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Manganese Schiff Base Complexes and their Biological Catalytic Applications

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ABSTRACT

Schiff bases are the compounds formed by the reaction between amines and carbonyl compounds. They are them self very important compounds of biological significances. They are also known due to their properties to form complexes with transitions metals. Manganese Schiff Base complexes are one of the important complexes having several catalytic activities. They work as catalysts in several organic reactions like transformation reactions, oxidation reaction, hydroxylation, epoxide formations etc. Also, they have significant applications in the field of biological chemistry. This short review selectively deals discussion on recent works on synthesis of manganese Schiff base complexes and their biological applications.

Keywords: *Manganese, Schiff base, Biological application, Catalysts, Transition metals*

INTRODUCTION

Schiff bases are the compounds result of the condensation of amines and carbonyl compounds. Actually, they can be prepared by the reaction of amine compounds (R-NH_2) with carbonyl compounds very easily with the release of water molecule to form either ketimines (obtained from the reaction of ketone and amine) or aldimines (obtained by the reaction of aldehyde and amines). These compounds are being extensively used as ligands for the synthesis of several types of metal complexes. Thus, they are promising ligands for coordination chemistry [1]. These complexes show strong catalytic applications like oxidation, epoxidation, hydroxylation and several biological applications [2].

Manganese is a transition metal which has tendency to form varieties of complexes with different types of ligands. They can form mixed ligand complexes [3], porphyrin complexes [4-8], Schiff base complexes [2] etc. Such complexes of manganese are significant from the point of view of their application as catalysts in organic syntheses, biological applications and pharmaceutical chemistry [2-6, 8-20].

Out of many types of complexes of manganese, it's Schiff base complexes and their biological activities and applications have a significant place [2, 13-21].This review article briefly deals the discussion on only recent manganese Schiff base complexes and their biological significances.

SCHIFF BASE COMPLEXES OF MANGANESE AND THEIR BIOLOGICAL APPLICATIONS

Researches on manganese Schiff base complexes are being conducted in majority by the researchers worldwide. This is only due to their broad synthetic as well as biological significances. Synthesis of important manganese Schiff base complexes and their biological applications have been discussed in the present short review dealing the research works of recent year 2019 and some of year 2020 (**Table1**).

Shaheen *et. al.* (2019) [13] synthesized the Schiff base complexes of different types of transition metals like copper, cobalt, manganese and zinc in the form Cu(II), Co(II), **Mn (II)**, and Zn(II). Schiff base used as ligand was derived from the condensation reaction between 5-aminosalicylic acid with *o*-vanillin. Solvent used for this Schiff base ligand synthesis was methanol. Schiff base used as ligand was named as (*Z*)-2-hydroxy-5-[(2-hydroxy-3-methoxy benzylidene) amino] benzoic acid. They used the methanolic solution of Schiff base ligand with $MnCl_2.4H_20$ and stirred for a fixed time. They obtained dark purple precipitate of the manganese complex. They further performed the antimicrobial activities for their synthesized complexes against *Escherichia coli, Pseudomonas aersginosa, Staphylococcus aureus, Shigellaflexneri, Protious vulgaris* and *Bacillus subtilus*. They used clarithromycin as standard drug for their experiments. They tested antimicrobial activities of their synthesized complexes at 100 ppm and 200 ppm concentrations of the complexes and found positive results for them [13]. A Schiff base was synthesized by Vinusha *et. al.* (2019) [14] using compounds like 5-amino-4H-1,2,4-triazole-3-thiol and 3-hydroxy-4-methoxybenzaldehyde and used as a ligand for the synthesis of transition metal complexes of Cu(II), Co(II), **Mn(II)**, Zn(II) and Ni(II). During Schiff base synthesis, they used equimolar amounts of 5-amino-4H-1,2,4-triazole-3-thiol and 3-hydroxy-4-methoxy benzaldehyde in ethanol for 6 hours at 60-70^0 C and obtained yellow precipitate of the ligand. They obtained the metal complexes by the reaction of ethanolic solution of metal chlorides with ethanolic solution of Schiff base ligand. Precipitates of metal

Table1. *Schiff base complexes and their biological applications*

S.N.	Metal Schiff Base Complexes	Schiff base ligand	Biological applications /studies (if any)	Ref
1	Cu(II), Co(II), **Mn(II)**, and Zn(II)	Derived from 5-aminosalicylic acid with *o*-vanillin	Antibacterial	13
2	Cu(II), Co(II), **Mn(II)**, Zn(II) and Ni(II) complexes	Schiff base derived from5-amino-4H-1,2,4-triazole-3-thiol and 3-hydroxy-4-methoxy benzaldehyde	Antibacetrial activity, antioxidant activity, inhibitory effect	14
3	**Mn (II)**, **(III) and (IV)**	Derived from diphenylamine-2,2′-dicarboxaldehyde and either diethylenetriamine or dipropylenetriamine	-	15
4	**Mn(II),** Co(II), Ni(II), and Cu(II)	Pyrimidinyl ligand, 2-(4,6-dimethylpyrimidin-2-ylamino)naphthalene-1,4-dione	Antibacerial, antifungal, DPPH radical scavenging studies	16
5	Cu (II), Zn (II), Co (II), Ni (II), **Mn (II)**, V (II) and *Au*(IIII)	Schiff base of salicyldehyde and 2, 4-dinitrophenylhydrazine	Antimicrobial, antioxidant and cytotoxic properties	17
6	Complexes of Cu and **Mn**	Chiral Schiff Base	Cytotoxicity and DNA/BSA intercation	18
7	**Mn(III)**	Salen	-	19
8	**Mn(III)**	Salen	Oxidation	20

Complexes were obtained. They used the synthesized complexes for biological testing as antibacterial activity against gram-positive as well as gram-negative bacteria. They used gram-negative bacteria namely, *Bacillus cereus, Micrococcus luteus, Staphylococcus aureus* while gram-positive bacteria namely, *Klebsiella pneumonia, Enterobacteraerogenes, Escherichia coli, Pseudomonas fluorescens, Pseudomonas aeruginosa* and *Salmonella enteritidis* for the antibacterial studies. They used amoxicillin as standard drug for this study. Their results were positive for many of thebacteria. Mn(II) complexes were able to inhibit bacteria as shown by their zone inhibition (mm) results and showed positive results for gram-positive bacteria like *Micrococcus luteus* and *Staphylococcus aureus* and for gram-negative bacteria like *Klebsiella pneumonia, Enterobacteraerogenes* and *Pseudomonas aeruginosa*. They also performed studies on antioxidant activity. They performed free radical scavenging activity using DPPH, ABTS and superoxides. Almost all complexes showed positive results for radical scavenging activities at different levels for each metal complexes. Antioxidant activity order for metal complexes and ligand was in order of Zn> Ni> Cu>Mn>Co>ligand. They also performed study on inhibitory effects on alpha-amylase and yeast alpha-glucosidase. Inhibition order for the metal and ligand was Zn>Ni>Cu>Mn>Co>ligand [14].

Wilson *et. al.* (2019) [15] synthesized three complexes of manganese having macrocyles of Schiff base out of which two were monomeric complexes as Mn(II) and Mn(III) and one was dimeric complex as Mn(IV). Schiff bases were differed in ring size with 14 membered ring*versus* 16 membered ring. Schiff bases were synthesized by the process of condensation of diphenylamine-2,2′-dicarboxaldehyde with either diethylenetriamine or dipropylenetriamine [15].

Festus *et. al.* (2019) [16] synthesized a series of transition metal complexes of Mn(II), Co(II), Ni(II), and Cu(II) using Schiff base ligand 2-(4,6-dimethylpyrimidin-2-ylamino)naphthalene-1,4-dione. This pyrimidinyl ligand was synthesized by using condensation process of 2-hydroxy-1,4-naphthoquinone and 2-amino-4,6-dimethylpyrimidine in methanol and refluxed for three hours. After cooling they got brown precipitate of the ligand. Now, this Schiff base ligand was used for the synthesis of aforementioned mixed metal (II) complexes with 2,2'-bipyridine using divalent metal acetate at 50–60°C. They used these complexes for the further studies of antibacterial, antifungal and radical scavenging properties. They used bacteria like *B. cereus, S. aureus, K. oxytoca, E. coli, P. mirabilis*, and *P. aeruginosa* microbes for antibacterial studies for Schiff base ligand as well as all synthesized complexes. They used a standard bactericide like 1-cyclopropyl-6-floro-1,4-dihydrido-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid (ciprofloxacin) for antibacterial studies. They further studied the *in vitro* antifungal properties for all synthesized complexes against *A. niger, A. flevus*, and *R. Stolonifer* using standard drug like diflucan. They found the better antimicrobial results for complexes. They also found the good results for radical scavenging ability [16].

Husaain *et. al.*(2019) [17] have synthesized metal complexes of Schiff base. Schiff base was derived from salicyldehyde and 2, 4-dinitrophenylhydrazine and this Schiff base was used for the synthesis of novel metal complexes of Cu (II), Zn (II), Co (II), Ni (II), **Mn (II)**, V (II) and Au (IIII). They used the complexes in the study of antibacterial, antifungal and antioxidant properties. For the study of antibacterial properties of the complexes, total four bacteria were used out of which two were gram-positive bacteria like *B. subtilis* and *S. aureus* while two of them are gram-negative bacteria like *E. coli* and *S. typhi*. They found better results for all the complexes in comparison to Schiff base ligand. They used four fungal sources for their study of antifungal properties of the complexes using fungal species like *C. albicans, R. stolonifer, T. viride* and *A. nigar*. They used potato dextrose agar as medium. They incubated the fungi for 48 hrs at 37°C. They performed studies on antifungal properties at two different concentrations. They used fluconazole as standard antifungal drug. Their antioxidant study was based on DPPH radical scavenging activity. Overall, their synthesized complexes showed good antimicrobial activities, antioxidant properties as well as cytotoxic activities [17].

Chang *et. al.*(2019) [18] synthesized the complexes of manganese and copper using chiral Schiff base. They synthesized the complexes having general formula [Mn(ONO-(S)L^1)$_2$], [Cu(ONO-(R)L^2)]$_4$·2CH_3OH and [Mn_3 (ONO-(S)L^3)$_4$(OAc)$_4$(H_2O)$_2$], where ligands used were H_2L^1 = (*S*)-2-phenyl-2-(2-hydroxy-5-chlorobenzylideneamino)ethane-1-ol, H_2L^2 = (*R*)-2-(2-hydroxy-5-chlorobenzylideneamino) butane-1-ol and H_2L^3 = (*S*)-2-phenyl-2-(2-hydroxy-3-methoxy benzylideneamino) ethane-1-ol, respectively. They studied the influence of these synthesized complexes in cytotoxicity and found that these complexes have higher cytotoxicity against HepG2, MDA-MB-231, and A549, three types of cancer cell lines than *cis*-platin [18].

Zhang *et. al.*(2020) [19] synthesized two new manganese (III) Schiff base complexes bridged by O–Se–O. Thegeneral formula of complexes were [Mn_2(salen)$_2$(L)](ClO_4) and {[Mn (salen)]$_2$(L)$_2$}·Y where salen was *N,N′*-bis (salicy lidene)-ethylenediamine while L used was 3,4,5-trifluoro benzeneseleninic acid, Y wassalicy laldehyde [19].

Neshat*et. al.* (2020) [20] synthesized salen based Schiff base complexes of manganese (III). Names of the salen ligands used during the synthesis were N,N'-bis (salicylidene)2,3-diaminopyridine, N,N'-bis (3-methoxy salicy lidene) 2,3-diaminopyridine, N,N'-bis (3,5-di-*tert*-butylsalicylidene)2,3- diaminopyridine and N,N'-bis (3,5-di-chloro-salicylidene) 2,3-diaminopyridine. These complexes have also been used for testing in catalytic application like oxidation of alcohols (primary as well as secondary). They optimized the reaction conditions and used various oxidants like O_2, H_2O_2 or *tert*-butyl hydroperoxide for the reaction. Additives used were as acetic acid and imidazole [20].

CONCLUSIONS

Above discussion demonstrates that manganese Schiff base complexes may be highly valuable for biological as well as several synthetic catalytic applications. This short review paper concisely deals the synthesis of new manganese Schiff base complexes and their biocatalytic application. They may be advantageous in field of pharmaceutical industries due to their biological functions as good antibacterial as well as antifungal agents.

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