



## Synthesis, Structural Characterization, Reactivity and Bioactivity Studies of Some Binuclear Salen Type Schiff Base Complexes of Manganese(III)

K.R. NATH BHOWMIK<sup>1,\*</sup>, R.N. DUTTA PURKAYASTHA<sup>2</sup> and S. ROY<sup>3</sup>

<sup>1</sup>Department of Chemistry, Ramthakur College, Agartala-799002, India

<sup>2</sup>Department of Chemistry, Tripura University, Suryamaninagar-799022, India

<sup>3</sup>Department of Chemistry, The ICFAI University Tripura, Kamalghat, Mohanpur, Agartala-799210, India

\*Corresponding author: E-mail: [kantinathbhowmik@gmail.com](mailto:kantinathbhowmik@gmail.com)

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Four new phenoxy bridged binuclear Salen type Schiff base complexes of manganese(III),  $[\text{MnLX}]_2$  with tetradentate Schiff base,  $\text{H}_2\text{L}$  [ $\text{H}_2\text{L} = \text{N,N}'\text{-O}$ -phenylene bis(salicylaldehyde)] containing anionic co-ligands, X (X = benzoate, *p*-hydroxy benzoate, *p*-aminobenzoate, 3,5-dinitrobenzoate) have been synthesized from manganese(II) acetate, Schiff base ( $\text{H}_2\text{L}$ ) and the corresponding co-ligands in methanol medium. Schiff base ligand ( $\text{H}_2\text{L}$ ) was obtained *in situ* by condensation of salicylaldehyde and *o*-phenylenediamine in aqueous methanol. Elemental analyses, FT-IR, molar conductance, UV-visible spectroscopic studies and magnetic moment measurements at room temperature were used to characterize the binuclear Schiff base complexes. The IR spectra of  $[\text{MnLX}]_2$  (X = benzoate, *p*-hydroxy benzoate, *p*-aminobenzoate, 3,5-dinitrobenzoate) complexes showed the characteristic absorptions due to coordinated azomethine nitrogen and phenolic oxygen atoms of the Schiff base. In addition, IR spectra of the compounds also suggest coordination of the co-ligands namely benzoate, *p*-hydroxy benzoate, *p*-aminobenzoate, 3,5-dinitrobenzoate in the respective complexes. A consistent presence of a band at *ca.* 755  $\text{cm}^{-1}$  in all the binuclear complexes arises due to (Mn-O-Mn) moiety originated from interactions of phenoxy oxygen and manganese atoms, resulted in dimeric structure of the compounds. The magnetic moment values ranging from 4.74-4.91 B.M. per manganese centre for the complexes suggest presence of Mn(III) ion in the complexes. The overall coordination geometry around the manganese centres is distorted octahedral. Redox behaviour of the synthesized complexes was ascertained from cyclic voltametric studies. The Schiff base complexes,  $[\text{Mn}(\text{L})\text{X}]_2$  (X = *p*-aminobenzoate, 3,5-dinitrobenzoate) have demonstrated their catalytic potentials in oxidizing selective organic substrates namely cyclohexene and styrene by hydrogen peroxide as oxidant. The oxidized products were characterized as *trans*-cyclohexane 1,2-diol and styrene epoxide, respectively. Complex **4** demonstrated a considerable level of effectiveness against a wide variety of pathogenic microorganisms.

**Keywords:** Mn(III) Schiff base complexes, Synthesis, Bioactivity study, Reactivity.

### INTRODUCTION

Metal complexes with Schiff base ligands are significant class of compounds with extensive applications in different spheres as catalysts [1], metalloenzyme models [2,3], metallomesogens [4], nonlinear optical materials [5], building blocks for supra-molecular structures [6], as well as antimicrobial [7], antiviral [8] or anticancer [9] agents. It has been emphasized in the literature that Schiff base complexes of manganese(III), though well known but still continue to attract attention because of their potential application in various sectors including magnetic materials and homogeneous catalysis [10-18]. Manganese(III)

complexes synthesized from the ligands of Schiff base are also studied significantly owing to their important role in several biological processes [19,20]. A contemporaneous field of work is concerned with the study of salen and salicylaldehyde type of ligands containing redox active metal centres such as Mn(III).

The factors that determine the geometry of the complexes formed by tridentate and tetradentate salen type Schiff bases with several metal ions depends on electronic configuration, repulsions of different ligand, size of metal ions and intrinsic rigidity from aromatic rings, *etc.* The salen type Schiff bases, usually coordinate to a metal through their imine nitrogen and another group usually oxygen, nitrogen or sulphur present on

the aldehyde moiety. These group of tridentate ligands is used extensively for the synthesis of mono-, di- and polynuclear complexes with first row transition metals [21-25] as well as precursors for the synthesis of unsymmetrical tridentate Schiff base complexes [26,27]. Complexes of tetradentate schiff base ligands usually formed by the condensation reaction between diamines and salicylaldehyde or salicylaldehyde derivatives often crystallizes as phenoxo-bridged dimmers, which may show a range of magnetic interactions depending upon bridged geometry [28-35] and these complexes may also show ferro or antiferromagnetic interactions [36-40]. The present work focuses on the syntheses, characterization and structural assessment of new phenoxo-bridged binuclear complexes of manganese(III) with *N,N'*-*O* phenylenebis(salicylaldimine) ligand. The catalytic potential of some synthesized complexes towards the oxidation of specific organic substrates was another objective of the present study. Additionally, the redox property of some of the synthesized complexes was also explored.

## EXPERIMENTAL

The chemicals were utilized without additional purification and were of the reagent grade. Distillation was done to purify the solvents before they were used. Infrared spectra were recorded as KBr discs using a Perkin-Elmer Spectrum100 FT-IR spectrometer. Perkin-Elmer model Lambda-25 was used to record the electronic spectra. The magnetic susceptibility measurements were carried out by Gouy's method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as standard. Studies of cyclic voltammetry were carried out using an Electrochemical Analyzer apparatus type CH620A. Antibacterial activity of the complexes was also screened by disc diffusion method [41,42] and a broth culture method. Carbon, hydrogen and nitrogen contents in the synthesized complexes were ascertained by elemental micro analysis. Complexometric titration with EDTA using Eriochrome black T as an indicator was used to estimate the manganese content in the complexes [43].

### Synthesis of Schiff base complexes

**Synthesis of  $[\text{Mn}(\text{L})(\text{X})]_2$  (1) [ $\text{H}_2\text{L} = \text{N}_2\text{N}'\text{-o-phenylenebis(salicylaldimine)}$ ] and  $\text{X} = \text{C}_6\text{H}_5\text{COO}^-$ ];  $[\text{Mn}(\text{L})(\text{X})]_2$  (2) [ $\text{H}_2\text{L} = \text{N}_2\text{N}'\text{-o-phenylenebis(salicylaldimine)}$ ] and  $\text{X} = [4\text{-(OH)C}_6\text{H}_4\text{COO}^-]$ ];  $[\text{Mn}(\text{L})(\text{X})]_2$  (3) [ $\text{H}_2\text{L} = \text{N}_2\text{N}'\text{-o-phenylenebis(salicylaldimine)}$ ] and  $\text{X} = [4\text{-(NH}_2\text{)C}_6\text{H}_4\text{COO}^-]$ ];  $[\text{Mn}(\text{L})(\text{X})]_2$  (4) [ $\text{H}_2\text{L} = \text{N}_2\text{N}'\text{-o-phenylenebis(salicylaldimine)}$ ] and  $\text{X} = [3,5\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{COO}^-]$ ]: Solution (A) was prepared by dissolving 0.245 g (1.0 mmol) of  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and 0.244 g (2.0 mmol)  $\text{C}_6\text{H}_5\text{COOH}$ /0.276 g (2.0 mmol) 4-(OH) $\text{C}_6\text{H}_4\text{COOH}$ /0.274 g (2.0 mmol) 4-(NH<sub>2</sub>) $\text{C}_6\text{H}_4\text{COOH}$ /0.424 g (2.0 mmol) 3,5-(O<sub>2</sub>N)<sub>2</sub> $\text{C}_6\text{H}_3\text{COOH}$  in 30 mL aqueous methanol. Another solution (B) was prepared by refluxing a methanolic solution (15 mL) of salicylaldehyde and *o*-phenylenediamine (molar ratio 1:0.5) for about 20 min. After combining the two solutions (A) and (B) so obtained, the resulting mixture was stirred for about 2 h, when dark brown microcrystalline product separated out. The product was isolated by filtration, washed with alcohol and dried *in vacuo* over anhydrous  $\text{CaCl}_2$  (Scheme-I). Single crystal of suitable quality for XRD**

studies could not be obtained even after several attempts.  $[\text{Mn}(\text{L})(\text{X})]_2$  (1): Yield 63%. Anal. calcd. (found) %: C, 66.13 (61.17); H, 3.91 (3.86); N, 5.71 (5.63); Mn, 11.20 (11.07). FT-IR (KBr,  $\text{cm}^{-1}$ ): 2963  $\nu(\text{CH})$ , 1608  $\nu(\text{C}=\text{N})$ , 1574s  $\nu_{\text{as}}(\text{COO})$ , 1373  $\nu_{\text{s}}(\text{COO})$ , 1312  $\nu(\text{CO})$ , 755  $\nu(\text{Mn-O-Mn})$ , 445  $\nu(\text{Mn-N})$ , 384  $\nu(\text{Mn-O})$ .

$[\text{Mn}(\text{L})(\text{X})]_2$  (2): Yield 67%. Anal. calcd. (found) %: C, 63.91 (63.83); H, 3.97 (3.93); N, 5.52 (5.51); Mn, 10.82 (11.03). FT-IR (KBr,  $\text{cm}^{-1}$ ) 2966  $\nu(\text{CH})$ , 1614  $\nu(\text{C}=\text{N})$ , 1579s  $\nu_{\text{as}}(\text{COO})$ , 1383  $\nu_{\text{s}}(\text{COO})$ , 1318  $\nu(\text{CO})$ , 755  $\nu(\text{Mn-O-Mn})$ , 506  $\nu(\text{Mn-N})$ , 380  $\nu(\text{Mn-O})$ .

$[\text{Mn}(\text{L})(\text{X})]_2$  (3): Yield 69%. Anal. calcd. (found) %: C, 64.04 (64.02); H, 4.18 (4.13); N, 8.30 (8.27); Mn, 10.84 (10.87). FT-IR (KBr,  $\text{cm}^{-1}$ ): 2963  $\nu(\text{CH})$ , 1608  $\nu(\text{C}=\text{N})$ , 1578s  $\nu_{\text{as}}(\text{COO})$ , 1378  $\nu_{\text{s}}(\text{COO})$ , 1317  $\nu(\text{CO})$ , 755  $\nu(\text{Mn-O-Mn})$ , 441  $\nu(\text{Mn-N})$ , 376  $\nu(\text{Mn-O})$ .

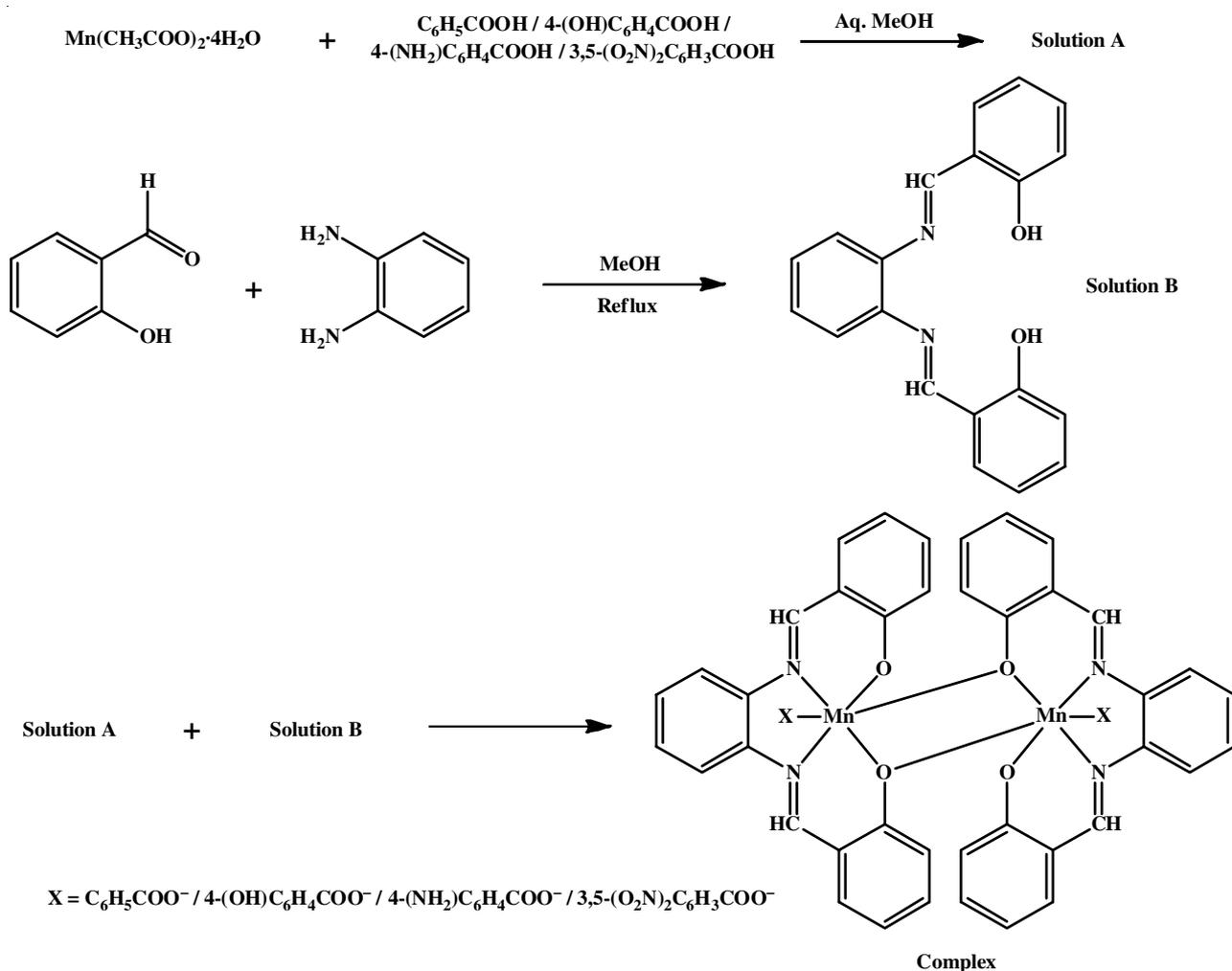
$[\text{Mn}(\text{L})(\text{X})]_2$  (4): Yield 71%. Anal. calcd. (found) %: C, 59.14 (59.11); H, 3.12 (3.09); N, 10.22 (10.20); Mn, 10.01 (10.07). FT-IR (KBr,  $\text{cm}^{-1}$ ): 2871  $\nu(\text{CH})$ , 1604  $\nu(\text{C}=\text{N})$ , 1569s  $\nu_{\text{as}}(\text{COO})$ , 1338  $\nu_{\text{s}}(\text{COO})$ , 1312  $\nu(\text{CO})$ , 742  $\nu(\text{Mn-O-Mn})$ , 441  $\nu(\text{Mn-N})$ , 371  $\nu(\text{Mn-O})$ .

### Catalytic oxidation of organic substrate with $\text{H}_2\text{O}_2$ as oxidant

**Catalytic oxidation of cyclohexene with  $\text{H}_2\text{O}_2$ :** In a 250 mL round bottom flask equipped with mechanical stirrer and thermometer was placed 30 mL (60 mmol) of 85% formic acid followed by the addition of 7.0 mL (6.2 mmol) of 30%  $\text{H}_2\text{O}_2$  slowly in small portions. To the resultant colourless solution, 0.03 g of  $[\text{Mn}(\text{L})(\text{X})]_2$  (1) was added, when the colour of the reaction mixture gradually changed to reddish brown. Maintaining the temperature of the reaction at *ca.* 45 °C by heating and alternately cooling the mixture in an ice bath, 5.1 mL (5.0 mmol) cyclohexene was gradually added to the above reaction mixture over a period of 20-30 min. After the addition of cyclohexene was complete, the reaction mixture was kept at ~40 °C for 1 h and then it was left for overnight at room temperature. The reaction mixture was distilled under low pressure to remove formic acid and water. To the remaining mixture, an ice cold solution of 4 g (10.0 mmol) of sodium hydroxide dissolved in 10 mL of water was added in small portions. The resultant mixture was warmed to 45 °C and added an equivalent amount (*ca.* 30 mL) of ethylacetate. The mixture was extracted thoroughly at *ca.* 45 °C with equal volume of ethylacetate, washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The removal of solvent was carried out using a rotary evaporator, until the volume becomes ~5 mL, when white solid product began to crystallize. The product was separated by filtration, washed 2-3 times with small portions of alcohol and dried *in vacuo* over anhydrous  $\text{CaCl}_2$ .

Similar reaction was also performed with the substrate without using the catalyst, *i.e.* complex  $[\text{Mn}(\text{L})(\text{X})]_2$  (1). Yield of the oxidation product ~0.359 g (oxidation in presence of catalyst), ~0.116 g (blank reaction) (m.p. of the product: 104 °C).

**Epoxidation of styrene:** Binuclear manganese(III) complex,  $[\text{Mn}(\text{L})(\text{X})]_2$  (3) ( $\text{X} = p\text{-aminobenzoate}$ ),  $[\text{Mn}(\text{L})(\text{X})]_2$  (4) ( $\text{X}$



Scheme-I

= 3,5-dinitrobenzoate), 0.003 g was dissolved in 10 mL of acetonitrile and to this solution 0.002 g ammonium acetate and 1 mL of styrene was added and the mixture was stirred for *ca.* 5 min. To a resultant reddish colour solution, 8 mL of 30%  $\text{H}_2\text{O}_2$  was added slowly in small portions, maintaining the molar ratio of catalyst:oxidant:co-catalyst:substrate as 1:2000:1000:1000, when colour of the reaction mixture becomes more intense. The mixture was further stirred for a period of *ca.* 4 h and then the organic layer was further extracted using petroleum ether (30 mL). The resulting ethereal layer was subsequently washed with water and dried over anhydrous sodium sulphate. The extracted layer so obtained was concentrated under vacuum until the volume reduced to about 2 mL. A short pad silica gel column was used to purify the crude product, which was produced by passing it through the column with an eluent combination of hexane and ether (1:1). The product, in liquid form, was obtained by reducing the pressure of the solvent during its evaporation.

## RESULTS AND DISCUSSION

New dimeric manganese(III) complexes with Schiff base of type  $[\text{Mn}(\text{L})(\text{X})]_2$ ,  $[\text{H}_2\text{L} = \text{N}, \text{N}'\text{-}o\text{-phenylenebis(salicylalimine)}$  and  $\text{X} = \text{benzoate}, p\text{-hydroxy benzoate}, p\text{-aminoben-$

zoate, 3,5-dinitrobenzoate), were synthesized and comprehensively characterized by elemental analyses, molar conductance measurements, FT-IR, electronic absorption spectroscopy and room temperature magnetic susceptibility measurements. The synthetic procedure followed involve reaction of a solution (A) prepared by dissolving manganese(II) acetate tetrahydrate and benzoic acid/*p*-hydroxybenzoic acid/*p*-aminobenzoic acid/3,5-dinitrobenzoic acid in aqueous methanol (methanol:water, ratio as 2:1), with a methanolic solution (B) of salicylaldehyde and *o*-phenylenediamine maintaining the molar ratio as 1:0.5 for 20-25 min. Complete aerial oxidation of Mn(II) to Mn(III) was achieved by mixing the two solutions (A) and (B) so obtained and stirring the resulting mixture for approximately 2 h. Dark brown microcrystalline solid was separated out of the reaction mixture, isolated by filtration and washed with small volume of ethanol several times. For the synthesized complexes diffraction quality single crystals could not be obtained even after several attempts. The complexes are stable in air but poorly soluble in polar solvents like ethanol and acetone, although they dissolve fairly in DMSO and acetonitrile. Compounds **1-4** in acetonitrile solution have molar conductance values in the range 10-12  $\text{ohm}^{-1} \text{cm}^{-1} \text{mol}^{-1}$ , suggesting their non-electrolytic nature. The elemental analyses data (Table-1) of the newly syn-

TABLE-1  
 ANALYTICAL DATA FOR THE COMPLEXES

Compound	Yield (%)	Molar conductance ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	$\mu_{\text{eff}}$ (B.M.)	Elemental analysis (%): Found (calcd.)			
				Mn	C	H	N
[Mn(L)(X)] <sub>2</sub> (X = benzoate)	63	10.12	4.74	11.07 (11.20)	66.17 (66.13)	3.86 (3.91)	5.63 (5.71)
[Mn(L)(X)] <sub>2</sub> (X = <i>para</i> -hydroxy benzoate)	67	11.65	4.83	11.03 (10.82)	63.83 (63.91)	3.93 (3.97)	5.51 (5.52)
[Mn(L)(X)] <sub>2</sub> (X = <i>para</i> -aminobenzoate)	69	10.51	4.91	10.87 (10.84)	64.02 (64.04)	4.13 (4.18)	8.27 (8.30)
[Mn(L)(X)] <sub>2</sub> (X = 3,5-dinitrobenzoate)	71	12.02	4.79	10.07 (10.01)	59.11 (59.14)	3.09 (3.12)	10.2 (10.22)

thesized complexes agrees well with the molecular composition of the compounds.

**Electronic spectra and magnetic moment:** The phenolate  $\rightarrow \text{Mn(III)}$  charge transfer and  $\text{Mn(III)} \rightarrow \text{imine (d} \rightarrow \pi^*)$  metal to ligand charge transfer transitions in the UV-visible spectra of the complexes **1-4**, observed in the region 331-365 nm and *ca.* 448-455 nm, respectively [44]. The room temperature (300 K) magnetic moments for the complexes **1, 2, 3** and **4** lying in the range 4.74-4.91 B.M. per manganese centre, indicating that all of the newly synthesized complexes contains manganese(III) ions.

**Infrared spectra:** The prominent absorption bands from the FT-IR spectra of the complexes **1-4** are presented in Table-2, which are comparable and exhibit a well resolved spectral pattern. The key features of the FT-IR spectra of the complexes, [Mn(L)X]<sub>2</sub> (X = benzoate, *p*-hydroxy benzoate, *p*-aminobenzoate, 3,5-dinitrobenzoate) show characteristic absorptions due to coordinated azomethine nitrogen and phenolic oxygen of Schiff base and carboxylate group of co-ligands *viz.* benzoate, *p*-hydroxy benzoate, *p*-aminobenzoate, 3,5-dinitrobenzoate. In all the complexes strong absorption in the region 1614-1604  $\text{cm}^{-1}$  were assigned as (C=N) stretching of Schiff base ligand, suggesting an imino nitrogen coordination. Appearance of strong absorptions at *ca.* 1579-1569  $\text{cm}^{-1}$  are assignable to  $\nu_{\text{asy}}(\text{COO}^-)$  modes of vibration of the carboxylate group and corresponding symmetric modes  $\nu_{\text{s}}(\text{COO}^-)$  was observed in the region 1383-1338  $\text{cm}^{-1}$ . The differences in frequencies between symmetric and antisymmetric  $\nu(\text{COO}^-)$  vibrations,  $\Delta\nu$ , larger than 200  $\text{cm}^{-1}$  in all the Mn(III) complexes under consideration, suggest the monodentate coordination of carboxylate group of the co-ligands in each case [45]. Phenolic C-O stretching modes of the metal bound Schiff base in these Mn(III) complexes were observed at *ca.* 1318-1312  $\text{cm}^{-1}$ . The appear-

ance of bands for  $\nu(\text{Mn-N})$  and  $\nu(\text{Mn-O})$  vibrations, in the ranges 506-445 and 384-371  $\text{cm}^{-1}$  respectively, provides additional evidence of the Schiff base ligand coordination to the metal. Consistent presence of a strong absorption band at *ca.* 755  $\text{cm}^{-1}$  in all the complexes **1-4** is attributed to vibration due to 'Mn-O-Mn' moiety originated from interaction of Schiff base's phenoxy oxygen atom and manganese centers, which resulted in dimeric structure of the complexes [46].

 TABLE-2  
 SIGNIFICANT FT-IR BANDS AND ASSIGNMENTS

Compound	FT-IR bands ( $\text{cm}^{-1}$ )	Assignment
[Mn(L)(X)] <sub>2</sub> , [H <sub>2</sub> L = N,N'-O-phenylene bis(salicylaldehyde) and X = benzoate, <i>para</i> -hydroxy benzoate, <i>para</i> -aminobenzoate, 3,5-dinitrobenzoate]	2963-2871	$\nu(\text{CH})$
	1604-1614	$\nu(\text{C=N})$
	1569-1579	$\nu_{\text{asy}}(\text{COO})$
	1338-1383	$\nu_{\text{sym}}(\text{COO})$
	1312-1318	$\nu(\text{CO})$
	742, 755	$\nu(\text{Mn-O-N})$
	441-445, 506	$\nu(\text{Mn-N})$
	371-384	$\nu(\text{Mn-O})$

**Electrochemical study:** Electrochemical behaviour of the synthesized complexes was ascertained from cyclic voltametric studies. Complexes display the cyclic response with anodic ( $E_{\text{p,a}}$ ) and cathodic ( $E_{\text{p,c}}$ ) peak potentials and  $E_{1/2}$  values in the range -2.0 to +2.0 V *vs.* SCE (Fig. 1). Complexes in acetonitrile solution were subjected to electrochemical studies. For the binuclear complex, **1** the  $E_{1/2}$  values of the redox couples was observed at 1.225 V, while the observed  $\Delta E_{\text{p}}$  value was found to be 1.15 V. The  $\Delta E_{\text{p}}$  value for complex **1** suggests that the redox process involving the Mn(III)/Mn(II) pair is irreversible. In case of complexes **3** and **4**, the cyclic voltagrams exhibit  $E_{1/2}$  values at *ca.* 1.37V and 0.95V with the corresponding  $\Delta E_{\text{p}}$

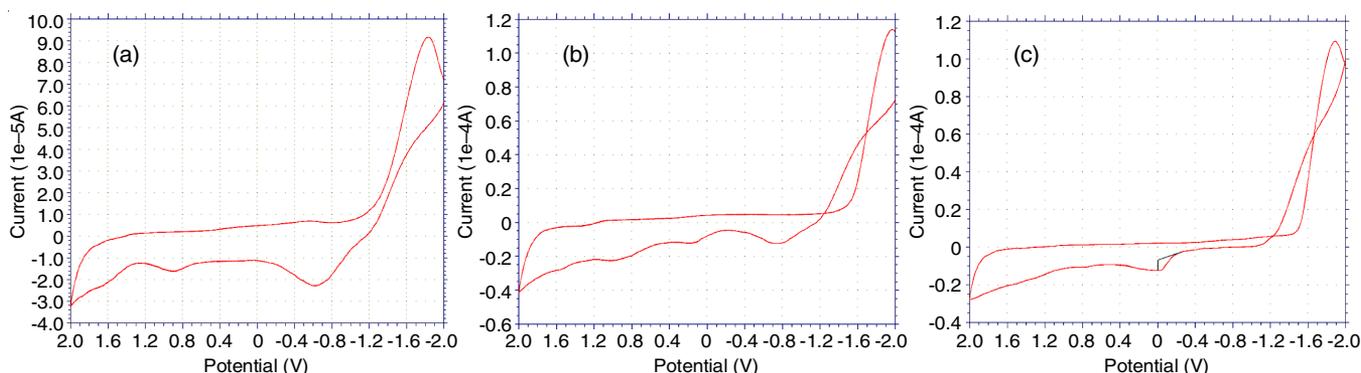
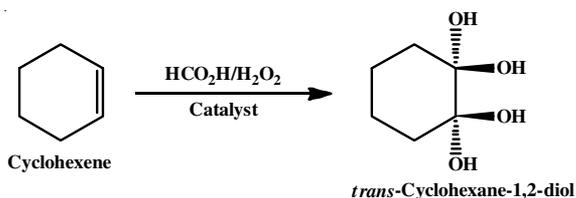


Fig. 1. Cyclic voltammogram of (a) [Mn(L)(X)]<sub>2</sub> (X = benzoate), (b) [Mn(L)(X)]<sub>2</sub> (X = *para*-aminobenzoate), (c) [Mn(L)(X)]<sub>2</sub> (X = 3,5-dinitrobenzoate)

values of 1.15 V and 1.9 V, respectively, thus suggesting an irreversibility of the redox processes. When the oxidation states of the complexes under discussion changes, the coordination geometry or coordination number may also changes as well, leading to irreversibility in the redox processes.

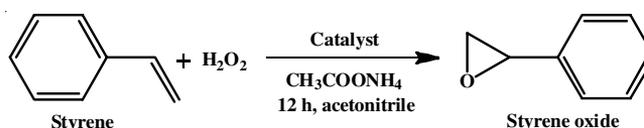
**Catalytic oxidation of cyclohexene with H<sub>2</sub>O<sub>2</sub>:** To assess the catalytic potential of the synthesized manganese(III) Schiff base complexes towards oxidation of selective organic substrates, the oxidation reaction were carried out involving cyclohexene and styrene as substrates, H<sub>2</sub>O<sub>2</sub> as oxidizing agent and complex **3** or **4** as catalyst. In case of styrene as substrate, the reaction was carried out in acetonitrile medium where as in case of cyclohexene reaction was performed in presence of aqueous formic acid solution. The white crystalline product was obtained by subjecting cyclohexene to a stoichiometric oxidation in the presence of formic acid (85% aqueous solution) using H<sub>2</sub>O<sub>2</sub> with complex **3**, followed by workup of the reaction solution. Melting point of the white crystalline product as obtained was 104 °C. The <sup>1</sup>H NMR spectrum of the complex in DMSO-*d*<sub>6</sub> showed signal at δ 1.05-2.08 and δ 3.5-3.6 and δ 8.2 ppm. The IR spectrum of the product show absorption band at 3442 cm<sup>-1</sup> is assignable to ν(OH), while the other significant absorptions were observed at *ca.* 2837 cm<sup>-1</sup> and in between 700-1600 cm<sup>-1</sup>.

Thus on the basis of the experimental results and a comparison with literature data [47], the identity of the compound was established as *trans*-1,2-cyclohexenediol. The product was obtained in reasonably good yield. However, a similar reaction without involvement of the catalyst *viz.* complex **3/4**, the yield of the product is much less in comparison to that obtained for oxidation using the manganese(III) complexes as catalyst.



**Epoxidation of styrene:** Epoxidation reaction of styrene was conducted in an acetonitrile medium at room temperature

using the Schiff base complexes, **3/4** as catalyst and 30% H<sub>2</sub>O<sub>2</sub> as oxidant. When the oxidant was added to solutions containing manganese(III) complex and substrates, the red colour became much more intense. This might be because an oxometallic intermediate was formed by the catalyst. The colour of the solution almost returns to its initial on completion of epoxidation reaction, which is indicative of the regeneration of catalyst took place. The product obtained was purified by column chromatography. <sup>1</sup>H NMR spectrum of the isolated liquid product in CDCl<sub>3</sub> exhibit signals at δ 3.3, 2.6 and 2.2 ppm, which compare very well with values of styrene epoxide [48]. Epoxidation of styrene as discussed was rather carried out in a qualitative manner. The results of the initial study are encouraging and further works in this regard are in progress in the laboratory. Thus, the catalytic potential of the synthesized manganese(III) complexes *viz.* **3/4** in oxidation of selective organic substrate by H<sub>2</sub>O<sub>2</sub> have been demonstrated.



**Antibacterial activity:** The minimum inhibitory concentration (MIC) and zone of inhibition are the metrics used to measure the antibacterial activity data. The disk diffusion and broth culture methods were used to screen the activity of free ligands and Mn(III) complexes against six human pathogenic bacteria including *Klebsiella pneumonia*, *Shigella flexneri*, *Shigella dysenteriae*, *Escherichia coli*, *Staphylococcus aureus* and *Streptococcus pneumonia*. Complex **4** shows significant antibacterial activity, however, ligand (H<sub>2</sub>L) is not active according to the results of the antibacterial screening. The zone of inhibition data (Table-3) show that complex **4** is active against *Klebsiella pneumonia*, *Shigella dysenteriae*, *Escherichia coli* and *Streptococcus pneumonia*. In all the cases, the MIC value found to be 400 µg/mL.

## Conclusion

It may be inferred that four new phenoxy bridged binuclear Schiff base complexes of manganese(III) with tetra-coordinating ONNO donor Schiff base ligand [H<sub>2</sub>L = N,N'-O-phenylenebis-

TABLE-3  
ANTIBACTERIAL ACTIVITY OF COMPOUND **4**

Bacterial strain		Concentration (µg/disc or µg/mL)				MIC (µg/mL)
		400	100	10	0	
<i>Klebsiella pneumonia</i>	Zone of inhibition (mm)	10.2 ± 0.55	8.5 ± 0.82	6.13 ± 0.37		
	O.D. at 600 nm	No growth	0.62 ± 0.27	1.03 ± 0.13	1.07 ± 0.23	400
<i>Shigella flexneri</i> 16	Zone of inhibition (mm)	8.56 ± 1.05	8.7 ± 1.4	6.77 ± 0.91		
	O.D. at 600 nm	No growth	0.46 ± 0.3	1.08 ± 0.13	1.11 ± 0.24	–
<i>Shigella dysenteriae</i> 1	Zone of inhibition (mm)	9.0 ± 1.0	8.2 ± 0.44	6.0 ± 0.0		
	O.D. at 600 nm	No growth	0.62 ± 0.21	0.79 ± 0.19	0.88 ± 0.31	400
<i>Escherichia coli</i>	Zone of inhibition (mm)	9.0 ± 1.4	7.5 ± 1.3	6.3 ± 0.57		
	O.D. at 600 nm	0.14 ± 0.18	0.77 ± 0.2	0.83 ± 0.22	0.96 ± 0.27	400
<i>Staphylococcus aureus</i>	Zone of inhibition (mm)	–	–	–		
	O.D. at 600 nm	No growth	0.67 ± 0.18	0.88 ± 0.09	0.79 ± 0.15	–
<i>Streptococcus pneumoniae</i>	Zone of inhibition (mm)	10.0 ± 0	9.0 ± 1.0	6.0 ± 0.0		
	O.D. at 600 nm	No growth	0.61 ± 0.39	1.05 ± 0.18	1.13 ± 0.15	400

(salicylaldehyde)] were synthesized from aqueous methanol medium. The Schiff base H<sub>2</sub>L obtained *in situ* from the condensation of salicylaldehyde and O-phenylenediamine. Spectral studies suggested that in complexes [Mn(L)X]<sub>2</sub> (X = benzoate, *p*-hydroxy benzoate, *p*-aminobenzoate, 3,5-dinitrobenzoate) two centrosymmetrically related manganese(III) centers were held by phenoxy bridges, which resulted in dimeric structure of the complexes. Electrochemical investigations of complexes **1**, **3** and **4** in acetonitrile solution show quasi-reversible to irreversible behaviour due to Mn(III)/Mn(II) couple. The catalytic potential of the newly synthesized binuclear complexes were also explored towards oxidation of selective organic substrates. Complexes, [Mn(L)X]<sub>2</sub> (X = *p*-aminobenzoate, 3,5-dinitrobenzoate) have demonstrated their catalytic potentials in oxidizing selective organic substrates *viz.* cyclohexene and styrene by H<sub>2</sub>O<sub>2</sub> as oxidizing agent. The oxidized products were ascertained as *trans*-cyclohexane-1,2-diol and styrene epoxide respectively. In addition, complex **4** exhibited considerable activity against several pathogenic bacteria in the antibacterial screening.

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#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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