COMPLEXES OF SCHIFF BASES WITH PENDANT AZAOXA-CROWN ETHER; SYNTHESIS AND SOME NOTEWORTHY RESULTS

Abstract

Considering the importance and extensive applications in numerous domains, fascination with the preparation of Schiff Bases having pendant azaoxa-Crown ether as well as related compounds has surged in recent times. Aza-oxa crown ether macrocycles have exciting potential to create supramolecular assemblies that are suitable for carrying out highly specific atomic functions.To change the ion binding potential, sensitivity, and specificity of the original aza-oxa crown ethers, ligands with an additional donor atom in the side chain were synthesized in a systematic manner by researchers around the globe. There are numerous applications for Schiff bases with attached azaoxa-crown ethers in catalytic processes. Coordination chemists are intrigued by Aza-oxa crown ethers having pendant Schiff bases because they behave as an ambis-dentate chelating framework. Through the Schiff base component, it can coordinate with transition metal ions of intermediary hardness (Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+} etc.), but the crown ether part complexes with alkali/ alkaline earth metal ions (Li^+, K^+, Na^+, Ba^{2+} etc.). Preparation of these modified crown ethers and their metal complexation primarily with transition metals, were thoroughly discussed in this chapter, with a focus upon their catalytic capabilities. Three key catalytic characteristics were addressed. These types of compounds nearly always have higher catalytic activity than the comparable regular Schiff base compounds, thus emphasizes their significance.

Keywords: Schiff base, macrocycles, Noteworthy complexes

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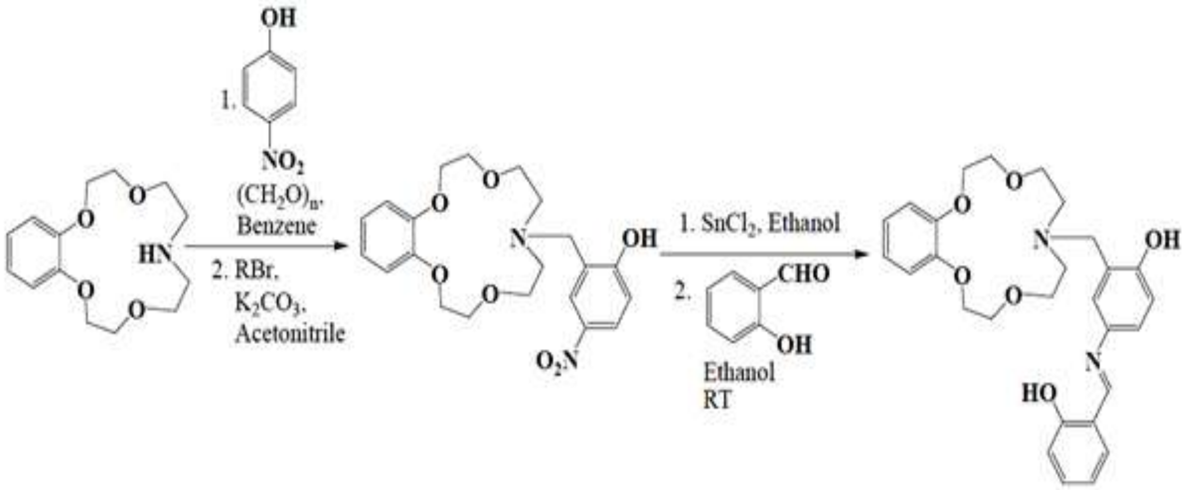
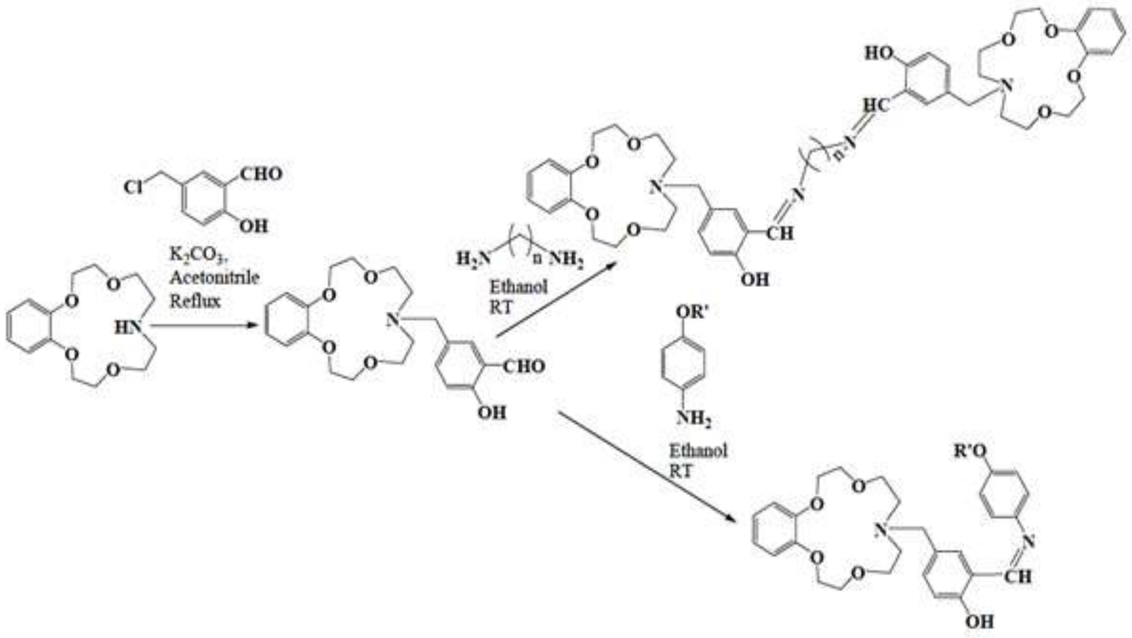
I. INTRODUCTION

Since the accidental discovery of crown ethers by Pedersen[1], supramolecular chemistry has grown by leaps and bounds, as their host-guest chemistry has been utilized in several practical applications[2]. Due to the importance and wide range of applications of complexes of Schiff bases with pendant azaoxa-crown ethers in diverse fields, demand of their synthesis has grown in recent years. Azaoxa-crown ether ligands with an additional donor atoms in their side chain framework are primarily synthesized to modify initial molecule' ion binding potential, sensitivity, and selectivity. Schiff bases along with crown ethers in one single backbone, provides the possibility of binding alkali/alkaline earth metal and transition metal ions together.In the disciplines of analytical chemistry[3], coordination chemistry[4], liquid crystalsand photochromism[5],catalytic chemistry[6], Schiff bases and their metal complexes have found extensive use. Transition metal complexes of Salicylaldimine Schiff bases have attracted a lot of attention recently for their potential applications as enzyme catalysis mimics[7] as well as oxygen carriers[8].

II. SYNTHESIS OF LIGANDS [SCHIFF BASES WITH PENDANT AZAOXA-CROWN ETHER]

A number of azaoxa-crown ether-containing mono- and di-Schiff bases [Scheme 1] were produced in order to study the impact of an azaoxa-crown ether ring with a unique stereo configuration and function on a number of significant characteristics, including the capacity for chelation with metal ions and bio-inspired efficiency[9].

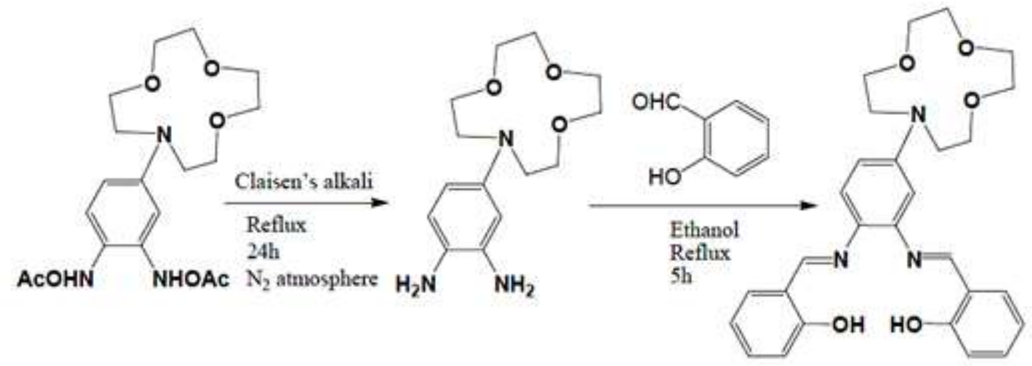




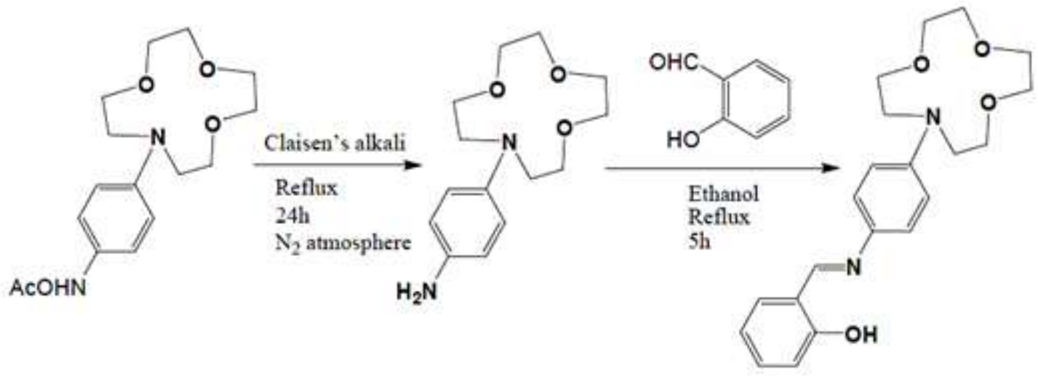
Scheme 1

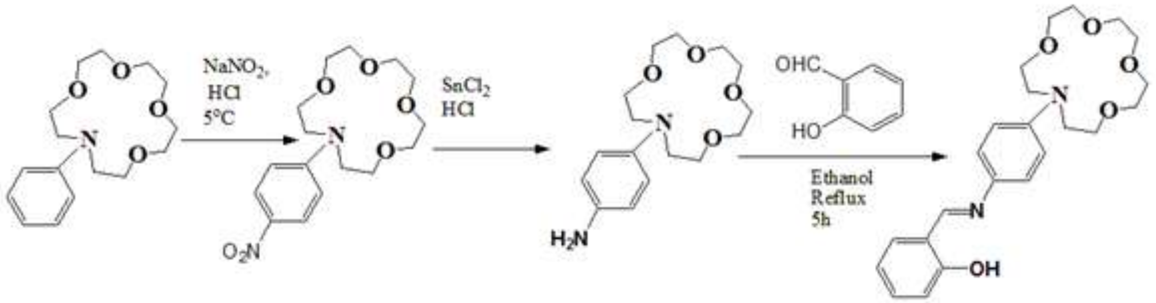
Lu et al. reported on the synthesis and investigation of numerous azaoxa-crown [12-crown-4/15-crown-5]-containing mono-/di-schiff base ligands[10] [Scheme 2]. They synthesized a series of Co(II) complexes with these ligands. Cation chelating properties and steadiness constants of these complexes were studied.

L_A



L_B

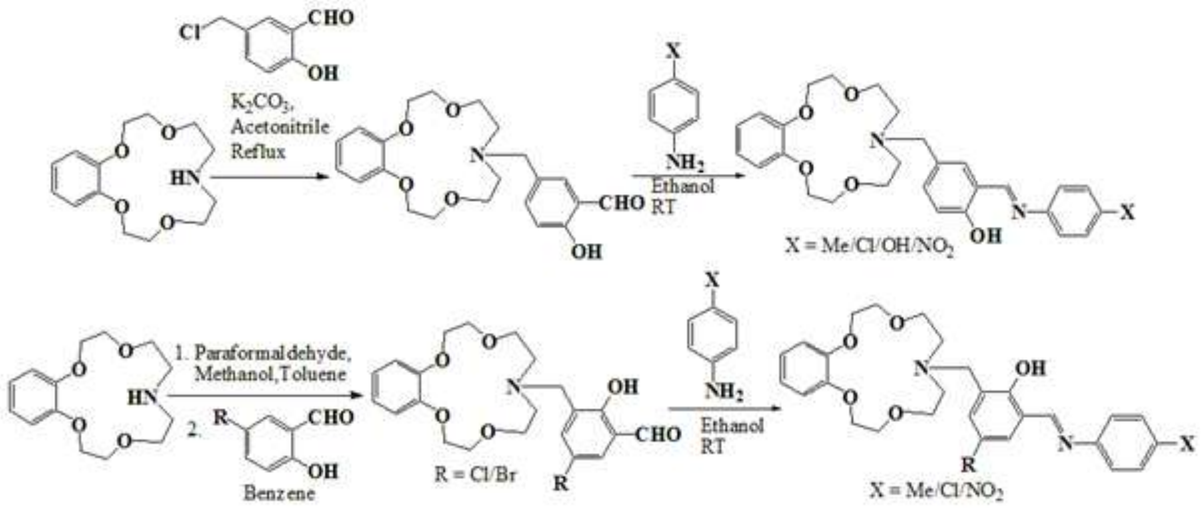




L_C

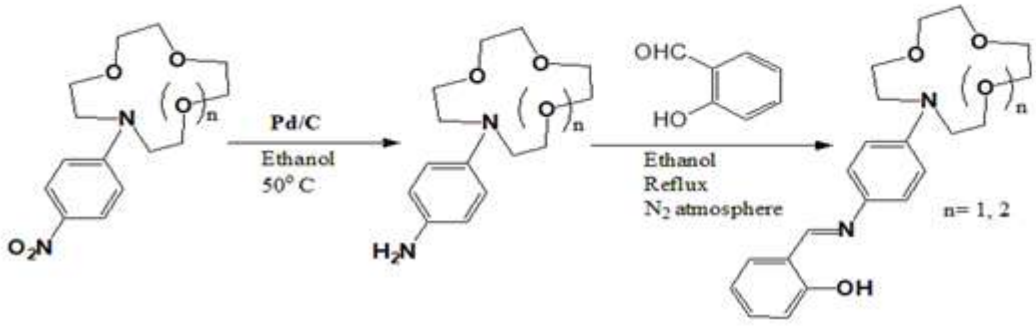
Scheme 2

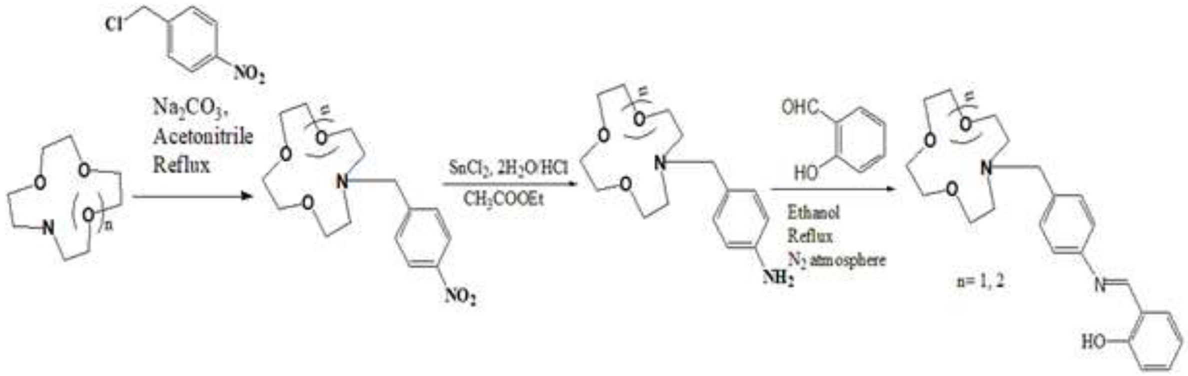
Series of uniqueazaoxa crowned salicylaldimine mono-Schiff bases[11][Scheme 3] were developed in order to examine the influence of the connected azaoxa crown ether ring's unique stereo configuration and activity on a number of significant characteristics, including their capacity to complex with metal ions and their bio-inspired catalytic efficiency.



Scheme 3

In the similar line, mono azaoxoappendedwith 12-crown-4 and 15-crown-5 moieties[Scheme 4] were synthesized by Zenget. al.[12]. Their Co(II) complexes have enhanced capacity to form dioxygen adducts with O_2, compared to uncrowned Schiff base complexes. In addition, better biomimetic catalytic activity too was seen for such complexes.

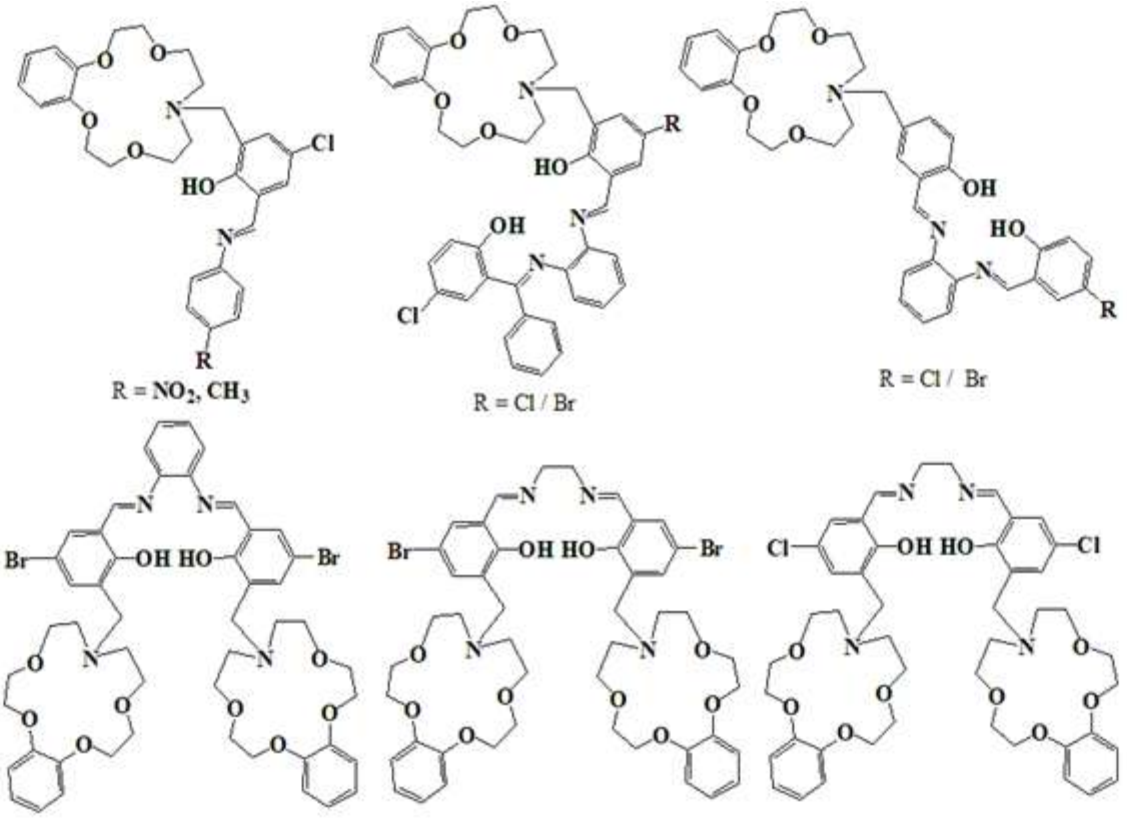


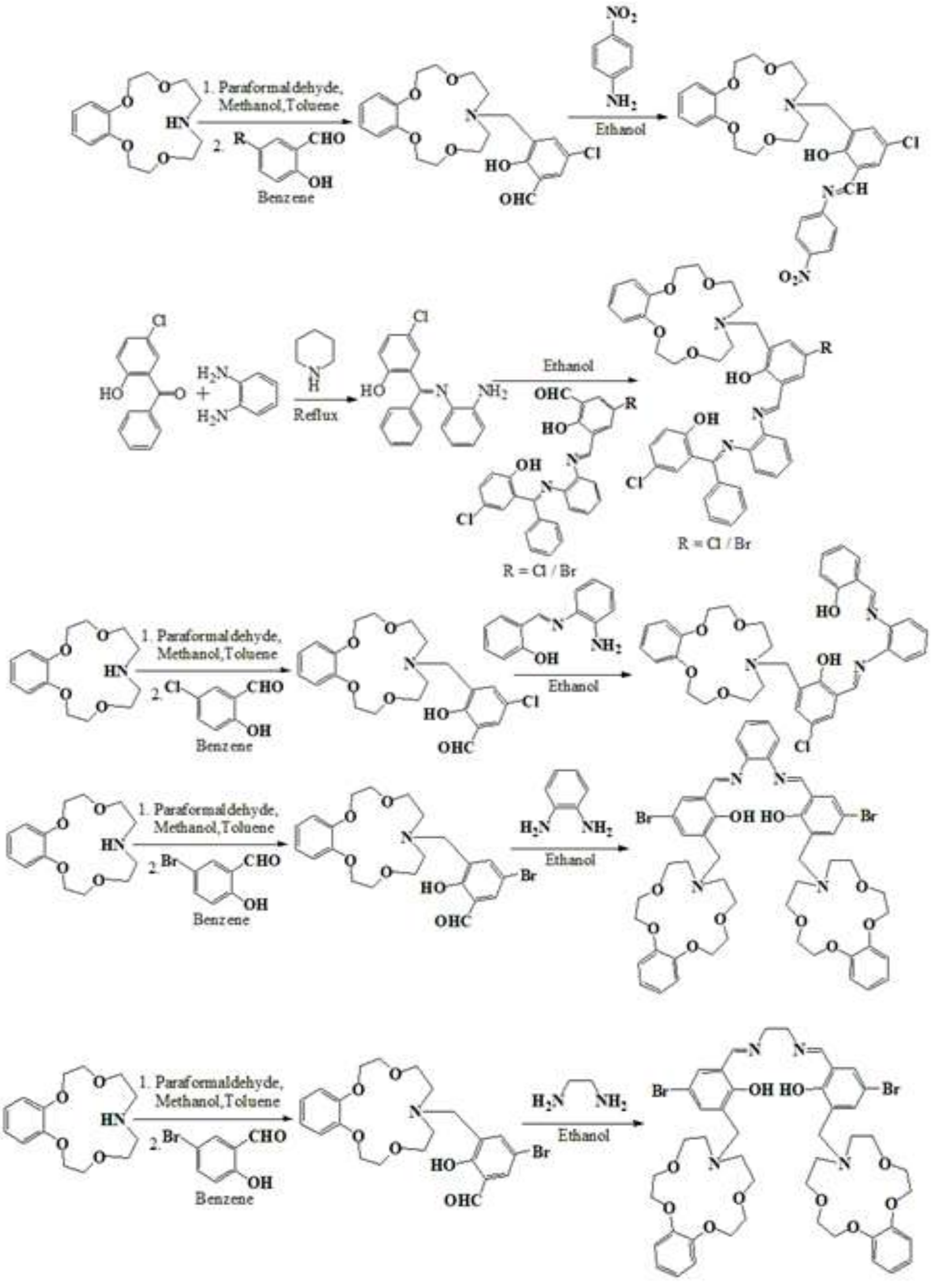


Scheme 4

More such works showing similar properties in the same field were reported by wei et. al.[13]. Data comparisons were also reported. Similar synthetic methodologies were employed for their synthesis as shown previously.

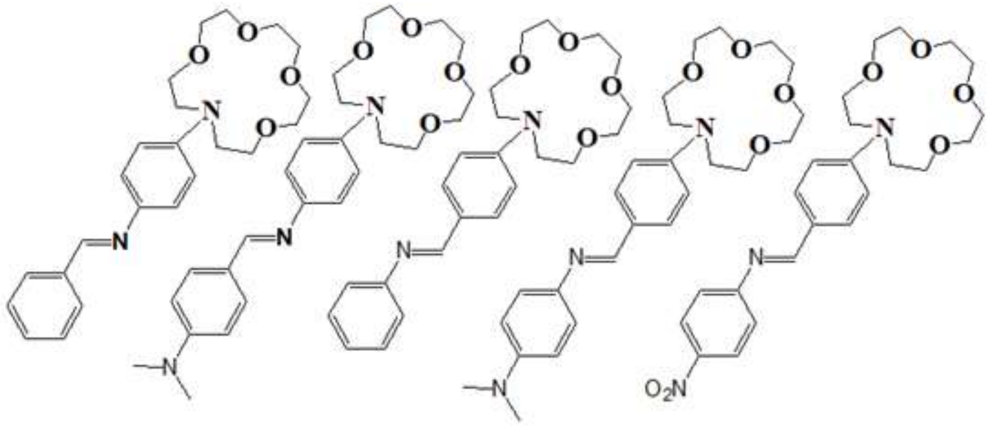
There have been studies on the chemical kinetics and mechanism of the hydrolysis of PNPP [p-nitrophenylpicolinate] catalysed using mono-Schiff base metal complexes containing benzo-azaoxa-crown ether pendants. These are used as hydrolase enzyme models. Scheme 5 displays the related ligand systems and their synthetic methodologies[14].





Scheme 5

UV-Vis spectroscopy is used to investigate the complex formation of a number of novel Schiff bases with the N-phenylaza-15-crown-5 structure with Group I and Group II metal ions (mainly Beryllium and Magnesium ions). The position of the N-phenylaza-15-crown-5 group in the ligand framework and the nature of the cation, are taken into consideration in order to estimate and analyse the associated stabilization constants. Related ligands[15] are depicted in Scheme 6.



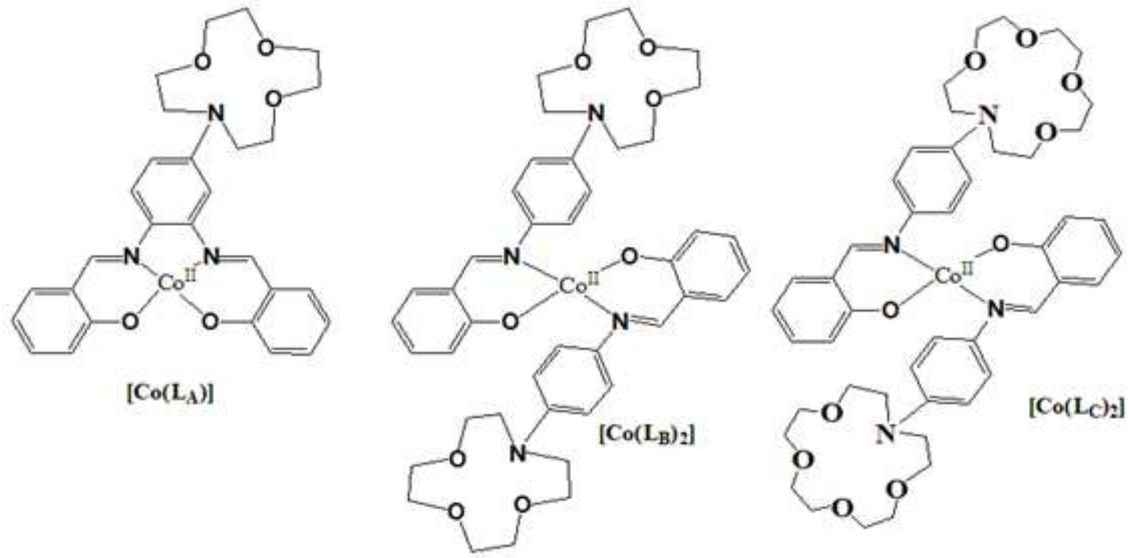
Scheme 6

Several other similar types of ligands are reported in literature. In the next section, some noteworthy metal complexes of these types of ligands will be discussed.

III. NOTEWORTHY COMPLEXES OF SCHIFF BASES WITH PENDANT AZAOXA-CROWN ETHER LIGANDS

Co^{II} complexes containing azaoxa-crown ether-basedsalicylaldimine Schiff base ligands were effectively synthesised as [Co(L$_A$)], [Co(L$_B$)$_2$], and [Co(L$_C$)$_2$][10]. L$_A$, L$_B$ and L$_C$ are depicted earlier in scheme 2. The complexes' cation-binding characteristics were investigated, and stability constants for Group I and Group II metal ions have been established. Meaningful correlation of the cation-binding characteristics between both the mono- and bis-Schiff base frameworks, and also with the molecule containing the monoaza-15-crown-5 pendant, ([Co(L$_C$)$_2$]), that has a dissimilar crown size, is made possible by the synthesising of the compounds of monoaza-12-crown-4, ([Co(L$_A$)] and [Co(L$_B$)$_2$]. Complex structures and their synthetic routes are shown in Scheme 7.

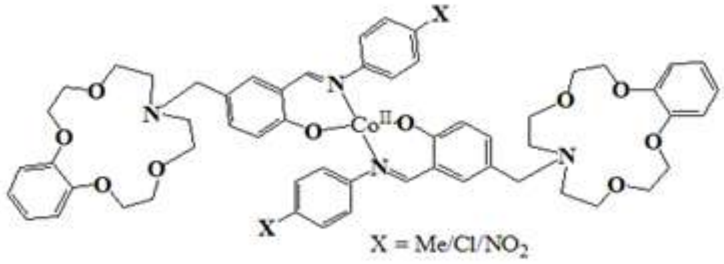
In 1,2-dimethoxyethane solution, oxygenation constants (K$_{O2}$) Co^{II} complexes, [Scheme 8] with azaoxa-crown pendants were evaluated over the range of temperature of -5^o-25^{o}C. According on these K$_{O2}$ values, ΔH_0 and ΔS_0 for oxygenation were derived. With regard to the regulation of O$_2$-binding capacities, the impacts of various substituent groups on the Schiff base ligand were investigated. The findings show that azaoxa-crown pendants significantly improve the dioxygenaffinities of Co^{II} complexes more than their comparable morpholino pendants do, and that sodium ion can also improve the azaoxa-crown pendant complexes' ability to bind oxygen.



Scheme 7

In order to catalyse the hydrolysis of p-nitrophenylpicolinate (PNPP), many mono-/bis-schiff base ligands with attached azaoxa crown-ether and their metal complexes [Co^{II} and Mn^{III}] were developed[14]. The kinetics and mechanism of the catalytic hydrolysis in buffer solution were also studied. Fe of such complexes and their synthetic routes are shown below [Scheme 9]. Synthesis of complexes are generally done by refluxing $Co(OAc)_2.4H_2O$ or $MnCl_2.4H_2O$ with corresponding ligand in ethanol in refluxing condition under nitrogen atmosphere.A hypothesized kinetic paradigm for the p-nitrophenylpicolinate breakdown is mediated by such complexes. On the kinetics of p-nitrophenylpicolinate hydrolysis, the impact of complex system and solution temperature has been studied. With pH, the rate rises.Mechanistic detail of hydrolysis is shown in scheme 10.

A



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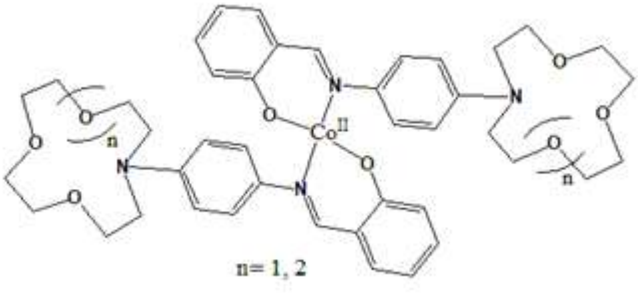
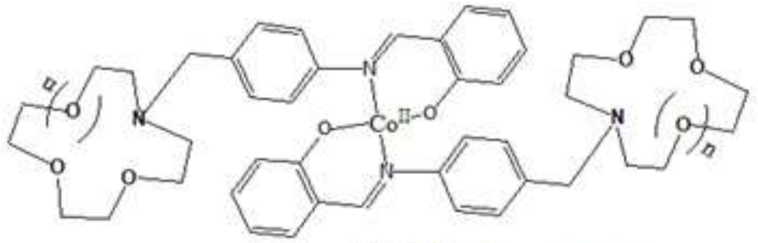


C

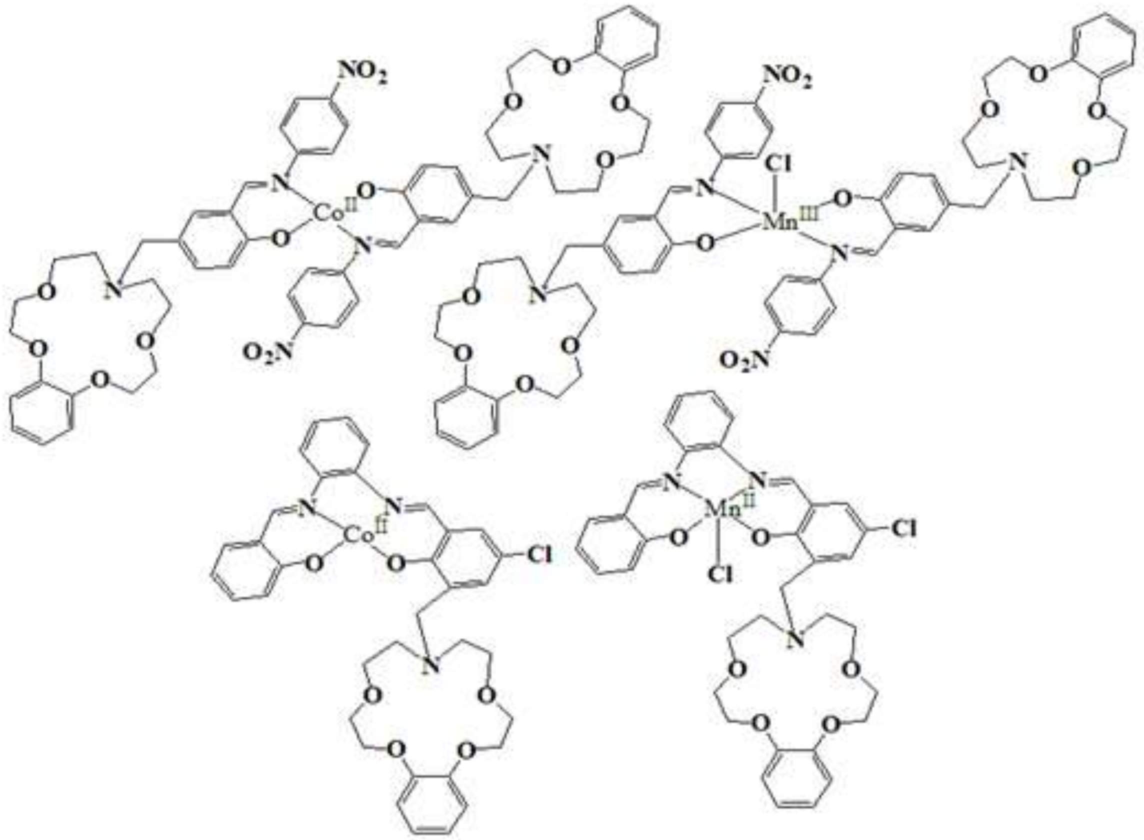


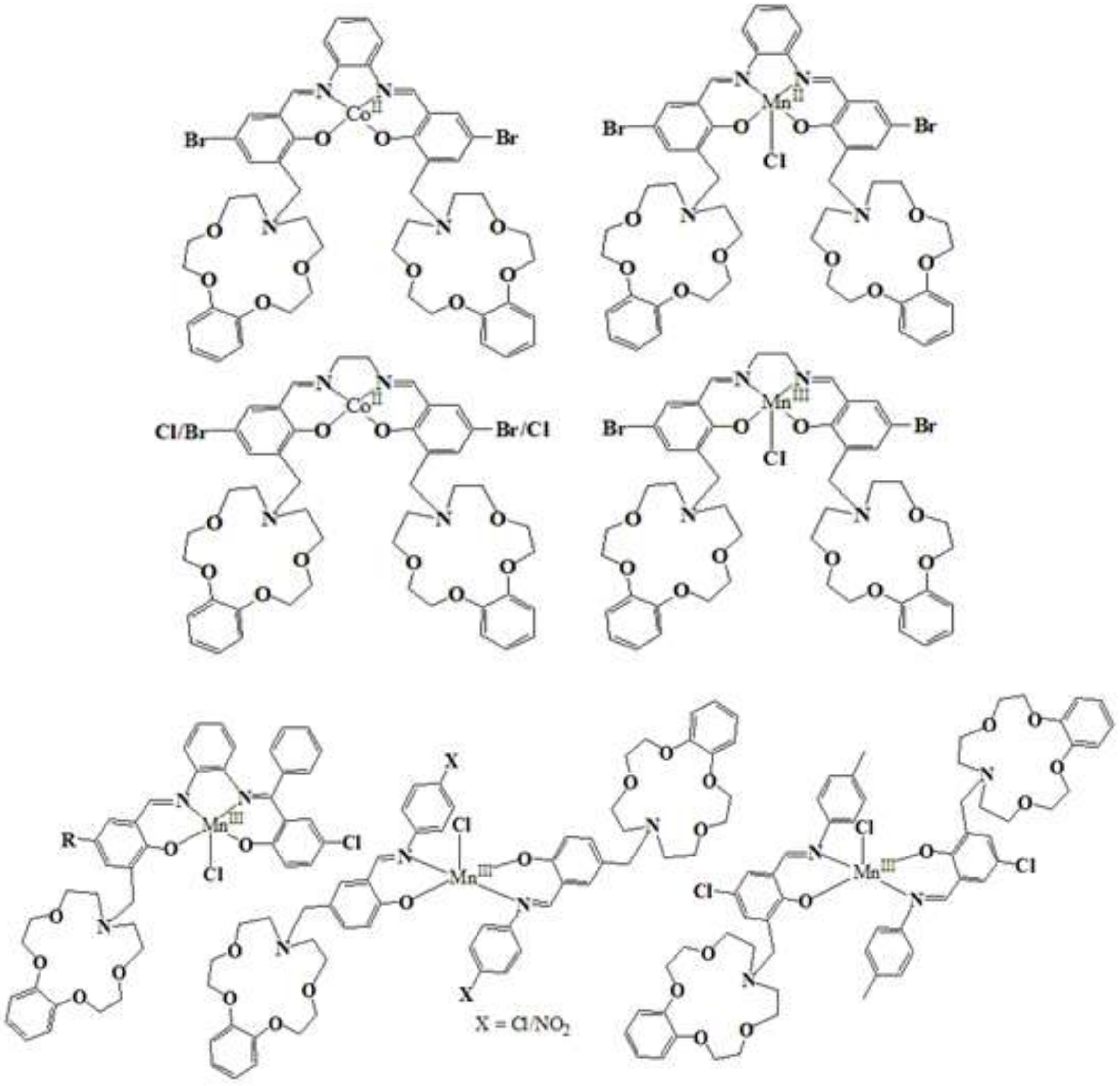
$$Co(OAc)_2.4H_2O + 2\ L \xrightarrow{\text{Ethanol, Reflux}} [Co(L)_2]$$

Scheme 8

$$Co(OAc)_2.4H_2O + 2\ L \xrightarrow[\text{N}_2\text{ Atmosphere}]{\text{Ethanol, Reflux}} [Co(L)_2]$$

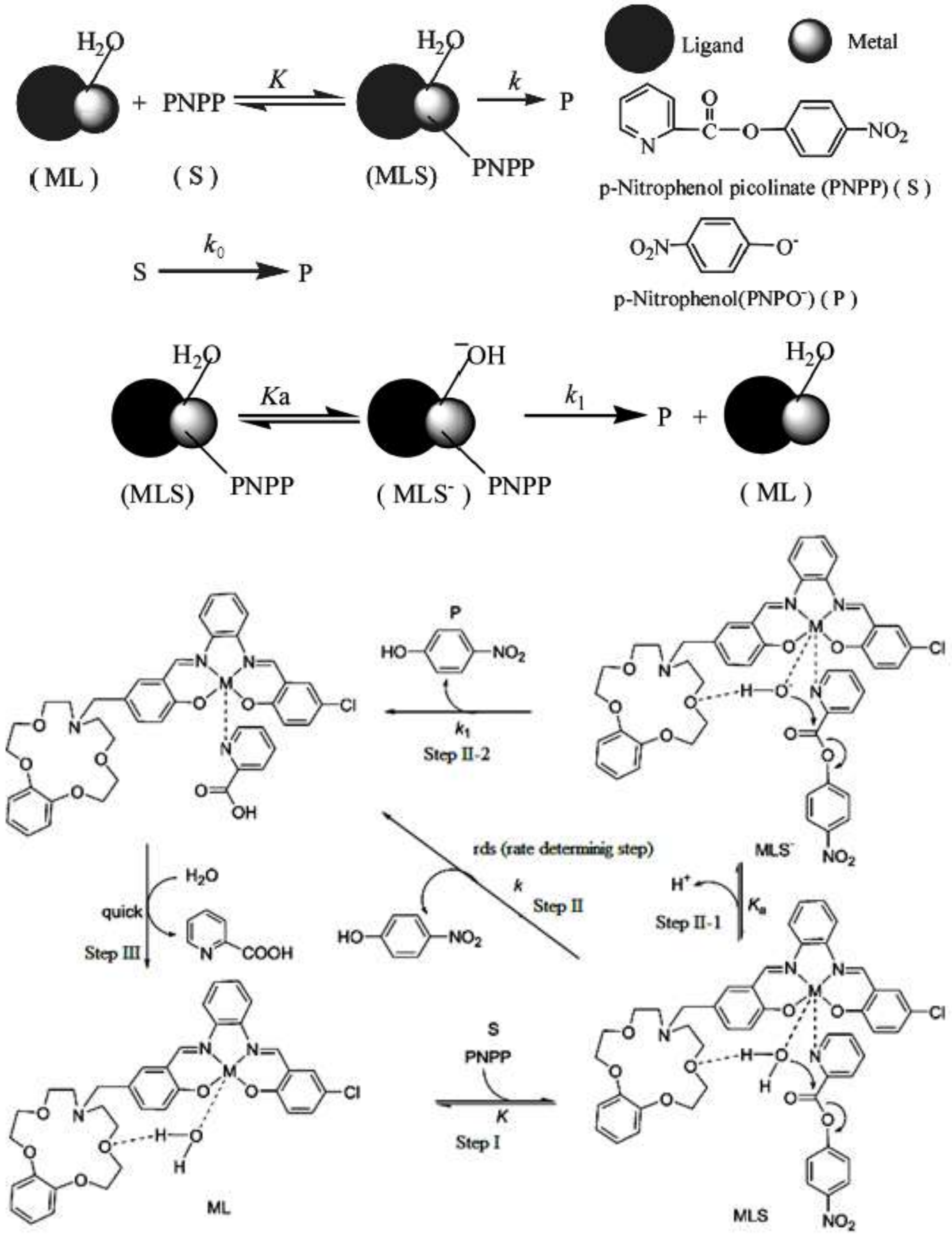
$$MnCl_2.4H_2O + 2\ L \xrightarrow[\text{N}_2\text{ Atmosphere}]{\text{Ethanol, Reflux}} [Mn(L)_2Cl]$$





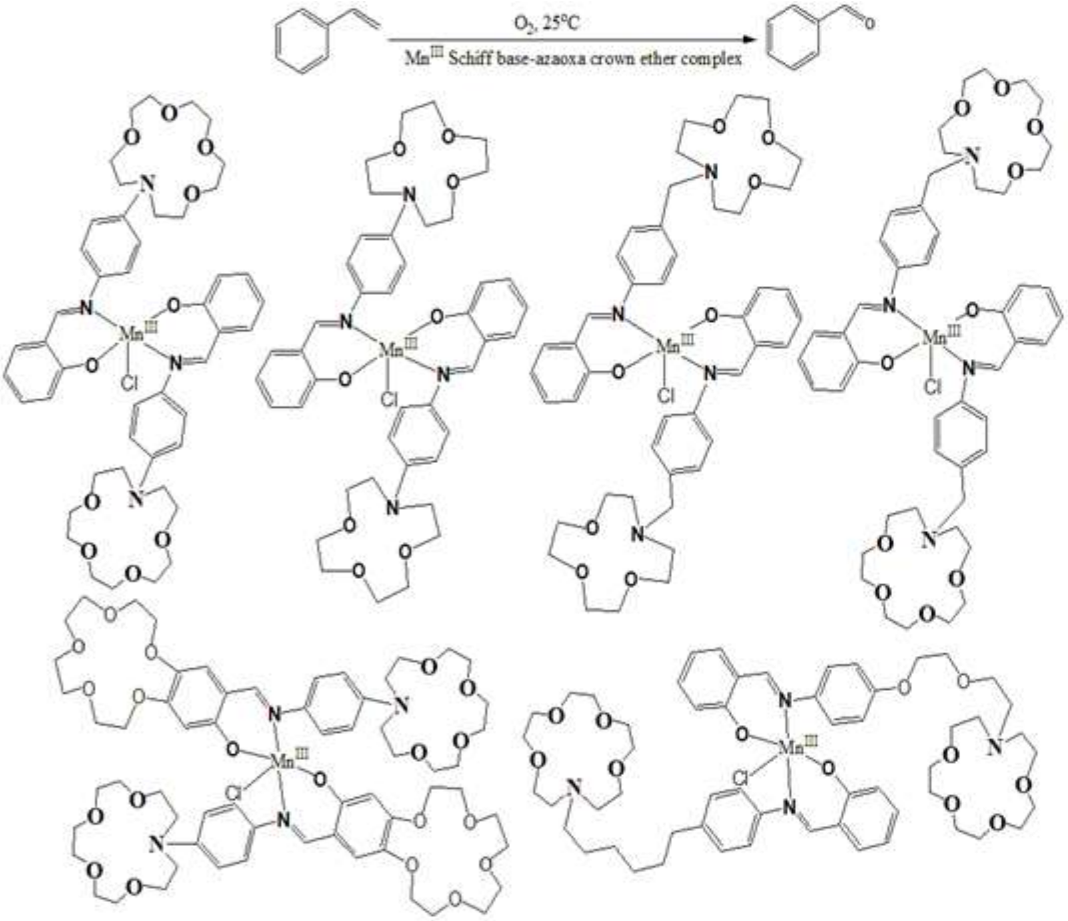
Scheme 9

All the above complexes show similar mechanistic pathway for hydrolysis of PNPP. The proposed mechanism is shown in Scheme 10 for catalytic hydrolysis of PNPP by one of Schiff-base complexes having attached azaoxa crown ether in buffer solution.The formation of the hydrated complex happens when H_2O is linked to the complex's metal ion.This hydrated complex might serve as the catalytic hydrolysis of PNPP's actual active species.The metal ion and crown ring work together to activate H_2O, resulting in the formation of the intramolecular hydrated complex (ML).The intermediary MLS is then produced by PNPP coordinating to this complex (Step I).The coordinated hydroxide then targets the PNPP carbonyl group with a first-order rate constant (k) in Step II, which is the rds (rate determining step) of the entire process.Eventually, H_2O quickly rebinds, releasing the coordinated picolinic acid from the metal (Step III).When the pseudo-first-order rate constant for the catalytic hydrolysis of PNPP is relatively independent of concentration of substrate, free hydroxyl ion (OH^-) may operate as a nucleophile.Hence, the hydrated complex (MLS^-) may represent the actual active species for the catalytic hydrolysis of PNPP if the pseudo-first-order rate constants for PNPP hydrolysis rise linearly with substrate concentration at any pH.



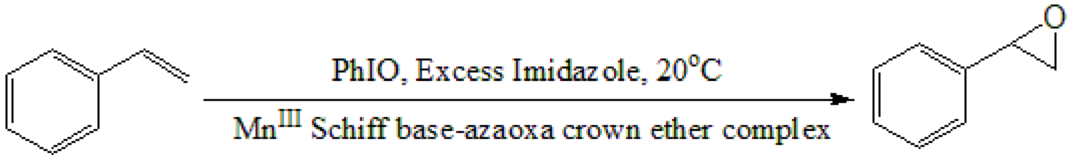
Scheme 10

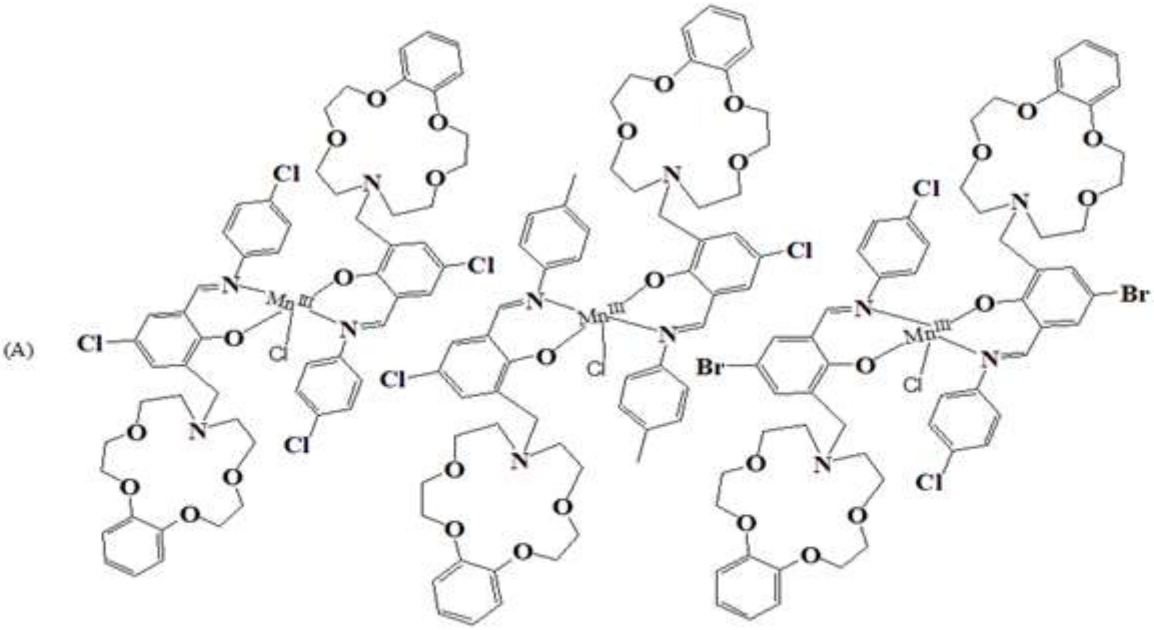
Different metal complexes of Schiff bases with pendant azooxa crown ether moiety are found to exhibit catalytic activity. Mainly, three types of catalysis reactions are reported; (1) oxidation of styrene to benzaldehyde[16], (2) epoxidation of styrene[17] and (3) oxidation of *p*-xylene to *p*-toluic acid[18]. The metal complexes listed in Scheme 11, Scheme 12 and Scheme 13, show catalytic oxidation of styrene to benzaldehyde, epoxidation of styrene and oxidation of *p*-xylene to *p*-toluic acid, respectively. Using Mn^{III} complexes of Scheme 11, styrene can be selectivelyoxidisedintobenzaldehydewith molecular dioxygen at room tempature and normal atmospheric O_2pressure.Alkali metal salt addition can increase conversion and turn over frequency (TOF).



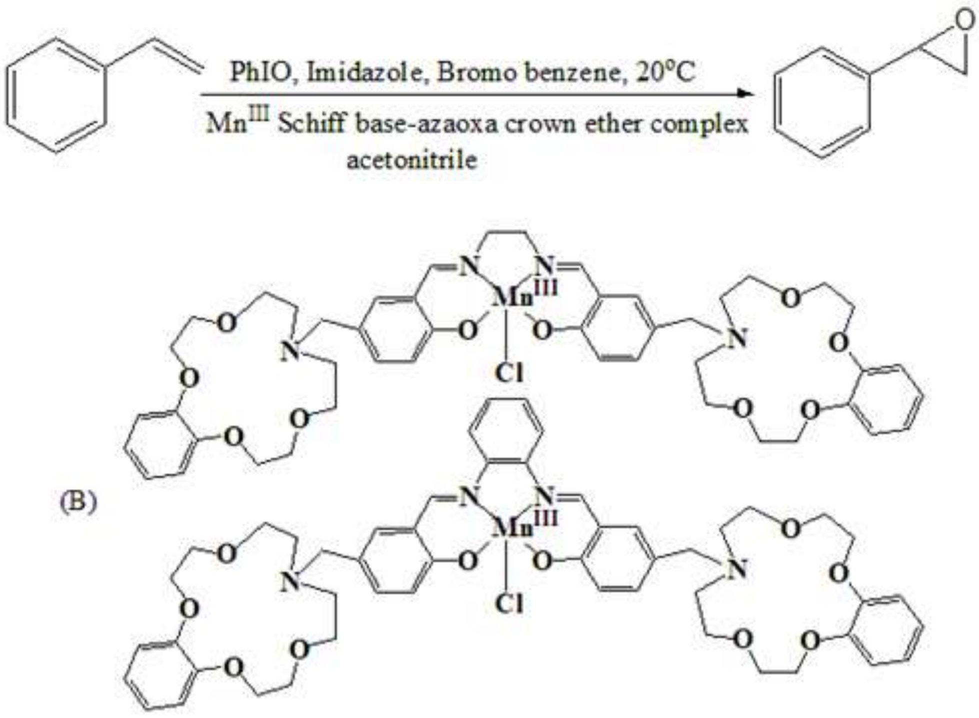
Scheme 11

Using excess imidazole as the axial ligand and iodosylbenzene as the catalyst, Mn^{III} compounds of Scheme 12 were used to catalyse the epoxidation of styrene (serving as analogues for monooxygenases) at standard pressure and 20°C. PhIO serves as the single-oxygen donor and no reaction occurs without PhIO, indicating no aerial oxidation.



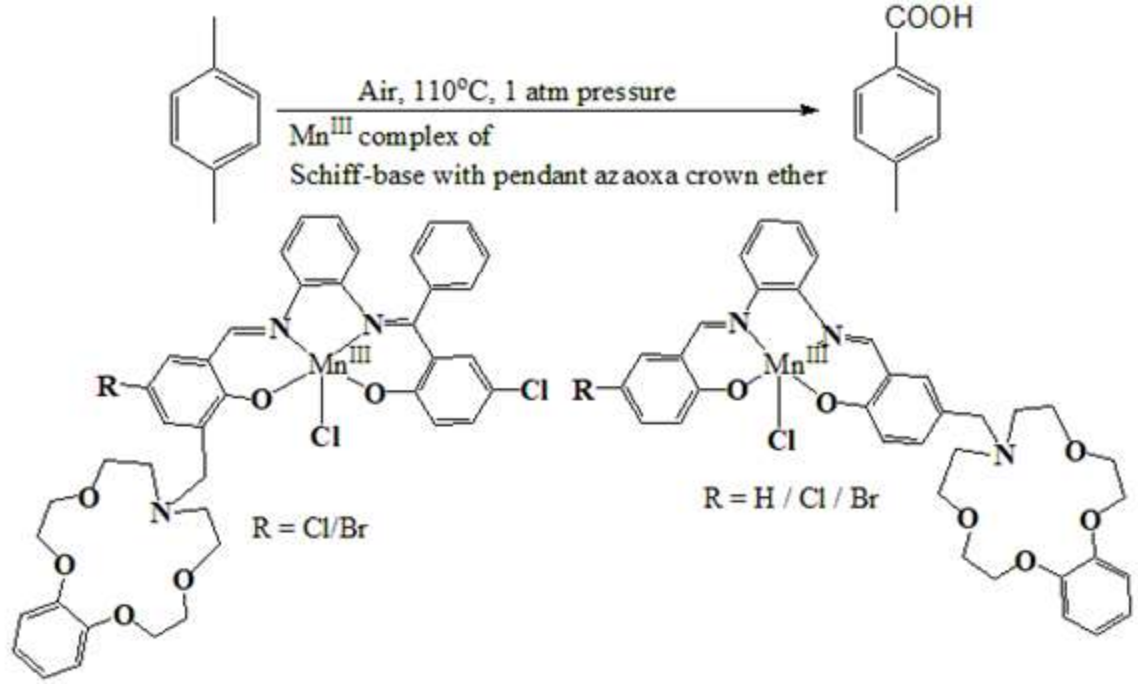


Similar type of epoxidation reaction occurs when acetonitrile solution of styrene, bromobenzene (internal stander), imidazole (axial ligand), PhIO as oxidation donor stirred for one hours in presence of below Mn^{III} Schiff base complexes with pendant azaoxa crown ether as catalyst.



Scheme 12

When mono-Schiff base Mn^{III} complexes with azaoxa-crown ether substitution[A, Scheme 12& Scheme 13] were present, air was effectively used to oxidisep-xylene to p-toluic acid at 120°C and standard air pressure. Significant levels of conversion and selectivity were attained. By comparing the complexes of morpholino pendant analogues with the azaoxa-crown ether pendant ligands, the impact of these compounds on the oxidation of p-xylene was also examined. Alkali metal ions were added to speed up the conversion.



Scheme 13

IV. CONCLUSION

Schiff base with pendant azaoxa-crown ethers have found variety of importance in catalysis. In this chapter, their synthesis and metal complexation with transition metals mainly, were described extensively, along with emphasis on catalytic properties. Three major catalytic properties were discussed. In almost all cases, these type of complexes got greater catalytic activity than corresponding normal Schiff base complexes, which indicates their importance.

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