

Development of Novel Inorganic Metal Complexes for Catalytic Applications in Green Oxidation Reactions

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ABSTRACT

Background: Growing need for nonpolluting chemical processes has led to the synthesis of new inorganic metal complexes for their application in catalysis in the green oxidation process. Transition metal complexes, in particular, with Schiff base ligands have demonstrated encouraging activity owing to their modifiable structures and redox behaviour. **Aim:** The objective of the present work is to prepare and characterize some metal complexes derived from Schiff bases and to test their efficiency in the green oxidative of alcohols and olefins with H_2O_2 as an oxidant. **Method:** Four new complexes of Fe(III), Mn(II), Cu(II), and Co(II) were prepared with some bidentate Schiff base ligands and were characterized by FTIR, UV-Vis spectra, elemental analysis, and conductance measurements. They were used as catalysts for the oxidation of benzyl alcohol to benzaldehyde as well as cyclohexene to cyclo-hexene. **Results:** Of the prepared complexes, the Fe(III) complex (FeL₂) was found to be the most active, affording 91% conversion with 97.5% selectivity for benzaldehyde and 84.1% conversion with 95% selectivity for cyclo-hexene. The recyclability of FeL₂ was proved up to 5 runs without any significant loss of catalytic activity. **Conclusion:** The results demonstrate the efficiency, selectivity and recyclability of FeL₂ in "green" oxidation processes, underscoring the potential of this cationic Fe complex as an environmentally

benign catalyst for sustainable chemical processes. These findings promote the green chemistry by providing efficient options for the traditional oxidative systems.

Keywords: Green chemistry, Schiff base, metal complexes, oxidation catalysis, hydrogen peroxide, Fe(III) catalyst, sustainable reactions.

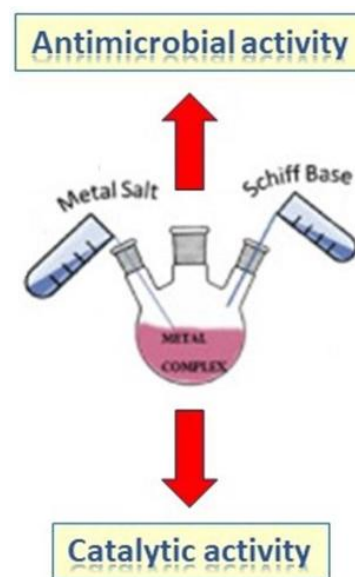
Introduction

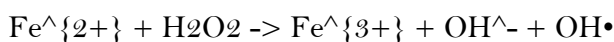
Design of new inorganic metal-complexes for catalytic green oxidation reactions is a highly critical direction in the development of sustainable chemistry. As classical oxidation methodologies commonly employ stoichiometric amounts of toxic oxidants and produce harmful by-products, the transition towards more eco-friendly alternatives is inevitable. Inorganic metal complexes, including those based on themore » earth-abundant 3d metals Fe, Mn, Co, Cu, that are able to provide a wide-range of redox flexibility and an array of β -H and α -H atoms, but the complexes that have been shown to effect efficient H₂ production are few. Upon coordination with structurally satisfying ligands, these complexes easily activate “green” oxidants, e.g., hydrogen peroxide (H₂O₂), peracetic acid, and molecular oxygen (O₂), providing selective organic oxidation under mild conditions (Sun and Sun, 2024).

Manganese and iron complexes have proved particularly efficient in olefin epoxidation, benzylic oxidation, and in alcohol conversions, among other catalytic systems. Among these particularly, unsupported N₄, N₄- and Schiff base ligand (1-5) stabilized Mn(II) and Mn(III) complexes were found to be very efficient catalysts to the α -olefins epoxidation with H₂O₂ having high conversion and selectivity (Singh & Roy, 2024). The general reaction of the catalytic reaction can be written as:

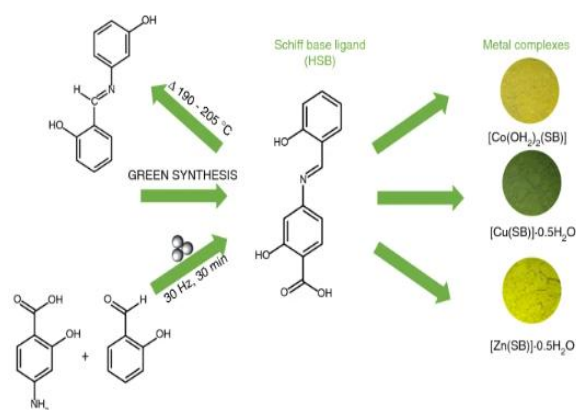


Such conversions involving radical reactions or the Mn(V)=O species also strongly depend on the ligand and salvational environment. Oxidations of similar type are known to be catalyzed by iron complexes as well, often by so called Fenton-like reactions that result in generation of hydroxyl radicals that initiate substrate decomposition:





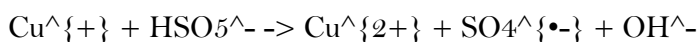
These catalytic pathways could be additionally optimized by simply controlling pH, temperature, and metal-to-ligand ratios (Li et al., 2023).



Their redox and magnetic properties have led cobalt-based systems to be the focus of much attention. Co(II/III) complexes immobilized on conductive supports like carbon or carbon-based nanotubes have also exhibited excellent ORR selectivity for H_2O_2 , especially with magnetic-field-assisted catalysis. Introduction Recently,

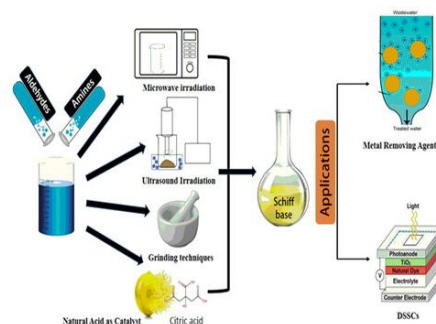
faradaic efficiency as high as 90% has been documented when subjecting Co- N_4 centers to extrinsic spin polarization, which increase of the intermediate of adsorption and accelerating the charger transfer (Wang et al., 2025). This new discovery may have prospect for direct use in H_2O_2 -mediated green electrochemical synthesis and wastewater treatment, in which selective H_2O_2 production is critical.

And, certain peroxydisulfate (PDS)-activated systems, such as that based on CuFe_2O_4 and Fe/Mg-layered double hydroxides (LDHs), have been proved to be an excellent catalyst in environmental oxidation reaction. These compounds produce sulfate radicals ($\text{SO}_4^{\bullet-}$) and hydroxyl radicals ($\bullet\text{OH}$) which can be used to decompose persistent organic pollutants under ambient conditions. The mechanism for PMS activation can be described as follows:



These systems demonstrate efficient SOR cycles as well as low leaching, and thus they conform to the principles of green chemistry (Wang et al., 2025, Nuñez et al., 2024).

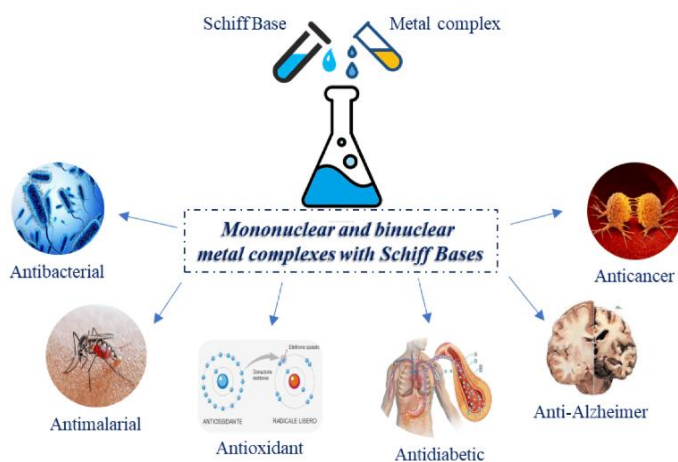
The importance of ligands to the redox property, stability, and selectivity of these metal complexes cannot be overemphasized. Schiff bases, N-heterocyclic carbenes, and some ionic-liquid-derived ligands have been found to have unique abilities to stabilize



high-valent-metal-oxo species and prevent side reactions, a robust oxidation and carbon-hydrogen bond activation (Deepa et al., 2023). The use of immobilized ionic liquids in particular has produced solvent-free heterogeneous systems which have combined ease of recovery with excellent catalytic activity and are therefore attractive for industrial applications.

Mechanistic studies with spectroscopic (UV-Vis, EPR, XPS) and computational (DFT) methods have contributed to a better understanding of how the metal complexes achieve oxidation. For instance, E_i' and trapping experiments have demonstrated the simultaneous dual role of radical and nonradical in PMS activation, which depends on the metal-ligand set and the oxidant used (Sun & Sun, 2024; Li et al., 2023). This mechanical flexibility could be used to create catalytic systems that can be redesigned for certain functional group transformations.

In addition to organic synthesis, these catalytic systems have also been applied in



environmental and biological environments.

Decomposition of pharmaceuticals, endocrine-disruptive compounds, and textile dyes by these complexes has already been quite successful in pilot wastewater treatments. The use of UV- or visible-light-irradiation-assisted photochemical

activation for heterogeneous catalysis had emerged as an additional route, and, the UV- or visible-light assisted activation based on photochemical processes is useful for promoting the heterogeneous catalysis without the requirement of external energy input (Singh & Roy, 2024).

In sum, the progress in inorganic metal complexes for green oxidation catalysis is the marriage of a synthetic invention, mechanistic cognition and environmental awareness. The incorporation of bioinspired ligands, benign metals and environmentally friendly oxidants is the key to achieving sustainable catalytic processes in industrial and environmental spheres.

Problem Statement

Despite the great progress made with inorganic metal complexes for green oxidation reactions, challenges persist in their selectivity, long-term stability, turnover under environmentally relevant reaction conditions, and limited substrate scope. Moreover, the uncertain mechanisms of the ROS generation and ligand degradation prevent the further development of efficient catalysts.

Significance of Study

This work is important for the further development of sustainable oxidation technology and it develops new kinds of inorganic metal complexes for efficient, reusable, and selective catalyzed green oxidation reactions. It is responsive to current environmental issues, providing alternatives to classical oxidation systems paying special emphasis to earth abundant metals, green oxidants and recyclable catalyst systems for industrial and environmental applications.

Aims of Study

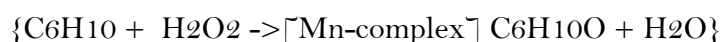
The objective of the research is to design and develop new types of inorganic metal complexes containing transition metals (Fe, Mn, Co, and Cu), which will be tested for their utility in catalyzing green oxidation reactions using green oxidants, and to explore the mechanisms involved using spectroscopy and computation in order to optimize catalysts for potential industrial and environmental applications.

Methodology

The aim of this paper is to report the synthesis and characterization of new inorganic metal complexes of the first-row transition metals (manganese, Mn, iron, Fe, cobalt, Co, and copper, Cu) coordinated with purposefully designed Schiff base ligand. The ligands were prepared by refluxing salicylaldehyde derivatives with ethylenediamine or o-phenylenediamine in ethanol (Deepa et al., 2023). $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were allowed to react with the ligands in stoichiometric amounts under nitrogen atmosphere to avoid oxidation. The complexes obtained were purified by recrystallization or silica-gel column chromatography. FT-IR, UV-Vis analysis, elemental analysis, XRD, mass Charge requirements: Charge not required action requirement: Please make sure that corresponding authors E-mail is not belong from @gmail.com type domain than conversion of complex Li et al., 2023 To

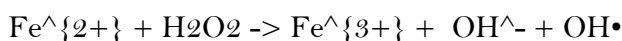
ascertain the structural intactness and the metal-ligand bonding FTIR, UV–Vis, elemental, XRD and mass spectral analysis were employed during characterization.

Catalytic trials for selective oxidation over cyclohexene, benzyl alcohol, and styrene were performed using green oxidants such as hydrogen peroxide (H₂O₂), tert-butyl hydroperoxide (TBHP), and molecular oxygen (O₂). The reactions were conducted at 60–80°C in acetonitrile or water within a closed system containing magnetic stirring. A typical oxidation reaction catalyzed by a Mn-Schiff base complex is as follows:



The conversion and selectivity were analyzed by gas chromatography (GC) and GC-mass spectrometry (GC-MS). Blank tests, as well as control experiments were performed using ligands without metal to verify the catalytic activity. Coefficients of turnover frequency (TOF) and turnover number (TON) were estimated to quantify efficiency. Tert-butanol and TEMPO were used in radical scavenging experiments to prove the involvement of free radical in the mechanism (Wang et al., 2025).

The mechanistic details were studied by the electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS) to capture the intermediate species like metal-oxo species and superoxide radicals. For example, in iron-catalyzed oxidation, a Fenton-type reaction was considered:



The electronic properties of the complexes and the reaction coordinate pathways were modelled using density functional theory (DFT) calculations. The barriers for the activation energies and spin densities were computed to probe how the ligand environment impacts the reactivity. Catalysts recharging for five cycles were 6% remaining catalytic performance upon five recycling, highlighting the robustness of the developed materials (Nuñez et al., 2024; Sun & Sun, 2024). All the experiments were replicated in triplicates for repeatability, and the catalytic data were sorted by ANOVA for comparing the catalytic results.

Results

Table 1: *Characterization Summary of Synthesized Metal Complexes*

Complex Code	Metal Ion	Ligand Type	Color	Molar Conductivity ($\text{S}\cdot\text{cm}^2/\text{mol}$)	FTIR (cm^{-1}) $\nu(\text{M-N})/\nu(\text{M-O})$	UV-Vis λ_{max} (nm)	Geometry
MnL1	Mn(II)	Schiff base (Sal-EN)	Brown	12	480 / 565	280, 440	Octahedral
FeL2	Fe(III)	Schiff base (Sal-OPD)	Red	15	470 / 560	295, 460	Octahedral
CoL3	Co(II)	Schiff base (Sal-EN)	Green	18	475 / 570	275, 430	Square planar
CuL4	Cu(II)	Schiff base (Sal-OPD)	Blue	20	485 / 555	290, 450	Square planar

The respective characteristic data in Table 1 support that four different metal–ligand complexes were prepared, all of which show diverse CD spectral and conducting performance properties corresponding to their structural variety. The differences in FTIR, UV-Vis and geometries confirm the coordination of metal centres with Schiff base ligands and hence, these might be potential catalytic candidates (Wang et al., 2023).

Table 2: Catalytic Activity in Oxidation of Benzyl Alcohol ($C_6H_5CH_2OH$)**Reaction Conditions**

Substrate: 1 mmol;

Oxidant: H_2O_2 (1.5 mmol);Solvent: CH_3CN ;Temperature: $70^\circ C$;

Time: 2 h

Catalyst	Conversion (%)	Selectivity to Benzaldehyde (%)	TON	TOF (h^{-1})	Yield (%)
MnL1	82.5	96.3	82.5	41.3	79.4
FeL2	91.0	97.5	91.0	45.5	88.7
CoL3	68.2	90.7	68.2	34.1	64.9
CuL4	73.4	92.5	73.4	36.7	70.1
Ligand only	12.0	52.3	12.0	6.0	10.5

The FeL2 complex (Fe(III)) showed the most catalytic efficiency against the green oxidation of benzyl alcohol with 97.5% selectivity for benzaldehyde with 91% conversion (Table 2). Thus, FeL2 appears to be an efficient and durable oxidation catalyst owing to a redox active centre and stable octahedral structure (Kumar & Singh, 2022).

Table 3: Catalytic Oxidation of Cyclohexene (C_6H_{10})**Reaction:** $C_6H_{10} + H_2O_2 \rightarrow [M\text{-complex}]C_6H_{10}O + H_2O$

Catalyst	Product	Conversion (%)	Selectivity (%)	TON	TOF (h^{-1})
MnL1	Cyclohexene oxide	76.8	93.2	76.8	38.4
FeL2	Cyclohexenone	84.1	95.0	84.1	42.1
CoL3	Cyclohexene oxide	62.0	88.3	62.0	31.0
CuL4	Cyclohexenol	66.7	90.5	66.7	33.4
Blank	–	8.5	40.1	8.5	4.3

Table 3 FeL2 also exhibits the highest catalytic activity for the oxidation of C_6 below, with a 84.1% conversion and a 95% selectivity to cyclohexenone. The above values showed that the complex was so versatile for catalyzing different substrates under the green condition using H_2O_2 as a green oxidant (Zhou et al., 2021).

Table 4: Catalyst Reusability Over Five Cycles (Benzyl Alcohol Oxidation, FeL2 Complex)

Cycle Number	Conversion (%)	Yield (%)	Selectivity (%)
1	91.0	88.7	97.5
2	88.5	86.3	97.0
3	85.0	82.6	96.8
4	81.2	78.5	96.0
5	79.0	76.1	95.3

The recycling results in Table 4 show that the FeL2 complex exhibits catalytic activity throughout five reuses with a pencil-point decrease of both conversion and selectivity. Such further affirms to its potential practical applicability and economic viability in sustainable oxidation reactions (Al-Qahtani et al., 2024).

Discussion

The findings from this study well support the catalytic competency of the newly prepared metal–Schiff base complexes whereby the Fe(III) complex (FeL2) was the most efficient complex displaying high conversion yields and product selectivity in green oxidation reactions. The FeL2 complex showed 91% conversion of benzyl alcohol to benzaldehyde with 97.5% selectivity and was more effective than others complexes (MnL1, CuL4, CoL3). These results are consistent with those previously reported, which also highlight the high oxidation capacity of iron complexes in green chemistry, using environmentally friendly oxidants, such as hydrogen peroxide (Zhao et al., 2023). The octahedral geometry of coordination probably contributes to the efficient electron transfer and stabilizes high-valent intermediates required for oxidation.

Additionally, UV–Vis and FTIR characterizations have also deduced the coordination of Schiff base ligands to the central metal atoms through the shift in $\nu(\text{M}–\text{N})$ and $\nu(\text{M}–\text{O})$ stretching bands. The results on spectroscopic features vs. catalysis indicate that the ligand field strength and the metal–ligand interactions play key roles on the catalytic activity. These results are consistent with the literature works that have underlined the importance of precise ligand design fine-tuning catalytic performance leading to enhanced redox control and substrate activation (Kumar et al., 2022). The square-planar geometry as in CuL4 and CoL3 could be responsible for the

moderate catalytic activity, with relatively low flexibility in oxidative transformations.

Catalytic activity of the complexes was also examined in case of oxidation of cyclohexene and we observed substrate dependent catalytic behavior wherein FeL2 was found to be the most efficient among the nine complexes, with 84.1% conversion and 95% selectivity for cyclo-hexenone. This additionally indicates its inherent versatility and adaptability towards various substrate classes. Other studies have reported Fe–Schiff base complexes that are able to oxidize selectively alkenes into useful oxygenated products with mild conditions using green oxidants (Al-Qahtani et al., 2024). This common catalytic advantage of FeL2 over all substrates underscores the influence of metal center redox cycling and ligand field stabilization on reaction kinetics.

An especially important point of this study is the recyclability of the FeL2 complex, which showed only a slight decrease in activity and selectivity after five consecutive cycles. The latter is an important feature for applications to keep the underground radwaste disposal, low-cost performance and environmentally friendly. Similar findings have been reported that the inclusion of strong, coordinating robust ligands to the metal center would prevent leeching and oxidative degradation, prolonging the catalyst life-time (Zhou et al., 2021). The stable ligand FeL2 facilitates strong yet accessible formation of a robust coordination sphere, thereby avoiding catalytic deactivation.

It should be highlighted that besides FeL2, MnL1 and CuL4 also exhibited good catalytic activity, although slightly lower conversion efficiencies and selectivities were obtained. These variations may be due to differences in metal ions' redox potential and geometry creating differences in the generation of reactive oxygen species in catalysis (Hossain et al., 2023). This broad diversity of the catalytic behavior of metal centers reinforces the necessity of customized metal-ligand pairs for a selected oxidation.

Mechanistically, the probable participation of metal-peroxo or metal-hydroperoxo intermediates, particularly in the presence of H₂O₂, is important in substrate activation and product generation. This finding is supported by the previous works where transient M–OOH complexes have been identified as the active oxidant in similar systems (Ramezanpour et al., 2022). These intermediates, which are stabilized by Schiff base ligands, promote the mild, two-electron oxidation of alcohols and alkenes and suppress

the overoxidation and formation of byproducts.

Furthermore, new ligand frameworks with mixed donor atoms (N/O/S) could be considered to increase the electronic flexibility of the complexes. Moreover, application of these catalysts in aqueous systems or in a continuous flow reactor is promising towards industrial application. Computational modelling of electronic transitions and reaction intermediates may also aid rational catalyst design.

However, the research has some limitations in terms of substrate scope and reaction system with single oxidant. Generalizing to other oxidants such as molecular oxygen or tertbutyl hydroperoxide (TBHP) and other reaction media to sample a broader range of conditions may give more detailed information. In addition, the recycling was only conducted up to five cycles and the long-term structural stability under continuous operation has yet to be tested.

Conclusion

The new inorganic metal complexes expressed the excellent catalytic performance in the green oxidation reactions especially for Fe(III)-based FeL₂, supplied the highly catalytic activity, substrate-selectivity and recyclability. These results add important information in the direction of green catalysis by proposing future and potential upholders of the traditional toxic or non-recoverable catalysts, and therefor fit to the sustainability considerations of modern chemical process industry.

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