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A Short Review on the Applications of Metal-Schiff Base Complexes in the Field of Catalysis and Magnetic Materials

Biplab Biswas

Department of Chemistry, Hooghly Mohsin College, Chinsurah 712101, WB, India

Abstract:

Schiff base complexes—which are characterized by the imine (-C=N-) functional group in ligands—have been attracting a lot of attention in coordination chemistry due to their structural flexibility, ease of synthesis, affordability, and variety of functional properties. Because of the variable coordination number and valency of transition metals, along with redox-active, and loosely bound ligands make these complexes highly efficient candidates as catalysts, whereas the unpaired electrons present in most of the transition metals make them magnetic in nature. The applications of Schiff base metal complexes as catalysts and magnetic materials have been described in this article.

Keywords: Schiff base, Transition Metal Complexes, Catalysis, Electrocatalysis, Magnetic materials,

1. Introduction

When primary amines condense with aldehydes or ketones, they produce Schiff bases, which are compounds containing an azomethine (-C=N-) bond [1]. Since their initial report by Hugo Schiff in 1864 [2], these compounds have been integral to coordination chemistry due to their strong metal-binding ability, ease of modification, and synthetic flexibility. A variety of mono- and polydentate Schiff base ligands may coordinate to transition metals to form coordination complexes since they can include N, O, S, and P donor atoms [3]. In some cases, several transition metals may form complexes with Schiff base ligands, which are coordinatively unsaturated, providing space for the substrates of a particular reaction, for which the substrate may interact more effectively depending on the orientation of the unoccupied sites. Coordinatively saturated complexes bearing loosely bound ligands may leave the coordinating site to make available the space required for the incoming substrates. The stability of the variable valencies of transition metals by Schiff base ligands also plays a determinant role in the reactions where oxidative addition and reductive elimination reactions serve as one of the steps involved in the overall reaction. Along with the variable valency of transition metals, redox-active ligands make these complexes a better candidate for a multi-electron carrier and thus promote electro-

catalytic activity. The presence of odd electrons in the transition metals of most of these complexes makes them magnetic in nature. Thus, Catalysis [4], electrocatalysis [5], and magnetism [6] all benefit greatly from their coordinative behavior, which offers exact control over the environment around the metal center, electronic structure, and metal center reactivity.

Recent advancements have expanded the potential application of Schiff base complexes to encompass energy-related applications, biomimetic systems, and asymmetric catalysis. Schiff base ligands offer exquisite control over the ligand field strength, redox characteristics, and stereoelectronic character due to their tunability by alteration of the substituent on the parent amine or the aldehyde [7]. The structure-activity relationship required to optimize complicated performance in catalytic and electronic applications is based on this modularity [8,9].

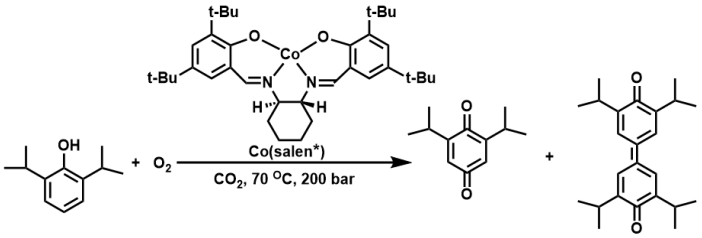
There are several fields of applications of Schiff base metal complexes. Among the many areas of interest, their roles in catalysis, electrocatalysis, and magnetic materials stand out as particularly impactful. In this concise review, we focus specifically on the applications of Schiff base complexes derived from transition metals, highlighting their importance in facilitating chemical transformations as catalysts and electrocatalysts, as well as their unique magnetic properties that make them valuable in the development of functional magnetic materials.

2. Schiff Base Complexes in Catalysis

Due to their convenient system of structural modification and stable coordination environment, Schiff base metal complexes are now multifunctional catalysts. The capacity to Schiff base complexes to fine-tune both steric and electronic properties makes them particularly effective in facilitating a wide range of chemical reactions. It has been discovered that Schiff base complexes, in particular, show strong catalytic activity for oxidation and reduction, C-C bond formation, different coupling processes, etc. These catalytic reactions show the broad application of Schiff base-based systems and are essential in both large-scale production and delicate chemical synthesis. The catalytic activity of the transition metal complexes arises due to the variable coordinating ability of the metals. The coordinatively unsaturated metals provide vacant sites for the substrate; as a result, the probability of interaction between the substrates increases, which increases the conversion rate and hence catalytic activity. In the case of coordinatively saturated complexes, the loosely bound ligands, such as solvents, halides, etc., provide binding sites for the incoming substrates by leaving the site of attachments. Again number of nuclearity of the metal centre also becomes important, as with the increase of the number of metal atoms number of such vacant sites for the incoming substrate increases, which can accommodate more substrate, increasing the activity many folds. Again, the orientations of such vacant sites, as well as the sites of loosely bound ligands that provide space for incoming substrate by leaving the complex, also play a crucial role in the interaction between the substrates. Solubility of the complexes also plays a vital role in selecting the type of catalysis to be utilised. In case of insolubility of the complexes, homogeneous catalysis can not be performed, and we need to utilise heterogeneous catalysis. The stability of variable oxidation states is one of the criteria for oxidative addition and reductive elimination for which transition metals are excellent candidates, and hence, transition metal Schiff base complexes show high catalytic activity, which involves those processes.

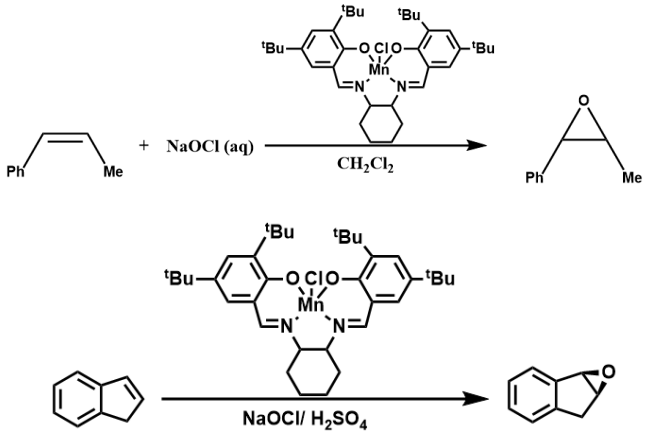
2.1 Oxidation Reactions

Catalytic oxidation processes have made extensive use of transition metal-Schiff base complexes such as Mn(III), Co(III) **(Scheme 1)**, and V(V) [10].



Scheme 1: Co-Schiff base-catalyzed olefin oxidation

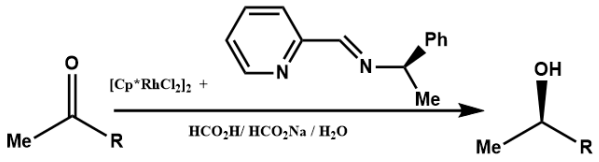
For instance, in olefin epoxidation, Jacobsen's Mn-Schiff base epoxidation catalysts exhibit excellent enantioselectivity [11]. These catalysts function by removing hydrogen from substrates or adding oxygen through high-valent metal-oxo intermediates **(Scheme 2)**.



Scheme 2: Mn-Schiff base-catalyzed epoxidation.

2.2 Reduction Reaction:

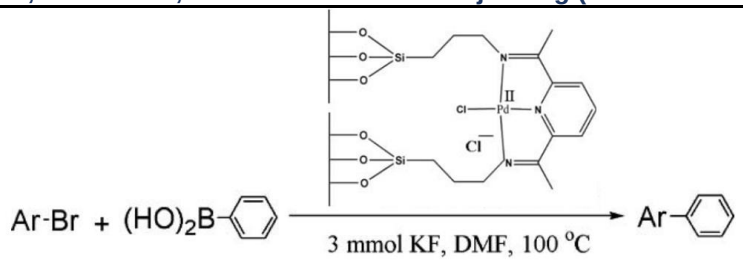
Schiff base complexes of transition metals are efficient catalysts for carrying out the difficult process of asymmetric reduction of dialkyl ketones to alcohols. Himeda et al. have shown that the activity of in situ-synthesised Schiff base complexes based on rhodium in catalyzing these asymmetric reductions is of great significance in the aqueous phase reduction [12].



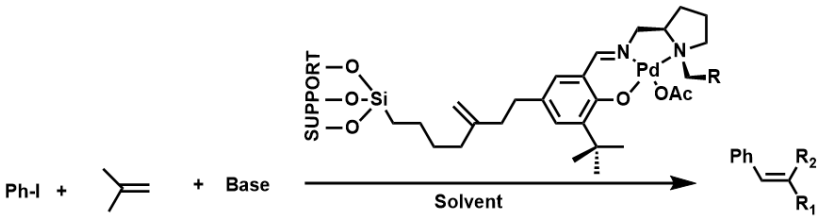
Scheme 3: Reduction of ketones using chiral rhodium complexes of different types of ligand

2.3 C-C Bond Formation and Cross-Coupling Reactions

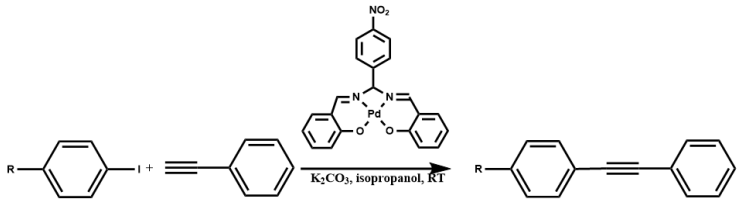
Schiff base complexes of Pd(II) and Ni(II) are effective pre-catalysts in reactions that produce C–C bonds, such as Heck, Sonogashira, and Suzuki-Miyaura couplings [13,14]. The electron-donating or electron-withdrawing groups on the ligands drive the oxidative addition and reductive elimination processes.



Scheme 4: Suzuki–Miyaura cross-coupling reaction of organoboron compounds with organic halides over Pd(II)-catalyst (IV), [13].



Scheme 5: The Heck reaction of aryl halides with olefins



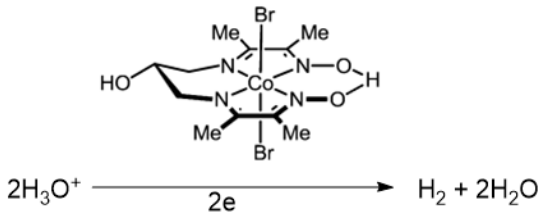
Scheme 6: Pd-Schiff base catalyzed Sonogashira reaction

3. Electrocatalytic Applications

The Schiff base complexes of transition metals capable of existing in variable oxidation states are highly efficient in catalysing electrocatalytic reactions. Because of these stable variable oxidation states, these complexes can participate in different electron transfer processes. Redox-active Schiff base ligands also facilitate electrocatalytic activity. The ability of Schiff base metal complexes to stabilize a variety of metal oxidation states, facile synthesis, and structural diversity have made them significant catlytic systems in electrocatalysis. They are excellent candidates for significant electrochemical processes because of their tunability of electronic and steric environments, which allows for fine control of catalytic activity. Schiff base complexes of transition metals have been particularly successfully assessed in energy-relevant, sustainable processes. Among these, Schiff base-based electrocatalysts have been found to be highly effective in important reactions like the oxygen evolution reaction (OER), carbon dioxide reduction (CO_2RR), and hydrogen evolution reaction (HER).

3.1 Water Splitting

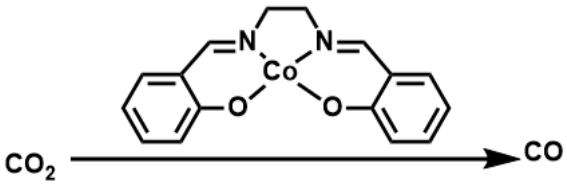
The oxygen evolution process (OER) and hydrogen evolution reaction (HER) can be catalyzed by the Schiff base complexes of Ni, Fe, and Co [15]. Multi-electron processes are facilitated by redox-active ligands, which enhance their activity [16]. For example, Co-Schiff base complexes with electron-rich ligands increase current densities and decrease overpotentials.



Scheme 7: HER reaction catalysed by Co-Schiff base complex

3.2 CO_2 Reduction

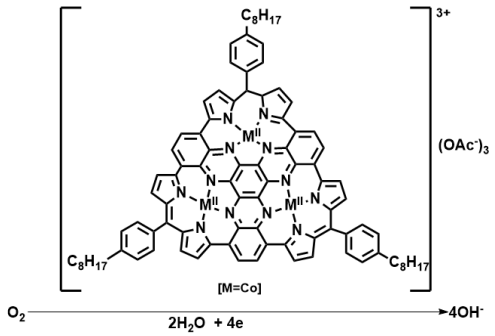
Electrochemical reduction of CO_2 to CO, formate, or methanol is catalyzed by Cu(II), Fe(II), and Mn(I) Schiff base complexes. The electron-rich ligand facilitates proton-coupled electron transport and stabilizes metal-CO_2 adducts mechanistically [17,18].



Scheme 8: Reduction of CO_2 to CO by Co(salen) complex

3.3 Fuel Cell Catalysis

Under alkaline conditions, Schiff base complexes, especially those of Fe and Co, show activity in the oxygen reduction process (ORR). Because of their cost-effectiveness and resistance to poisoning, these catalysts are being studied as platinum alternatives [19].



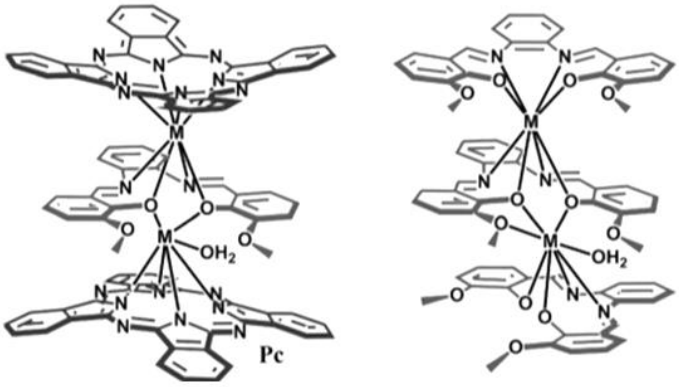
Scheme 9: Oxygen reduction reaction

4. Schiff Base Complexes as Magnetic Materials

Transition metal Schiff base complexes have drawn a lot of attention in molecular magnetism mainly because of the presence of unpaired electrons in these metals, along with the diverse nuclearities and geometries. They are excellent for studying magnetic processes at the molecular level because of their structural flexibility and ligand environment adjustability. Schiff base metal complexes have been extensively studied for their applications in magnetic exchange coupling, spin crossover systems, and single-molecule magnets (SMMs). These properties not only help us understand fundamental magnetic behavior, but they also make it possible to develop molecular materials for spintronics, quantum computing, and information storage. We are surrounded by magnetic materials since magnets are found in almost every electrically powered devices. Magnetic material is, therefore, very significant.

4.1 Single Molecule Magnets (SMMs)

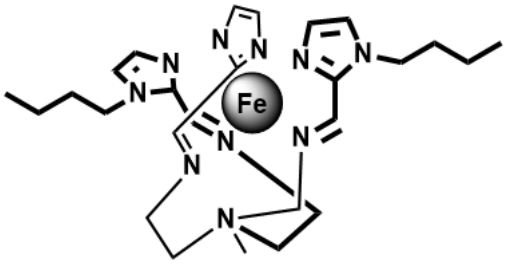
Molecular compounds known as single molecule magnets (SMMs) are created when an intrinsic energy barrier is present. This barrier allows the molecules to retain their magnetic moment even after the external magnetic field is removed. Significant magnetic anisotropy and spin-orbit coupling are the causes of the slow magnetic relaxation observed in lanthanide-Schiff base complexes (such as Dy(III) and Tb(III)) [20]. Their ligand field and coordination geometry contribute to the blocking temperatures and energy barriers.



Scheme 10: SMM containing Schiff base complex (M = Dy, Gd)

4.2 Spin Crossover Complexes

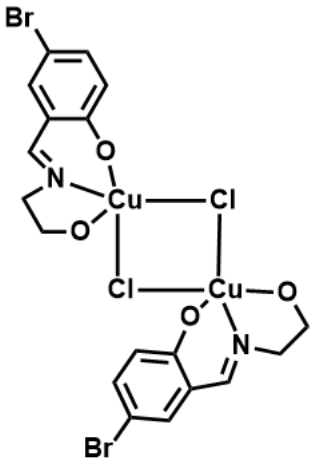
Spin crossover between low-spin and high-spin forms is generated thermally or optically in Fe(II) complexes containing N4 or N2O2 Schiff base donors [21]. Molecular switches and memory units both make use of this phenomena.



Scheme 11: Spin crossover in Fe-Schiff base complex

4.3 Magnetic Exchange Coupling

Depending on the metal-ligand-metal angles and bridging modes, dinuclear and polyuclear Schiff base complexes show either ferromagnetic or antiferromagnetic exchange [22]. These species are ideal for studying as catalysts in different reactions, magnetic communication, and exchange mechanisms.



Scheme 12: Ferromagnetic exchange coupling in bis(l-chloro)-bridged copper(II) Schiff base complex:

5. Conclusion

Schiff base complexes continue to be a cornerstone of coordination chemistry, with a growing number of applications. Their structural diversity and tunable properties allow them to be used in a variety of catalytic, electrocatalytic, and magnetic materials. Their full potential is still being unlocked by ongoing advancements in ligand design, synthesis, and computational modeling.

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