

Versatile Catalytic Applications of Manganese(II,III) Schiff Base Complexes (Review)

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Abstract—Manganese forms a big number of complexes with Schiff bases that are extensively used as catalysts of oxidation, epoxidation, decarboxylation, coupling reactions, decomposition, urease inhibitory, catalase activity, anticancer activity, antibacterial activity, and many more. To the best of our knowledge, though some catalytic applications of such complexes are reported but hardly as independent reviews. The presented below review deals with various catalytic applications of novel Schiff base Mn(II,III) complexes.

Keywords: Mn(II,III) complexes, Schiff bases, catalysis, biomimetic catalyst, stereo-selective oxidation, epoxidation, decomposition, antifungal activity, anticancer activity

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INTRODUCTION

Schiff bases, also known as imines or azomethines, can be obtained by reactions of a primary amine with an aldehyde or ketone under specific conditions. These are nitrogen containing compounds in which the C=O group is replaced by the C=N bond [1]. Complexes of multidentate ligands with transition metals have attracted close attention as those ions can exist in variable oxidation states and exhibit wide range of applications in biological, clinical, analytical, and pharmacological fields [2–4]. Azomethine nitrogen and other donor atoms play a vital role in coordination chemistry of Schiff bases [5], that are also known as biomimetic catalysts [6–10]. Coordination chemistry of manganese has been studied extensively due to occurrence of its complexes in the active sites of many enzymes [11, 12]. In addition, they act as catalysts in many important reactions whenever manganese forms complex with different ligands [13–18]. In the current review only manganese-Schiff base complexes that found catalytic applications are presented. Such complexes are categorized in accordance with their specific activities and brought together in the table.

Oxidation reactions catalyzed by Schiff base complexes of Mn(II,III). Among various catalytic

applications of Mn-Schiff base complexes that have been determined over recent years, one of the most important is catalysis of oxidation reactions.

Saikia et al. [19] functionalized the Mn(salen)Cl complexes grafted on SBA-15 molecular sieves with propylamine, propylthiol and propylsulphonic acid groups. Support and the type of organo-functional groups influenced upon the oxidation state, redox behavior and chemoselectivity of the Mn-complexes were studied in the oxidation reaction of limonene. The extent of Mn-ions +3 to +2 reduction on different supports decreased in the order SBA-15-pr-SH > SBA-15-pr-SO₃H > SBA-15-pr-NH₂. The 100% chemo- and regio-selective process for 1,2-limonene epoxide was catalyzed by Mn(salen)Cl supported on propylthiol-functionalized SBA-15. According to the authors, the reason behind the efficient selective catalytic activity was probably high electron density at the site of manganese ions and the consequent lower redox potential of manganese-complexes upon immobilization. The catalytic activity could be enhanced by solvents, additives and co-reagents (*iso*-butyraldehyde) that facilitated formation of Mn²⁺ ions. Some of Mn-complexes leached out of the solid phase in the course of the reactions, and the extent of this decreased in the

Catalytic applications of different types of manganese complexes

Complexes of manganese	Catalytic applications	References
Mn(salen)Cl supported on propylthiol-functionalized SBA-15	Formation of 1,2-limonene epoxide	[19]
Mn(III) Schiff base complex	Oxidative coupling of aromatic thiols into corresponding disulfides. Synthesis of symmetrical disulfides	[20]
Mn(III) Schiff base complex	Oxidative decarboxylation of arylacetic acids to corresponding aldehydes or ketones	[21]
Phenol based Schiff base complex of Mn(II)	Oxidation of benzyl alcohol and styrene	[22]
Salophen complexes of Mn(III)	Efficient oxidation of hydrocarbon	[23]
Mn(III) tridentate Schiff base complex	Oxidation of olefins and sulphides	[24]
Octahydra-schiff base complexes of transition metal encapsulated in nanopores of zeolite-Y; [M([H]8-N4O4)]@NaY	Oxidation of cyclohexane	[25]
Mn(III) complexes with four dentate N2O2 Schiff base ligand	Decarboxylation of carboxylic acids	[26]
Chiral dimeric Mn-complex	Asymmetric oxidation of sulphides	[27]
Mn(II) ion complexes	Oxidation of 2,6-di- <i>tert</i> -butyl diphenquinone	[28]
4-Hydroxy salophen; [(OH) ₂ -salophen], complex of manganese grafted on the walls of MWNTs	Aerobic oxidation of para-xylene in the absence of added halogen promoter	[29]
Mn(II) complexes of azo-linked Schiff base	Oxidation of cyclohexene	[30]
Water soluble manganese-salen complex	Chemo-selective oxidation of thioanisole	[31]
Mn(II) Schiff base complexes	Oxidation of benzoin to the corresponding benzil	[32]
Mn(II) and Co(II) complexes of carbazoles containing Schiff bases	Oxidation of styrene and cyclohexene	[33]
Mn(III) Schiff base complex	Oxidation of benzyl alcohol	[34]
Mixed ligand dinuclear Mn(II,II) complexes	Microwave assisted oxidation of alcohols	[35]
Mononuclear Mn(II) complexes	Oxidation of <i>o</i> -aminophenol	[36]
Schiff base metal complexes of Mn(II) and Co(II)	Oxidation of cyclohexane and benzyl alcohol	[37]
Homogeneous and heterogeneous catalysts of Manganese	Cyclohexane oxidation	[38]
Mn, Cu and Ni complexes with pyridine carboxaldehyde derived Schiff bases	Oxidation reaction of cyclohexene and styrene	[39]
Novel Schiff base complex of Mn(III) covalently immobilized as support on silica coated magnetic cobalt nanoparticles	Oxidation of alcohols and sulphides to corresponding aldehydes and sulfoxides	[40]
Mn(III) chiral Schiff base complexes supported on MCM-41	Enantio-selective oxidation of 2-naphthol to <i>R</i> - and <i>S</i> -BINOL(1,1'-bi-2-naphthol)	[41]
Mn(III) salophen acetate, [Mn(salophen)OAc], supported on hydroxyapatite coated magnetic nanoparticle, Hap-Fe ₂ O ₃	Oxidation of alcohols	[42]
Mn-Schiff base complex supported on magnetic nanoparticles	Oxidation of alcohol to aldehyde	[43]

Table (Contd.)

Complexes of manganese	Catalytic applications	References
Chromium and manganese Schiff base complexes immobilized on modified nanoporous MCM-41	Catalytic oxidation of sulphides to sulphoxides	[44]
Manganese and cobalt Schiff base complexes immobilized on cobalt magnetite nanoparticles	Oxidation of sulphides	[45]
Hydrazone Schiff base Mn(II) complexes	Highly selective epoxidation of cyclohexene	[46]
Mn-based materials	Enantio-selective heterogeneous catalysts in epoxidation of α -methylstyrene	[47]
Non-heme Mn(II) complex	Epoxidation of olefins	[48]
Mn(III) and Mo(IV)-salen complexes immobilized on a silica surface	Catalytic epoxidation of olefines (cyclooctene and cyclohexene)	[49]
Mn(salen)Cl containing <i>tert</i> -pentyl at the 3,5 position of the salen ligand	Epoxidation and hydroxylation	[50]
Mn(III) complexes obtained with H ₂ salen derivatives	Effective catalysts in epoxidation reactions of <i>E</i> - and <i>Z</i> -stilbene isomers	[51]
Acetylacetonate-based Schiff bases/Mn(II) homogeneous system [Mn(II)/LA and Mn(II)/LB systems]	Catalytic alkene epoxidation	[52]
SiO ₂ -immobilized Mn(II) complexes	Heterogeneous catalyst for alkene epoxidation	[53]
Mn(II) three mononuclear complexes with two N ₂ O coordination spheres	Epoxidation of <i>E</i> -stilbene and styrene	[54]
Manganese Schiff base complexes immobilized on inorganic support	Epoxidation of cyclo and linear alkenes	[55]
[Mn(III)-L-SBA-15]	Oxidation of bulky alkenes like 1,2-dihydronaphthalene	[56]
Mn(III)-salen complex	Efficient catalyst in <i>E</i> -stilbene and styrene epoxidation	[57]
Heterogeneous Mn(III) salen complex	Asymmetric epoxidation of unfunctionalized olefins	[58]
Pyridine Schiff base-Mn(II) complexes	Epoxidation of cyclohexene	[59]
Mesoporous propylthiol group-functionalized silica supported Mn(III) salen complexes	Epoxidation of styrene	[60]
Mn-salen based hybrid catalysts	Effective, selective and re-usable catalyst in epoxidation of alkenes including styrene, cyclohexene and 1-phenyl cyclohexene	[61]
Schiff base complexes of manganese	Epoxidation of styrene	[62]
Heterogeneous Mn(II)-catalysts	Epoxidation of alkene	[63]
Tridentate Schiff based Mn(III) and Fe(III) complexes	Epoxidation of olefins	[64]
Mn(II) salophen supported on a nanosilica triazine dendrimer	Efficient catalyst in epoxidation of different cyclic and linear alkenes	[65]
Encapsulated SALEN- and SALHD- Mn(III) complexes in an Al-pillared clay	Active catalysis in cyclohexene epoxidation; addition of sodium bicarbonate as co-catalyst led to enhanced conversion (100%) and selectivity (70%)	[66]

Table (Contd.)

Complexes of manganese	Catalytic applications	References
Mn(II) and oxovanadium VO(IV) complexes	Catalytic oxidation of alkene in the presence of hydrogen peroxide	[67]
Mn(III) complexes	Epoxidation of styrene	[68]
Mn(II) complexes	Epoxidation of olefins	[69]
Manganese-Schiff base complexes	Peroxidase and catalase activities	[70]
Mononuclear Mn(III)-complex of salen and salpn	Catecholase like activity	[71]
Dinuclear [Mn(III) ₂ (μ -1,3-OAc) ₂ L ₂]	Efficient catalyst for oxidation of 3,5-di- <i>tert</i> -butylcatechol to its quinone	[72]
Novel Mn(salen) complexes	Antioxidant therapy	[73]
Mononuclear Mn(III)-complex of Schiff base	Catecholase activity	[74]
Mononuclear Mn(III) complexes	Catecholase activity in oxidation of 3,5-di- <i>tert</i> -butyl catechol	[75]
Manganese salts in combination with several Schiff base ligands	Autoxidation and oligomerization of ethyl linoleate	[76]
Transition metal Schiff base complexes of Mn(II)	Potent inhibitors against jack bean urease	[77]
Thiocyanato-coordinated Mn(III) complexes	Urease inhibitory activity	[78]
Mn(III) Schiff base complexes of a salen type ligand	Considerable anticancer activity against the studied cell lines	[79]
Crowned Schiff base Mn(III) complexes	Metal promoted hydrolysis of bis(<i>p</i> -nitrophenyl) phosphate	[80]
Mn(III) Schiff base complexes	Water photolysis	[81]
Manganese Schiff base complexes	Photodegradation	[82]
Mn(III) Schiff base complexes	Conversion of veratryl alcohol to veratraldehyde	[83]
Dimanganese tetrakis-Schiff base complex [Mn(II) ₂ L] ²⁺	Catalytic water oxidation	[84]
Schiff base mononuclear manganese complex [Mn(Habph) ₂]	Corrosion inhibition	[85]
Mn(II) Schiff base complexes immobilized on nano-silica as catalysts	Ozone decomposition	[86]
Schiff based Mn(II), Cu(II) and Co(II) complexes	Decomposition of hydrogen peroxide	[87]
Mn(II) Schiff base complex	Quantitative analysis of dopamine in the presence of ascorbic acid and uric acid	[88]
2,4-Dihydroxyacetophenone based Co(II), Cu(II), Mn(II), and Ni(II) complexes	DNA cleavage	[89]
Mn(II) Schiff base complex	Photoactive material due to its specific fluorescence properties	[90]
Schiff base complexes of Mn(II)	Catecholase-like and phenoxazinone synthase-like catalytic activity	[91]
Mn(II) Schiff base complex	Antibacterial activity	[92]

Table (Contd.)

Complexes of manganese	Catalytic applications	References
Novel nanostructured Schiff base complex	Cyclocondensation–Knoevenagel condensation–Michael reaction of phenylhydrazine with ethyl acetoacetate and various aromatic aldehydes	[93]
Acetylacetone and leucine derived Schiff base complex of Mn(II)	Antifungal activity	[94]
Metal-Schiff base complexes	Antifungal activity	[95]
Mn(III) Schiff base dicyanamide complexes	Peroxidase activity	[96]
Cu(II) and Mn(II) quinoline Schiff base complexes	Antibacterial and antifungal activity	[97]
Schiff base complexes of Fe(II), Mn(II), Zn(II), and Ru(II)	Antioxidant properties	[98]
Divalent Schiff base metal complexes of metals Mn, Co, Ni, and Zn	Antibacterial and antifungal activity and good antioxidant properties	[99]
Schiff base complex of Mn(III)	Strong DPPH (2,2-diphenyl-1-picrylhydrazyl) radical-scavenging activity	[100]

order: SBA-15-pr-NH₂-Mn(salen)Cl > SBA-15-pr-SO₃H-Mn(salen)Cl > SBA-15-pr-SH-Mn(salen)Cl [19].

Golchoubian and Hosseinpoor [20] used Mn(III) Schiff base complex for the oxidative coupling of aromatic thiols under aerated and mild reaction conditions. Products of the oxidative coupling were the corresponding disulphides. The method was particularly efficient for symmetrical disulphides.

Quadridentate Schiff base ligand bis(2-hydroxybenzene)phthalimide (BHBPDI) and its Mn(III) and Fe(III) complexes were used in oxidative decarboxylation of a variety of arylacetic acids using tetrabutylammonium periodate as an oxidant. The reaction was carried out in DCM at room temperature. Rapid and effective oxidative decarboxylation of arylacetic acids to the corresponding aldehydes or ketones with high yields was achieved in the presence of [Mn(III)(BHBPDI)Cl]–imidazole–(*n*-Bu)₄(NIO₄) [21].

The synthesized complexes of Mn(II) and Co(II) containing Schiff base ligands [22] were used in oxidation of benzyl alcohol and styrene by hydrogen peroxide. Styrene oxidation resulted in very poor yields of products. Benzyl alcohol oxidation under the

action of mononuclear complexes was found to be more efficient than dinuclear complexes.

Bahramian et al. [23] successfully immobilized the salophen complexes of Mn(III) on natural diatomite for the first time, and used these efficiently as catalysts in alkene epoxidation and hydrocarbon hydroxylation under the action of sodium periodate as an oxidant (Fig. 1).

Bagherzadeh et al. [24] designed a simple oxidation system using Mn(III) tridentate Schiff base complex, Mn(N–OPh–Sal)(acac)(EtOH) (N–HOPh–HSal = *N*-hydroxyphenyl-salicylienamine, Hacac = acetylacetone), and urea hydrogen peroxide as terminal oxidant for oxidation of olefins and sulphides. Catalytic studies showed that in short span of reaction, conversion rate was up to 90% for olefins and 96% for sulphides at room temperature. The study supported the accelerating effect of strong π -donor axial ligands such as imidazole on the processes of oxidation [24].

Niasari et al. [25] synthesized the octahydro-Schiff base complex of some transition metals including Mn(II). The complexes were encapsulated in nanopores of zeolite-Y. These host-guest nanocomposite materials have been tested in the catalytic

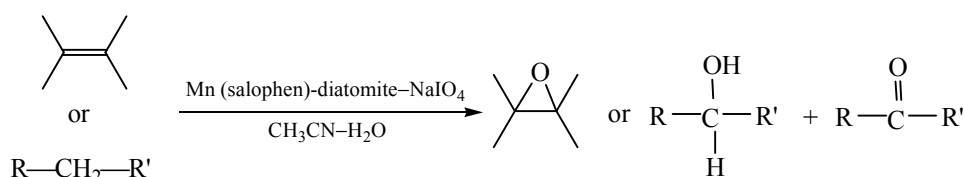


Fig. 1. Epoxidation reaction catalyzed by the salophen complexes of Mn(III) [23].

processes with cyclohexane. The host-guest nanocomposite materials could be recycled and utilized as partial oxidation catalysts. It was observed that catalytic activity of encapsulated catalytic systems $\{M([H]_8-N_4O_4)\}@NaY$; was higher than that of uncapsulated complex, $[M([H]_8-N_4O_4)]$ [25].

Mn(III) Schiff base complex based on N_2O_2 Schiff base ligand of bis(2-hydroxyacetophenone)-1,2-propanediimine was synthesized by Nasr-Esfahani et al. [26], and used in the efficient biomimetic decarboxylation of some carboxylic acids. In those processes tetrabutyl ammonium periodate was used as a mild oxidant in chloroform medium.

Salen-type ligands anchored by 9,9-dimethylxanthene-4,5-diyl spacers were used in synthesis of dimanganese(III) complexes by Hirotsu et al. [27]. The complexes were presented in two types of structures, cyclic and acyclic. The cyclic dimanganese(III) complex was synthesized with a microcyclic ligand obtained by [2+2] Schiff-base condensation of 5,5'-(9,9-dimethylxanthene-4,5-diyl)bis(salicylaldehyde) with 1,2-diaminobenzene. A similar dimanganese(III) complex with stereogenic centers was synthesized by the metal-assisted condensation reaction using (1*R*,2*R*)-1,2-diaminocyclohexane. Metal-assisted stepwise condensation reactions using the xanthene-bridged bis(salicylaldehyde), (1*R*,2*R*)-1,2-diaminocyclohexane monohydrochloride, and salicylaldehydes gave acyclic dimanganese(III) complexes coordinated by one xanthene spacer. Chiral dimeric complexes when used as catalysts in given asymmetric oxidation of sulphides with enantiomeric excess (5 to 19%) upon addition of 4-(dimethylamino)pyridine, led to increased enantiomeric selectivity (39% *ee*). The corresponding mononuclear catalyst did not demonstrate such effect [27].

The Schiff bases with two chlorine atoms grafted on each salicylaldehyde or salicylketone molecules and $-H$, $-CH_3$ or $-CH_2CH_3$ in the azomethinic position were synthesized as ligands, and coordinated with Mn(II) [28]. The complexes were capable to support oxidation of 2,6-di-*tert*-butyl diphenoquinone (THBuDQ).

Niasari et al. [29] managed to anchor covalently the hydroxyl functionalized Mn(III) Schiff base complex $\{Mn[(OH)_2\text{-salophen}]Cl\}$ $[(OH)_2\text{-salophen}] = (N,N'$ -bis(4-hydroxysalicylidene)phenylene-1,2-diamine) on modified multi-wall carbon nanotubes (MWNTs); $[Mn((OH)_2\text{-salophen})Cl]@MWNTs$. For aerobic oxidation of para-xylene, manganese complex with 4-hydroxy salophen, grafted on the walls of MWNTs

was used with *tert*-butylhydroperoxide (TBHP) as the initiator at low temperature. Toluic acid, toluyl aldehyde and toluyl alcohol were obtained as major products. Due to no color change in the course of reaction, the MWNTs-grafted complex could be easily separated and reused many times whereas the neat complex initiated lower conversion and showed color change in the course of the reaction [29].

Lashanizadegan and Zareian [30] studied the catalytic performance of azo-based Schiff base complexes of Mn(II), Cu(II) and Co(II). The complexes were used in oxidation of cyclohexene in the presence of *tert*-butylhydroperoxide. The major products obtained were 2-cyclohexene-1-one and 2-cyclohexene-1-ol [30]. Conversion under the action of Mn(II) complex reached 57% for 2-cyclohexene-1-one.

Allard et al. [31] synthesized the new water soluble manganese salen complex, Mn(III)-*N,N'*-ethylenebis(2-hydroxy benzylimine)-5,5'-dicarboxylic acid (1-Mn), which was used as a catalyst in oxidation of sulphides. 1-Mn acted as a catalyst in chemoselective oxidation of thioanisole by hydrogen peroxide in aqueous medium giving the corresponding sulphoxide with high yield [31].

Safari et al. [32] used *N,N'*-bis(salicylidene)ethylenediaminemanganese (II) in oxidation of benzoin into corresponding benzils in acetonitrile medium at room temperature.

Mn(II) And Co(II) complexes of carbazoles containing two new Schiff bases, (*Z,Z*)-*N,N'*-bis[(9-ethyl-9*H*-carbazole-3-yl)methylenepropane-1,3-diamine (L^1) and (*Z,Z*)-*N,N'*-bis[(9-ethyl-9*H*-carbazole-3-yl)methylene]-2,2-dimethylpropane-1,3-diamine (L^2), were synthesized and characterized by Bal and Bal [33]. The complexes were used in oxidation of styrene and cyclohexene. Oxidation of styrene was characterized by higher selectivity than that of cyclohexene [33].

Kargar [34] synthesized Mn(III) Schiff base complex by the reaction of 6,6'-diethoxy-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilomethylidene)]diphenol with $Mn(OAc)_2 \cdot 4H_2O$. The product was successfully applied as a catalyst in oxidation of benzyl alcohol by (*n*-Bu)₄NIO₄. Substituents on the complex molecules did not affect the oxidation process [34].

Three different hydrazone derived Schiff bases were synthesized by condensation of benzohydrazide, 2-aminobenzohydrazine or 2-hydroxybenzohydrazide with 2,3-dihydroxybenzaldehyde. These were used in

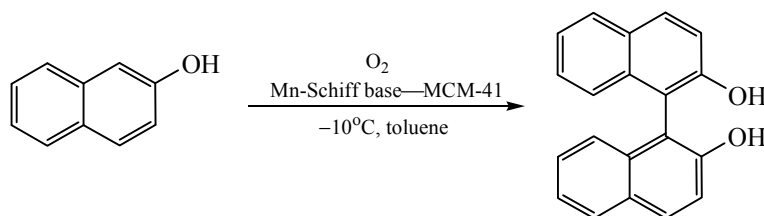


Fig. 2. Simplified enantiomeric oxidation of 2-naphthol catalyzed by Mn(III) chiral Schiff base complexes supported on MCM-41 [41].

synthesis of six new mixed ligand dinuclear Mn(II,III) complexes by Sutradhar et al. [35]. The complexes were tested as catalysts in the microwave assisted oxidation of alcohols.

Anangamohan [36] synthesized two new mononuclear Mn(II) complexes, $[\text{Mn}(\text{L}^1)\text{Cl}_2] \cdot 2\text{MeOH}$ (**1**) and $[\text{Mn}(\text{L}^2)\text{Cl}_2]$ (**2**), where L^1 and L^2 are the tetradentate Schiff base ligands. The complexes were successfully tested in oxidation of *o*-aminophenol. Catalytic efficiency of the complexes depended on the steric contribution of the ligands and electrochemical response of the metal [36].

Parrey and Hashmi [37] synthesized two Schiff base metal complexes of Mn(II) and Co(II) and used these as catalysts of oxidation of cyclohexane and benzyl alcohol by hydrogen peroxide.

Khalil et al. [38] prepared Mn(salen) complex supported on fumed silica. To explore the effect of interaction nature between the active sites and the nature of surface on the catalytic activity, direct and multistep grafting methods were used. The silica surface was silylated and the metal complexes were modified in order to achieve different metal complex-surface interactions. Cross linker was used to provide covalent bonding. Homogeneous and heterogeneous catalysts were used for testing oxidation of cyclohexane by *tert*-butylhydroperoxide (TBHP) [38].

Bal et al. [39] had synthesized and characterized manganese, copper and nickel complexes with two pyridine carboxaldehyde derived Schiff bases. They studied the role of these complexes in oxidation of cyclohexene and styrene and determined that complexes of manganese and nickel were relatively more efficient.

A novel Schiff base complex of Mn(III) was synthesized and covalently immobilized on silica coated magnetic cobalt nanoparticles by Azar et al. [40]. Oxidation of alcohols and sulfides proceeded under mild conditions with high yield.

Bania et al. [41] synthesized three efficient and reusable Mn(III) chiral Schiff base complexes supported on MCM-41 that were used as catalysts in enantioselective oxidation of 2-naphthol to *R*- and *S*-BINOL (1,1'-bi-2-naphthol) in the presence of oxygen. The complexes promoted the homo-coupling reaction with oxygen, which gave bi-naphthols with enantioselectivity up to 91%. Both homogeneous and heterogeneous chiral catalysts were found to show similar catalytic activities. The heterogeneous counterparts demonstrated better recyclability and storage stability. The catalytic oxidation process was affected by oxygen partial pressure, nature of solvents, temperature, and amount of the catalyst. High temperature and highly polar solvents had adverse effects on the catalytic oxidative process (Fig. 2) [41].

Saffar-Teluri [42] performed the synthesis of Mn(III) salophen acetate, $[\text{Mn}(\text{salophen})\text{OAc}]$, supported on hydroxyapatite coated magnetic nanoparticles, Hap- Fe_2O_3 . The newly synthesized efficient heterogeneous catalyst was used in oxidation of alcohols with NaIO_4 . The complex was characterized by high reusability in the oxidation reactions without any loss of its catalytic activity.

Mn-Schiff base complex supported on magnetic nanoparticles was synthesized by Zhou et al. [43]. Their catalyst was used in oxidation of alcohols to corresponding aldehydes or ketones. The highly selective catalyst led to high yields in DMSO at 110°C when *tert*-butyl hydroperoxide was used as an oxidant. The catalyst could be easily isolated by using an external magnet and reused five times without significant loss of activity.

Nikoorazm et al. [44] synthesized the complexes of chromium and manganese Schiff base that were immobilized on modified nanoporous MCM-41. The complexes demonstrated selectivity in catalytic oxidation of sulphides to sulphoxides. These were also efficient in the oxidative coupling of thiols to corresponding disulphides.

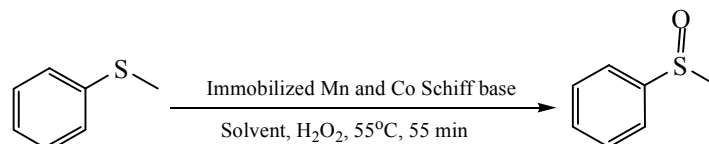


Fig. 3. Simplified scheme of oxidation reaction of sulphide [45].

Saremi et al. [45] developed a selective heterogeneous catalyst by immobilization of manganese and cobalt Schiff base complexes on cobalt magnetite nanoparticles. The catalytic activity of such complexes was studied under different conditions of oxidation of sulphides to sulphoxides. The catalyst supported high yields and was reusable (Fig. 3).

Epoxidation reaction. Mn-Schiff base complexes demonstrated high catalytic efficiency in epoxidation reactions.

Pouralimardan et al. [46] synthesized five dissymmetric tridentate Schiff base ligands by reaction of benzhydrazide with the appropriate salicylaldehyde and pyridine-2-carbaldehyde. Such ligands were found to contain mixed donor sets of ONN and ONO. The Mn(II) complexes of these ligands (Mn-L^{1-5}) were studied as catalysts in epoxidation of cyclohexene by iodosylbenzene.

Silva et al. [47] synthesized a modified Jacobsen-type catalyst, which possessed the hydroxyl group on the aldehyde fragment of salen ligand. The complex of this ligand was determined to be active and enantioselective heterogeneous catalysts in epoxidation of α -methylstyrene using NaOCl as an oxidant.

Nehru et al. [48] proposed a mechanism of non-heme Mn(II) complex catalyzed oxidation reaction. The complex was effective in epoxidation of olefins by iodosyl benzene and in oxidation of olefins, alcohol and alkanes by peracetic acid.

Luts et al. [49] studied the catalytic effect of homogeneous Mn(III)- and Mo(IV)-salen complexes immobilized on silica surface in epoxidation of cyclooctene and cyclohexene by *tert*-butyl hydroperoxide (TBHP) and hydrogen peroxide (HP). The immobilized enzymes showed stable catalytic activity in manifold reuses. The epoxide products were synthesized with >95% selectivity [49].

Mirkhani et al. [50] studied the effect of bulky substitution on catalytic activity of a manganese-salen complex. They evaluated the effect of *tert*-pentyl group at the positions 3- and 5- on the salen ligand of the complex Mn(salen)Cl upon epoxidation of alkenes

and hydroxylation of alkanes at room temperature. Sodium periodate was used as a source of oxygen. The influence of axial ligands in oxidation of cyclooctene was also studied. According to the experimental results, catalytic activity of the complex increased in the presence of bulky substituent in 3- and 5- positions of the salen ligand [50].

Qurari et al. [51] synthesized three manganese complexes with H_2 -salen derivatives, Mn(III) tetradentate Schiff base complexes. The complexes were tested in epoxidation of *E*- and *Z*-stilbene isomers. The complete conversion of *E*-stilbene into *Z*-stilbene oxide was achieved, while oxidation of *Z*-stilbene gave a mixture of products in which benzaldehyde was dominating.

Stamatis et al. [52] synthesized two new symmetrical acetylacetonate-based Schiff bases (L_A and L_B) and developed the acetylacetonate-based Schiff bases-Mn(II) homogeneous system for epoxidation of olefins by hydrogen peroxide. Mn(II)- L_A and Mn(II)- L_B showed the remarkably effective and selective catalytic activity towards epoxides in the presence of ammonium acetate.

Stamatis et al. [53] studied also epoxidation reaction of alkenes by hydrogen peroxide using SiO_2 -immobilized Mn(II) complexes. The developed heterogeneous catalysts preserved the coordination and catalytic properties of the catalyst vs the competitive H_2O_2 dismutation [53].

Guha and Das [54] used three mononuclear complexes of Mn(II) as catalysts in epoxidation of *E*-stilbene and styrene by PhIO and NaOCl in four different solvents. It was observed that catalytic efficiency of the complexes was influenced by their own structural features, substrates, solvents, and terminal oxidant. Two different types of intermediates, such as $\text{O}=\text{Mn(IV)(L)(X)}$ and Cl-O-Mn(II)(L)(X) [$\text{X} = \text{NO}_3-\text{SCN}-\text{N}(\text{CN})_2$] were observed in the presence of the aforementioned oxidants. Acetonitrile was used as the most suitable solvent [54].

Ghorbanloo et al. [55] developed an efficient, highly selective, robust, stable, and reusable

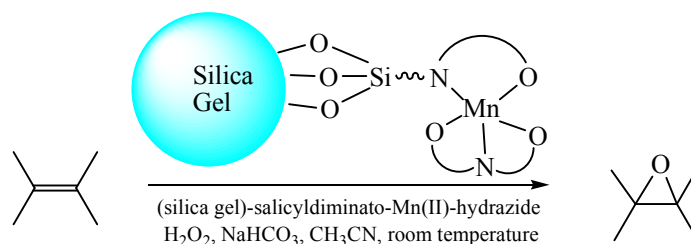


Fig. 4. Epoxidation reaction catalyzed by silica gel-immobilized Mn(II)-hydrazone complex (Redrawn) [55].

heterogeneous manganese Schiff base complex which was immobilized on an inorganic support. The developed catalyst was efficient in clean epoxidation by aqueous hydrogen peroxide and acetonitrile in the presence of aqueous sodium bicarbonate. This was particularly efficient in epoxidation of cycloalkenes. Selectivity of the process was 87–100%. The catalytic system was also active in epoxidation of linear alkenes (Fig. 4) [55].

Sharma et al. [56] synthesized a heterogeneous catalyst by covalent anchoring of the complex chloro (*S,S*)(-)[*N*-3-*tert*-butyl-5-chloromethylsalicylidene]-*N'*-[3',5'-di-*tert*-butylsalicylidene]-1,1'-binaphthyl-2,2'-diamine Mn(III) over modified mesoporous surface of SBA-15. The catalyst was effective in oxidation of 1,2-dihydronaphthalene and bulky alkenes [56]. It was observed that [Mn(III)-L-SBA-15] catalyst was more active than the homogeneous catalyst [Mn(III)-L].

Kar and Ghosh [57] synthesized a new complex of Mn(III) which consisted of cationic units $[\text{Mn}_2(\text{salen})_2 \cdot (\text{HCOO})]^+$ joined together by weak Mn...O(phenoxido) interactions forming an alternating phenoxido and format-bridge 1D polymer. The complex was tested as an efficient catalyst in epoxidation of alkenes like *E*-stilbene and styrene by PhIO (terminal oxidant) (Fig. 5).

Ji et al. [58] used different oxidants for comparative epoxidation of not functionalized olefins. For this purpose, they synthesized asymmetric Mn(III) salen complexes that were immobilized on mesoporous silica.

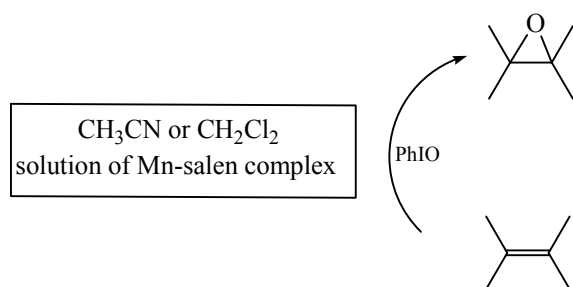


Fig. 5. Epoxidation by the manganese salen complex [57].

Under the action of the catalyst, oxidation by NaClO was characterized by higher conversion than oxidation by *m*-CPBA (*m*-chloroperbenzoic acid) (Fig. 6).

Different Mn(II) complexes were synthesized using novel pyridine Schiff bases by Li et al. [59]. The complexes were used as catalysts in the auto-oxidation of cyclohexene under optimized reaction conditions, that were determined to be low temperature under atmospheric oxygen pressure.

Ma et al. [60] performed epoxidation of styrene catalyzed by mesoporous propylthiol group-functionalized silica supported Mn(III)-salen complexes with different pore morphologies. The developed material was characterized by excellent catalytic performance in epoxidation of styrene by aqueous NaClO. The pore size and structural ordering affect upon the catalytic activity of the materials were studied.

Ma et al. [61] prepared highly ordered mesoporous manganese-salen-based hybrid catalysts, Mn(salen)-C₃N₂-Schiff-SBA-15 and Mn(salen)-C₄N₂-Schiff-SBA-15, and used these in catalytic epoxidation of

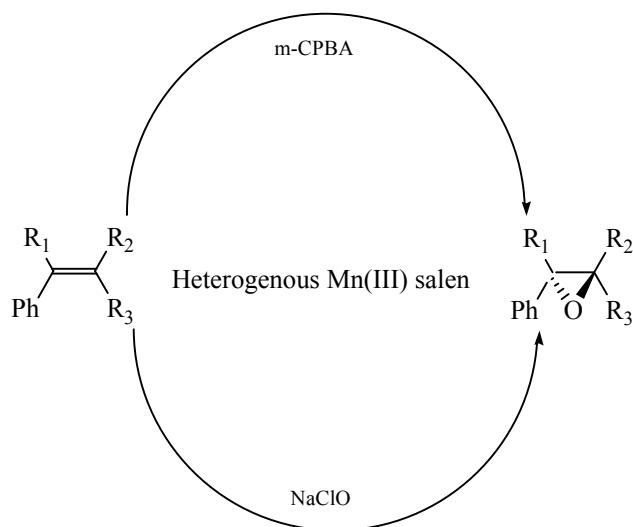


Fig. 6. Epoxidation by heterogeneous Mn(III) salen complex (Redrawn) [58].

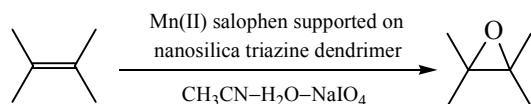


Fig. 7. Epoxidation of alkene catalyzed by Mn(II)-salophen complex supported on a nanosilica triazine dendrimer [65].

alkenes. The catalytic epoxidation of styrene, cyclohexene and 1-phenyl cyclohexene was carried out efficiently by NaOCl. The catalysts had high selectivity and reusability.

Erdem and Guzel [62] synthesized Schiff base complexes of manganese and studied their catalytic properties in the epoxidation of styrene. They synthesized the product in good yield by optimizing the reaction conditions.

Mavrogiorgou et al. [63] functionalized the activated carbon by covalently anchoring Mn(II)-Schiff base catalysts [Mn(II)-L@ACox] that were applied in alkenes oxidation. The catalysts were selective towards epoxidation by hydrogen peroxide in the presence of ammonium acetate as a co-catalyst. The reusable heterogeneous catalysts Mn(II)-L@ACox were kinetically faster than homologous Mn(II)-L@SiO₂ [63].

Adhikari et al. [64] synthesized tridentate Schiff based Mn(III) and Fe(III) complexes that demonstrated the catalytic activity in epoxidation of styrene, *E*-stilbene, 1-octene, and cyclooctene by PhIO and TBHP with excellent yields of products.

Fardjahromi et al. [65] synthesized Mn(II) salophen complex supported on a nanosilica triazine dendrimer and used it in epoxidation of different cyclic and linear alkenes by sodium periodate. The heterogeneous catalyst showed high stability and reusability (Fig. 7).

Garcia et al. [66] performed the bicarbonate assisted epoxidation of cyclohexene catalyzed by SALEN- and SALHD-Mn(III) complexes encapsulation in an Al-pillared clay. They successfully encapsulated the [Mn(3,5-dtSALEN)Cl] (**1**) and [Mn(3,5-dtSALHD)Cl] (**2**) complexes (3,5-dtSALEN = *N,N'*-bis(3,5-di-*tert*-butylsalicylaldehyde)ethylenediamine; 3,5-dtSALHD = *N,N'*-bis(3,5-di-*tert*-butylsalicylaldehyde)-1,2-cyclohexanediamine) within natural bentonite. The synthesized catalysts were active in epoxidation of cyclohexene by hydrogen peroxide. Presence of sodium bicarbonate as co-catalyst enhanced the process up to 100% conversion and 70% selectivity. Catalysts were stable and reusable in up to two catalytic cycles [66].

Rayati et al. [67] synthesized Mn(II) and oxovanadium VO(IV) complexes that were encapsulated with nanocavities of zeolite Y. Such encapsulated complexes were used for the catalytic oxidation of alkene by hydrogen peroxide.

Li et al. [68] synthesized two salen-type Schiff base *N,N'*-bis(5-nitrosalicylidene)ethane-1,2-diamine derived Mn(III) complexes and studied their catalytic efficiency in oxidation of styrene by PhIO and NaOCl. The process was characterized by high level of conversion and selectivity.

Bikas et al. [69] synthesized Mn(II) complexes of hydrazone based NNO-donor ligands and studied their catalytic role in epoxidation of olefins by *tert*-butylhydroperoxide.

Catalase like and catecholase activities. Fernandez et al. [70] studied the influence of geometry around manganese ion on peroxidase and catalase activities of Mn(III) Schiff bases complexes. Peroxidase and catalase activities of μ -aqua manganese-Schiff base dimers increased according to the tetragonal distortion of the octahedral geometry around the metal ion center.

Synthesis and characterization of three Mn(III) complexes, [MnL¹(OOCH)(OH₂)] (**1**), [MnL²(OH₂)₂]·[Mn₂L₂²(NO₂)₃] (**2**), and [Mn₂L₂¹(NO₂)₂] (**3**), where H₂L¹=H₂Me₂; Salen= 2,7-bis(2-hydroxyphenyl)-2,6-diazaocta-2,6-diene and H₂L² = H₂Salpn = 1,7-bis(2-hydroxyphenyl)-2,6-diazahepta-1,6-diene was carried out by Seth et al. [71]. Upon structural studies, it was determined that complex **1** was mononuclear while complex **2** contained a mononuclear cationic and dinuclear nitrite bridge anionic units, and complex **3** was a phenoxido bridged dimer containing the terminally coordinated nitrile. All three complexes demonstrated excellent catecholase like activity with 3,5-di-*tert*-butylcatechol (3,5-DTBC) as the substrate. Kinetic measurements indicated that the rate of catechol oxidation matched the saturation kinetics with respect to the substrate and first order kinetics with respect to the catalyst [71].

Synthesis and characterization of mononuclear [Cu(II)(HL)₂] (**1**) and dinuclear [Mn(III)₂($\mu_{1,3}$ -OAc)₂L₂] (**2**) [H₂L = *N*-(2-Hydroxypropyl)-3-methoxysalicylaldehyde] complexes have been performed by Mitra et al. [72]. Both complexes in the presence of molecular oxygen in methanolic solution were found to be efficient catalysts of oxidation of 3,5-di-*tert*-butylcatechol.

SOD- and catalase-mimetic activities were exhibited by manganese (Salen) complexes. Noritake et al. [73] synthesized the novel Mn(Salen) complexes pursuing enhancement of the catalytic activity. They observed the superior catalase like activity and retaining moderate SOD-like activity. The studied compounds were found to be useful in antioxidant therapy [73].

Schiff base compartmental ligand *N,N'*-ethylenebis(3-ethoxysalicylaldehyde) was used by Chakraborty et al. [74] in the synthesis of five mononuclear Mn(III) compounds [Mn(III)L(OAc)]·DMF (**1**), [Mn(III)L(Cl)(H₂O)]·2H₂O (**2**), [Mn(III)(N₃)(H₂O)] (**3**), [Mn(III)L(NCS)(H₂O)] (**4**), and [Mn(III)L(NCSe)(H₂O)]·MeCN (**5**). All five complexes were determined to be mononuclear with Mn(III) center occupying the N(imine)₂O(phenoxo)₂ compartment. The synthesized Mn(III) complexes demonstrated catecholase activity with turnover (*k*_{cat}) number ranging 17.0–41.7 h⁻¹ (for **1–5**) in DMF and 16.9–137.3 h⁻¹ (for **2–5**) in MeCN [74].

Dutta et al. [75] synthesized four mononuclear manganese complexes and studied their catecholase activity following oxidation of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butylbenzoquinone.

Alkyd paints. Liu et al. [76] studied autoxidation and oligomerization of ethyl linoleate catalyzed by manganese salts in combination with several Schiff-base ligands. The studies suggested that there were different combinations that showed relatively high catalytic activity in autoxidation of ethyl linoleate.

Urease inhibitory activity. Shi et al. [77] studied the urease inhibitory activity of metal complexes of Schiff bases. They synthesized six new transition metal complexes and determined that three complexes showed efficient inhibition against *jack bean* urease. Among those [Mn₃(SALPD)₂(OAc)₂] was determined to be the most active.

Zhang et al. [78] prepared two complexes of thiocyanato coordinated Mn(III) with bis-Schiff bases from starting materials, *N*-ethylethane-1,2-diamine and *N*-(2-hydroxyethane-1,2-diamine), that were tested in urease inhibition.

Anticancer activity. Damercheli et al. [79] synthesized four new salen type Mn(III) Schiff base complexes derived from *meso*-1,2-diphenyl-1,2-ethylenediamine and studied their *in vitro* anticancer activity. They evaluated this activity using MTT and

apoptosis assays against human breast (MCF-7) and liver (Hep G2) cancer cells, and determined the complexes to be significantly active against both types of cell lines.

Miscellaneous catalytic activities. Apart from aforementioned reactions and applications, the Schiff base complexes of manganese demonstrated some other catalytic functions in a number of ways of which some were determined to be highly useful.

Jiang et al. [80] studied the metal promoted hydrolysis of bis(*p*-nitrophenyl)phosphate using crowned Schiff base Mn(III) complexes. They used these complexes in the Gemini surfactants [bis(hexadecyldimethylammonium)hexane bromide (abbreviation 16-6-16, 2Br⁻)] solution to catalyze the process of hydrolysis. Three types of micelles, namely 16-6-16, CTAB (hexadecyltrimethylammonium bromide) and LSS (*n*-laurooylsarcosine sodium) were tested in hydrolysis of bis(*p*-nitrophenyl)phosphate. Gemini 16-6-16 micelles were determined to be the most active.

Gonzalez-Riopedre et al. [81] synthesized four Mn(III) Schiff base complexes of general formula [Mn^{*n*}(H₂O)₂]₂(ClO₄)₂·*m*H₂O (*n* = 1–4; *m* = 0, 1). The complexes were used in the study of water photolysis. Evolution of oxygen was measured in aqueous media in the presence of *p*-benzoquinone while reduction of it was monitored by UV-spectroscopy.

Wu et al. [82] combined two manganese Schiff base complexes [Mn(salen)(H₂O)₂]₂Na₃[IMo₆O₂₄]·18H₂O and [Mn(salpn)(H₂O)₂]₂Na₃[IMo₆O₂₄]·10H₂O and A-type Anderson heteropolymolybdates, and studied their photo catalytic properties. Both compounds demonstrated good catalytic activity in photo degradation of RhB upon UV irradiation.

Gonzalez-Riopedre et al. [83] synthesized six Mn(III) Schiff base complexes incorporating dianionic hexadentate Schiff base ligands (H₂L¹⁻–H₂L⁴⁻) and different anions, and used these in the study of oxidation of veratryl alcohol, which is lignin model compound. The biomimetic catalysts were used in conjunction with chlorine-free inexpensive co-oxidants. They achieved 30% conversion of veratryl alcohol into veratraldehyde upon air flow using the catalyst (0.5%).

A dimanganese tetrakis-Schiff base complex [Mn(II)₂L]²⁺, synthesized by Kal et al. [84], demonstrated catalytic activity in water oxidation. Cyclic voltagrams of [Mn(II)₂L]²⁺ in propylene carbonate showed current increase starting at +1.3V vs.

Fc^{+0} . Water molecule was added as a limiting reagent. The current showed the first order dependence on H_2O and $[\text{Mn}(\text{II})_2\text{L}]^{2+}$, indicative for electrocatalytic water oxidation. The rate of O_2 evolution was proportional to $[\text{Mn}(\text{II})_2\text{L}]^{2+}$.

Mishra et al. [85] synthesized a Schiff base mono-nuclear manganese complex $[\text{Mn}(\text{Habph})_2]$ in which Schiff base was 2-amino-benzoic acid [1-(2-hydroxy-phenyl)propylidene]hydrazide (H_2abph). The complex demonstrated appreciable corrosion inhibition properties.

Schiff base complexes of general formula $\text{Mn}(\text{L}^{1-5})_2$ with nanosilica-immobilized hydroxyaldimine, where $\text{L}^1 = \text{salicylaldehydinepropyl}$; $\text{L}^2 = 5\text{-bromosalicylaldehydinepropyl}$; $\text{L}^3 = 2\text{-hydroxynaphthaldehydinepropyl}$; $\text{L}^4 = 2\text{-hydroxy-3-methoxybenzaldehydinepropyl}$; $\text{L}^5 = 2\text{-hydroxy-3,5-dichloroacetophenoneiminepropyl}$, were synthesized by Rakytska et al. [86]. The complexes demonstrated activity in ozone depletion at low temperature. Reactivity of the ligands was in the order $\text{L}^5 < \text{L}^2 < \text{L}^3 < \text{L}^1 < \text{L}^4$. The number of catalytic cycles for synthesized complexes was in the order $\text{Mn}(\text{L}^3)_2 \gg \text{Mn}(\text{L}^4)_2 > \text{Mn}(\text{L}^1)_2 > \text{Mn}(\text{L}^2)_2 > \text{Mn}(\text{L}^5)_2$ [86].

Zhang et al. [87] synthesized Mn(II), Cu(II) and Co(II) complexes with water soluble azo Schiff base ligand containing the crosslinking reactive group 3,5-bis[(2-hydroxy-4'-sodiumsulphatoethylsulphonyl)azobenzenemethylenimine]benzoic acid (BHSABA), and studied their activity in decomposition of hydrogen peroxide.

Gorczyrski et al. [88] performed a facile synthesis of Mn(II) Schiff base complex $[\text{Mn}_2(\text{H}_2\text{L})_2](\text{ClO}_4)_2$ and used it in preparation of voltammetric sensor for quantitative analysis of dopamine in the presence of ascorbic and uric acids. The analytical study enabled the selective detection of these compounds coexisting in a mixture.

2,4-Dihydroxyacetophenone based Co(II), Cu(II), Mn(II), and Ni(II) complexes were synthesized by Ashokan et al. [89]. The complexes exhibited good antibacterial activity as well as high efficiency towards DNA cleavage.

Synthesis of metals, including manganese, complexes with tridentate-ONS-Schiff base ligand was performed by Ayoub et al. [90]. The complexes acted as photoactive materials due to their specific fluorescence properties.

Adhikary et al. [91] synthesized the Schiff base complexes of Mn(II), such as $[\text{Mn}(\text{HL})_2] \cdot 2\text{ClO}_4$ (**1**),

$[\text{Mn}(\text{HL})(\text{N}(\text{CN})_2)(\text{H}_2\text{O})_2] \cdot \text{ClO}_4$ (**2**) and $[\text{Mn}(\text{HL})(\text{SCN})_2]$ (**3**) {LH = 4-*tert*-butyl-2,6-bis[(2-pyridin-2-yl-ethylimino)methyl]phenol}, and studied the experimental and theoretical aspects of their catalytic properties. They evaluated the effect of synthesized complexes on biorelevant catecholase and phenoxazinone catalytic activity. The study revealed that radicals formation was responsible for their catecholase-like and phenoxazinone synthase-like catalytic activity instead of metal centered redox action.

Babu et al. [92] demonstrated the synthesis of binuclear Mn(II) complexes of a new Schiff base ligand, $[\text{Mn}(\text{II})_2(\text{L})(\text{H}_2\text{O})_4] \cdot x\text{H}_2\text{O}$ (where ligand was based on amino acids and *o*-phthalaldehyde), and their role in antibacterial activity. All the synthesized metal complexes demonstrated moderate to good antibacterial activity against gram positive bacteria *B. Subtilis* and *S. aureus*, and two gram-negative bacteria, *E. Coli* and *K. pneumoniae*.

Moosavi-Zare et al. [93] synthesized a novel nanostructured Schiff base complex, Mn-[4-chlorophenyl-salicylaldehyde-methylpyranopyrazole] Cl_2 . The complex was used as a catalyst in cyclocondensation-Knoevenagel condensation-Michael reaction of phenylhydrazine with ethyl acetoacetate and various aromatic aldehydes.

Mohammed et al. [94] synthesized acetylacetone and leucine derived Schiff base complex of Mn(II), which was determined to have momentous antifungal activity against the tested species, *Candida albican* and *Sacchromyces cerevisiae*. Complexes synthesized by George and Lokhande [95] using different metals, including Mn(II), also exhibited antifungal activity enhanced upon the complex formation. Their study was based on the fungal species *Alternaria brassicae*, *Aspergillus niger*, *Fusarium oxysporum*.

Bermezo et al. [96] synthesized Mn(III) Schiff base dicyanamide complexes and studied their peroxidase type activity in hydrogen peroxide mediated reaction. Two of the synthesized complexes showed good peroxidase activity.

Sudha and Karunamoorthi [97] synthesized Cu(II) and Mn(II) quinoline Schiff base complexes and determined those to be antibacterial and antifungal active.

Turan and Buldurun [98] synthesized complexes of Fe(II), Mn(II), Zn(II), and Ru(II) and studied their antioxidant properties. Among those, Mn(II) Schiff base complex demonstrated low antioxidant properties.

Chioma et al. [99] synthesized heteroleptic divalent metal complexes of Mn(II), Co(II), Ni(II), and Zn(II) of general formula $[M(L)(bipy)(Y)] \cdot nH_2O$ (L = pyrimidine Schiff base ligand, bipy = 2,2'-bipyridine, Y = OAc) and studied their antimicrobial and antifungal activity. Mn(II) Schiff base complex and as well as other complexes demonstrated high level of activity along with good antioxidant properties. The complexes exhibited efficient DPPH (diphenyl-1-picrylhydrazyl) scavenging activity [99]. Schiff base complex of Mn(III) synthesized by Chahmanna et al. [100] showed moderate antibacterial but strong DPPH (2,2-diphenyl-1-picrylhydrazyl) radical-scavenging activity.

There are some more reviews that could be helpful for closer approach to manganese complexes and their catalytic properties [101–108].

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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