption.

Beyond the conventional applications, the use of these complexes into optoelectronics, chemical and electrochemical sensors and photocatalysis highlights their multidisciplinary potential integrating molecular chemistry and material science. A transition from phenomenological observation to a computationally – aided understanding of structure – activity relationships is required for the optimization of the performance of the N_2O_2 Schiff base complexes.

Conflict of Interest:

The authors have no conflicts of interest regarding this investigation.

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