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Importance of Transition Metal Complexes with Salen-Based Ligands: A Review

Prerna Swati[*] and Ashok Kumar Yadav[#]
[*] Research Scholar, University Department of Chemistry, North Campus, B. N. Mandal University, Madhepura , P.O- Singheshwar , PIN -852128, Bihar, India-
[#]Professor & Head (Retd.) , University Dept. of Chemistry , North Campus, B. N. Mandal University, Madhepura , P.O- Singheshwar , PIN -852128, Bihar, India-
Email: prernaswati.sg@gmail.com, yadavkrashok@yahoo.co.in

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Abstract : Salen-based Schiff base ligands and their transition metal complexes have a wide range of applications in various fields like catalysis, sensors, materials science and even medicine. A transition metal is an element with a partially-filled d subshell or the capacity to produce cations with an incomplete d subshell. Salen-type salicylaldimine Schiff bases are very common to the synthetic inorganic chemists as very useful ligands for the synthesis of various transition and non-transition metal complexes. It makes an important contribution to iron absorption and maintains health blood vessels, bones, nerves, and an effective immune system. These metal complexes were screened for their biological activities such as in vitro antibacterial and anti-oxidant activity. The Salen-based complexes are also crucial components or architectural motifs in recent detectors, nonlinear absorptional devices, solar cells and the development of bio-inorganic chemistry catalysis, electromagnetism and diagnostic imaging. The Salen- type ligands thus closely resemble metallo-proteins. A good quality of work has been reported on synthesis and structural investigation of different types of Schiff bases and their complexes. These compounds also find catalytic applications ranging from asymmetric epoxidation, solid phase extraction of metal ions, polymerization and for the preparation of ion selective electrodes. The modified electrodes were screened as electrocatalysts for the determination of some biological compounds, such as dopamine, catechol, cysteine and uric acid.

(Keywords : Salen based Schiff base ligands, transition metal complexes).

Introduction

Schiff base ligands are organic compounds containing an azomethine (–HC=N–) functional group formed by condensation of aldehydes or ketones with primary amines[1,2]. These ligands are widely employed in coordination chemistry because of their simple synthesis, strong metal-binding ability, and structural tunability[2,3]. Salen ligands, typically N, N'-bis (salicylidene) ethylenediamine, are tetradentate ligands possessing an N_2O_2 donor set capable of stabilizing transition metals in square-planar, square-pyramidal, or octahedral geometries[2,3]. This coordination environment closely resembles the active sites of many metalloenzymes, enabling biomimetic behavior in catalysis and biological systems[4,5].

Transition metals are elements with partially filled d-orbitals that can form cations with incomplete d-subshells, allowing redox flexibility, ligand exchange, and catalytic activity[1,5]. The combination of transition metals with Salen ligands produces complexes with enhanced stability, electronic versatility, and functional diversity. The growing interest in Salen-metal complexes arises from their :

- Simple and modular synthesis[2,3]
- Strong chelating ability and thermal stability[2,4]

- Tunable redox and electronic properties[6]
- Potential as eco-friendly alternatives to conventional catalysts[5,7]

As a result, Salen-based transition metal complexes have become indispensable in catalysis, sensing technologies, materials science, medicinal chemistry, and bioinorganic research[8,9].

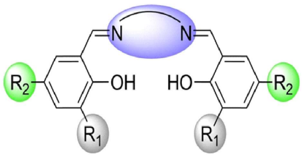

Fig.1 General structure of Salen ligand

2. Methodology

This review is based on an extensive survey of peer-reviewed literature obtained from reputed scientific journals and databases. The collected studies focus on:

- Synthetic strategies for Salen ligands and their metal complexes[1-3]
- Structural and spectroscopic characterization techniques[2-10]
- Applications in catalysis, biological systems, sensors, and materials science[5-9]

Emphasis is placed on correlating ligand structure with functional performance, recent advances, and future research potential.

3. Structural Characteristics of Salen Ligands

Salen ligands possess a rigid and planar N_2O_2 chelating framework that plays a crucial role in their coordination behavior[2,3].

Chelation: Nitrogen and oxygen donor atoms form stable five- and six-membered chelate rings upon metal coordination, increasing complex stability[2].

Planarity: The planar geometry promotes electron delocalization, enhancing redox activity and catalytic efficiency[2].

Substituent tunability: Functional groups on the aromatic rings or diamine backbone allow control over solubility, steric effects, stereoselectivity, and electronic properties[3,6].

Metal–ligand interaction: Strong σ-donation and π-interaction influence magnetic, optical, and catalytic behavior[4].

Salen ligands readily coordinate transition metals such as Mn, Fe, Co, Ni, Cu, Zn, V, and Cr, leading to diverse functional complexes[2,5,6].

4. Synthesis of Salen Ligands and Metal Complexes

Synthesis refers to the chemical procedures used to prepare Salen ligands and their coordination compounds with transition metals in a controlled and reproducible manner[1,2].

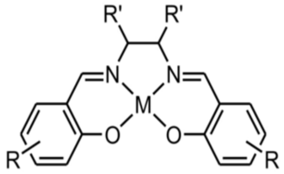

Fig.2

A square planar metal–salen complex. The M denotes the metal atom; R and R' denote precursor ingredients.

4.1 Synthesis of Salen Ligands

Salen ligands are synthesized by condensation of salicylaldehyde (or substituted derivatives) with diamines such as ethylenediamine under reflux in alcoholic solvents[1,2]. The reaction proceeds with elimination of water, forming azomethine linkages. This method is high-yielding and allows structural modification to tune ligand properties[2,3].

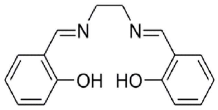

Fig.3 Salen Ligand

$2\,(C_7H_6O_2)$ + $(C_2H_8N_2)$ — Condensation → $(C_{16}H_{16}N_2O_2)$ + $2H_2O$
Salicylaldehyde Ethylenediamine H_2Salen

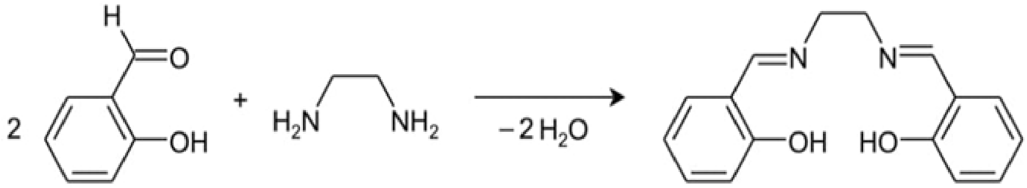

Fig.4

4.2 Formation of Transition Metal Complexes

Metal complexes are obtained by reacting Salen ligands with metal salts such as chlorides, acetates, or nitrates in methanol or ethanol[2,3]. The resulting complexes are typically stable and intensely colored.

Characterization techniques include:

- FT-IR spectroscopy for azomethine (C=N) and metal–ligand vibrations[2,10]
- UV–Vis spectroscopy for ligand-field and charge-transfer transitions[2]
- NMR spectroscopy for ligand confirmation[3]
- X-ray diffraction for structural determination[10]
- Magnetic susceptibility and ESR for electronic configuration analysis[6]

5. Applications of Salen-Based Transition Metal Complexes

Applications refer to the practical utilization of Salen-metal complexes based on their chemical reactivity, electronic behavior, and biological activity[4-6].

5.1 Catalysis

Catalysis is the process by which the rate of a chemical reaction is increased by a substance known as a catalyst, which remains chemically unchanged after the reaction. In coordination chemistry, transition metal complexes act as efficient catalysts because their variable oxidation states and flexible coordination environments allow stabilization of reaction intermediates and lowering of activation energy[1,2].

Salen-based transition metal complexes are particularly effective catalysts due to their rigid tetradentate N_2O_2 chelating framework, which provides high structural stability and precise control over the metal center's electronic environment[2,6]. These features enable selective activation of substrates and controlled reaction pathways. Metal–Salen complexes, especially those of manganese, cobalt, chromium, and iron, have been widely employed in asymmetric epoxidation of alkenes, polymerization reactions, oxidation processes, and hydrolytic transformations[1,6,11].

Salen-metal complexes, particularly Mn-, Co-, and Cr-Salen systems, are widely employed in:

- Asymmetric epoxidation of alkenes with high enantioselectivity[1,6,11]
- Polymerization and oxidation reactions[6,7,12]
- Green and recyclable catalytic transformations[5,6]

Their modular ligand framework enables fine control over stereoselectivity and reaction efficiency.

5.2 Biological and Medicinal Applications

Biological and medicinal applications refer to the use of metal complexes in living systems for therapeutic, diagnostic, and biochemical purposes. Salen-based transition metal complexes are particularly important in this field because their rigid coordination geometry, redox activity, and structural resemblance to natural metalloproteins enable effective interaction with biological targets[4,7].

Salen-metal complexes have been reported to exhibit significant antibacterial, antifungal, antioxidant, and anticancer activities, which arise from metal–ligand synergism that enhances lipophilicity and facilitates penetration through biological membranes[8,13]. Coordination of the metal ion to the Schiff base framework promotes interactions with DNA, proteins, and enzymes, leading to inhibition of microbial growth and suppression of tumor cell proliferation[13,14].

In medicinal chemistry, Salen complexes function as bioinorganic models and enzyme mimics, reproducing the structural and functional features of metalloenzymes such as catalase, superoxide dismutase, and cytochrome oxidase[4,17]. Their redox-active nature allows participation in oxidative stress regulation and reactive oxygen species scavenging, which is relevant for therapeutic and protective biological roles[7,8]. Furthermore, structural modification of the Salen ligand enables control over toxicity, selectivity, and biological performance, making these complexes promising candidates for drug design and biomedical applications[7,14].

Salen-metal complexes exhibit:

- Antibacterial and antifungal activity through metal–ligand synergy[7,13]
- Antioxidant behavior via free-radical scavenging and enzyme mimicry[8,13]
- Anticancer potential through DNA and enzyme interaction[13,14]
- Metal coordination enhances lipophilicity, cellular uptake, and biological effectiveness[4,5].

5.3 Sensors and Electrochemistry

Sensors are devices that detect and measure specific chemical or biological substances, while electrochemistry involves studying chemical processes that involve electron transfer. Salen-metal complexes act as electroactive materials in sensors due to their redox-active centers, high stability, and tunable electronic properties. These complexes are widely used in detecting biomolecules, heavy metals, and environmental pollutants through changes in electrical signals such as current, potential, or conductivity[6,9,10,15].

Salen-metal complexes are used in:

- Modified electrodes for detection of dopamine, catechol, cysteine, uric acid, and heavy metal ions[9,10,15]
- Electrocatalytic systems with improved sensitivity and selectivity[10,15]
- These sensors find applications in environmental monitoring and medical diagnostics.

5.4 Materials Science and Photonics

Materials science focuses on the design and development of substances with tailored physical, chemical, and electronic properties, while photonics deals with the manipulation and application of light. Salen-metal complexes contribute to these fields by offering tunable optical absorption, charge-transfer behavior, and magnetic properties. Structural modification of the ligand allows precise control over electronic transitions, enabling applications in nonlinear optics, light-harvesting systems, molecular electronics, and optoelectronic materials[12,16].

Salen-metal complexes are employed in:

- Organic solar cells and charge-transfer materials[12]
- Nonlinear optical (NLO) devices and molecular magnets[12,16]
- Electromagnetic and nanostructured materials[16]
- Ligand modification allows precise control over optical and electronic behavior.

5.5 Bioinorganic and Biomimetic Chemistry

Bioinorganic chemistry studies the role of metal ions in biological systems, while biomimetic chemistry focuses on designing synthetic compounds that imitate natural biological functions. Salen-based transition metal complexes act as effective enzyme models due to their structural similarity and redox behavior comparable to metalloenzymes such as catalase and cytochrome oxidase[4,7,17]. Their tunable coordination environment enables investigation of metal-mediated biological processes and development of artificial enzyme systems[7,8,14].

Salen-metal complexes act as:

- Enzyme mimics of catalase, cytochrome oxidase and superoxide dismutase[4,7,17]
- Models for electron transfer and oxygen activation[17]
- Tools for understanding enzyme mechanisms and DNA interaction[14]

6. Discussion

Salen-based transition metal complexes are versatile due to their rigid N_2O_2 chelation, tunable electronic properties, and structural stability[1-7]. These features make them highly effective in catalysis, biological applications, sensors, and materials science[2,5,6,12,16]. Challenges remain, including improving biological stability, developing green and scalable synthesis methods, and performing comprehensive safety evaluations for biomedical use[4,7,13].

Future directions involve designing smart and nanostructured catalysts, advanced photonic and electrochemical devices, and biomimetic systems that mimic enzyme functions[5,9,12,16,17]. Salen complexes continue to bridge synthetic chemistry with biological functionality, offering a platform for innovation in chemical, biomedical, and material sciences[4,7,17].

7. Conclusion

Salen-based transition metal complexes represent a cornerstone of modern coordination chemistry. Their stable coordination geometry, tunable electronic properties, and biomimetic nature enable applications across catalysis, medicine, sensors, materials science, and bioinorganic chemistry[1-7,12,16]. Continued research will further expand their role in sustainable technologies and advanced functional materials.

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