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Epoxidation and catechol oxidation catalytic processes promoted by manganese(III) complexes of salen-type ligands

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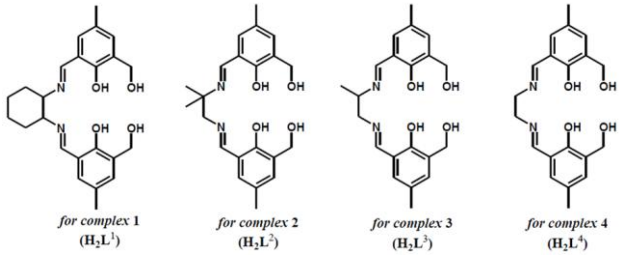
Four new mononuclear manganese(III) complexes namely **1**, **2**, **3** and **4** of salen-type ligands H_2L^1-H_2L^4 (ligands were obtained *in situ* via Schiff-base condensation of 2-formyl-6-hydroxymethyl-4-methylphenol and amines cyclohexane-1,2-diamine, 2-methylpropane-1,2-diamine, propane-1,2-diamine and ethane-1,2-diamine, respectively) have been synthesised and characterised by routine physicochemical techniques. **1** is further characterised by X-ray single crystal structure analysis. Catalytic efficiencies of the complexes as epoxidation catalysts (substrates: styrene and (*E*)-stilbene; terminal oxidants: PhIO/NaOCl; solvent: MeCN /dicholorometane) and as catalysts for oxidation of catachol (substrates: 3,5-di-*tert*-butylcatechol (3,5-DTBC); solvent: methanol) have been evaluated. In both cases the catalytic efficiency increases on going from **4-1** although the actual mechanisms in those two catalytic reactions are completely different. However, the observations have been rationalized on the basis of steric and electronic factors exerted by the alkyl substituents present on the imine back-bone of the salen-type ligands. This study also verifies that there is at least another active epoxidizing species, [Cl–O–Mn(III)(salen)X] in addition to the discrete Mn(V)=O(salen) species in epoxidation of olefins depending upon the terminal oxidants employed.

Keywords: Mononuclear Manganese(III) complexes, Catecholase activity, Epoxidation catalyst

Manganese ions are present in the active site of various metalloenzymes and play a vital role in controlling a large variety of biological reactions[1]. Since this metal is able to exhibit a wide numbers of oxidation states ranging from 0 to +7 in its complexes[2], it is not surprising that this property has been exploited by many living systems containing manganese dependent enzymes in performing diverse redox functions. Thus manganese complexes have attracted particular interest as synthetic structural mimic of the active site of a range of metalloenzymes, (*viz*, superoxide dismutase[3], manganese dioxygenase[1], catalase[4,5], ribonucleotide reductase[6], arginase[7], oxygen evolving complex (OEC) of photo system II etc.[8-12]) and to understand their catalytic activities in many organic reactions[13–17]. In the field of the catalytic oxidation of organic substrates by transition-metal complexes, several manganese Schiff-base complexes have been investigated as epoxidation catalysts[18-32] and a few numbers have been studied for their catecholase activity [33-37].

Previously our group synthesized some mononuclear manganese complexes of Schiff-base ligand and studied their epoxidation[38] and catecholase[39] activities where the aldehyde used was 2,6-diformyl-4-methyl phenol. Here, we have chosen 2-formyl-6-hydroxymethyl-4-methylphenol as aldehyde with the curiosity to see the effect of alcohol group at 6 position instead of aldehyde groups on the catalytic activities of the corresponding salen-type Schiff-base complexes of manganese(III). In this paper, we report the catalytic properties of a series of manganese(III) complexes of type $[Mn(L^{\mathbf{1-4}})(H_2O)Cl]$ (L = salen-type ligand) bearing different alkyl substituents at the imine side of the Schiff-base ligand back-bone. A chemical drawing of the ligand system H_2L^1-H_2L^4 used to synthesize complexes **1-4** is depicted in Scheme 1.

Catalytic activities of manganese(III) Schiff-base catalysts have been assessed in terms of (i) catechol oxidation where the substrate is 3,5-di-*tert*-butylcatechol (3, 5-DTBC) and (ii) epoxidation where substrates are (*E*)-stilbene and styrene with PhIO and



Scheme 1 — Chemical drawing of the ligand systems

NaOCl as terminal oxidants in different organic solvents. The steric and electronic effect of alkyl substituents present at the imine side of the Schiff-base ligand's back-bone on the catalytic efficiency of the corresponding manganese(III) complexes has also been thoroughly investigated and rationalized.

Materials and Methods

Experimental

2-formyl-6-hydroxymethyl-4-methylphenol[40] and Iodosylbenzene (by hydrolysis of iodobenzene diacetate with NaOH solution)[41] were prepared according to the literature method. Manganese(II) chloride tetrahydrate (Sigma Aldrich), cyclohexane-1,2-diamine (Merck), 2-methylpropane-1,2-diamine (TCI), propane-1,2-diamine (Merck), ethane-1,2-diamine (Fluka), iodobenzene diacetate (Aldrich), sodium hypochlorite solution (Aldrich), *E*-stilbene (Aldrich) and Styrene (Aldrich) were purchased from commercial sources and used as received. The solvents used were of AR grade and were distilled prior to complex preparation.

Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Perkin Elmer 240C analyzer. Infrared spectra (4000-400 cm^{-1}) were recorded at 28 °C on a Shimadzu FTIR-8400S using KBr as a medium. ^1H NMR spectra (300 MHz) were recorded using $CDCl_3$ as medium on a Bruker AV300 Supercon NMR spectrometer using the solvent signal as the internal standard in a 5 mm BBO probe. Electronic spectra were obtained at 25 °C using a Shimadzu UV-3101PC spectrophotometer in methanol and acetonitrile medium. The magnetic susceptibilities were measured at 27 °C using a Magway MSB Mk1 magnetic susceptibility balance made by Sherwood Scientific Ltd. Conductance was measured using Systronics Conductivity Meter 306.

Syntheses of the complexes

All the Schiff-base complexes **1-4** were synthesized *in situ* by adopting identical procedure. The ligands L^1-L^4 were synthesised through 2:1 condensation reaction of 2-formyl-6-hydroxymethyl-4-methylphenol and the respective amines (cyclohexane-1,2-diamine, 2-methylpropane-1,2-diamine, propane-1,2-diamine and ethane-1,2-diamine) in ethanol medium. To the resulting Schiff-bases an aqueous solution of $MnCl_2.4H_2O$ was added and stirred overnight to get the desired complexes.

$[MnL^1Cl(H_2O)_2]$ (1)

Yield 63%. Anal. calcd. for $MnL^1(H_2O)Cl\cdot H_2O$: C, 53.89; H, 6.02; N, 5.24. Found: C, 53.81; H, 6.01; N, 5.17.

$[MnL^2Cl(H_2O)_2]$ (2)

Yield 55%. Anal. calcd. for $MnL^2(H_2O)Cl\cdot H_2O$: C, 51.92; H, 5.54; N, 5.50. Found: C, 51.87; H, 5.48; N, 5.48.

$[MnL^3Cl(H_2O)_2]$ (3)

Yield 69%. Anal. calcd. for $MnL^3(H_2O)Cl\cdot H_2O$: C, 53.96; H, 5.29; N, 5.66. Found: C, 53.93; H, 5.21; N, 5.54.

$[MnL^4Cl(H_2O)_2]$ (4)

Yield 67%. Anal. calcd. for $MnL^4(H_2O)Cl\cdot H_2O$: C, 49.95; H, 5.02; N, 5.82. Found: C, 49.81; H, 5.07; N, 5.78.

X-ray crystal structure determination

X-ray diffraction data were collected at room temperature (293(2) K) on a Nonius DIP-1030H system by using Mo-Kα radiation (λ = 0.71073 Å). Cell refinement, indexing and scaling for the data set were performed by using Denzo and Scalepack programs[42]. The structure was solved by Patterson/ direct methods and subsequent Fourier analyses[43] and refined by the full-matrix least-squares method based on F^2 with all observed reflections[43]. The Fourier map evidences the presence of a lattice water molecule. Hydrogen atoms were positioned at geometrical calculated positions except those of the water molecules. All the calculations were performed using the WinGX System, Ver 1.80.05[44].

Crystal data for 1

$C_{24}H_{32}ClMnN_2O_6$, M = 534.91, triclinic, space group $P\bar{1}$ (No. 2), a = 8.809(10), b = 11.616(3), c = 13.255(3) Å, α = 74.48(1), β = 82.97(2), γ = 73.64(2) °, V = 1252.4(5) $Å^3$, Z = 2, ρ_{calcd} = 1.419 g/cm^3, μ(Mo-Kα) = 0.675 mm^{-1}, $F(000)$ = 560. Final R = 0.0461, *wR2* = 0.1124, S = 0.880 for 315 parameters and 14412 collected reflections, 3997 unique [R(int) = 0.0380], of which 2405 with $I > 2\sigma(I)$, max positive and negative peaks in ΔF map 0.361 and -0.198 e $Å^{-3}$.

Results and Discussion

Synthesis procedure and characterization

The salen-type Schiff-base ligands H_2L^1-H_2L^4 were synthesised through the classical condensation reaction between aldehyde (2-formyl-6-hydroxymethyl-4-methyl phenol) and the amines cyclohexane-1,2-diamine, 2-methylpropane-1,2-diamine, propane-1,2-diamine and ethane-1,2-diamine, respectively in ethanol medium. An aqueous solution of manganese(II) chloride was then added to the each of the prepared Schiff-base ligand *in situ* to obtain the four complexes **1-4.**

The IR spectra of all the complexes show bands in the range of 1618-1632 cm^{-1} and 1550-1554 cm^{-1} due to the presence of azomethine group and for skeletal vibration, respectively. The effective magnetic moments exhibited by the complexes are in the range of 4.80 to 4.85 B. M. at 27 °C which are very much consistence with the spin only value (4.90 B. M.) for high spin mononuclear Mn^{III}. The molar conductivities shown by the complexes in methanol were <80 Ω^{-1} cm^2 mol^{-1} at 25 °C, suggesting the complexes to be non-electrolytes. Thus it can be said that the chloride ion is located within the coordination sphere of the molecule.

Description of structure of complex 1

The X-ray diffraction analysis of $[Mn(L^1)(H_2O)Cl].H_2O$ (1) shows that the independent crystallographic moiety comprises a neutral complex and a lattice water molecule. The molecular structure of the complex (Fig. 1) shows that the metal in a distorted octahedral geometry, a selection of the coordination bond distances and angles are reported in Table 1. The side view of the complex demonstrated in Fig. 2 depicts the disposition assumed by the phenolato rings with respect to the equatorial coordination plane. The Mn-O and the Mn-N bond distances are only slightly different in length, being of 1.905(2), 1.888(2) Å and of 1.993(3), 1.979(3) Å, respectively. These values agree with data reported for similar complexes[36]. A water molecule and a chloride reside at the axial positions at significantly longer distances [Mn-O(1w) = 2.258(2), Mn-Cl(1) = 2.5572(14) Å]. The tetradentate Schiff base ligand does not assume a planar conformation but the phenolate groups are bent on opposite direction with respect the N_2O_2 equatorial plane and form a dihedral angle of 17.6(1) and 21.6(1)° with the latter. This arrangement contrast with the planar geometry of the compartmental ligand L found in $[MnL(H_2O)_2]Cl$[37], where L has a methylethylene bridge in between the N atoms instead of the cyclohexyl group of the present complex. This conformation may be dictated by packing forces in order to accomplish the interactions described below. The complexes are arranged about a centre of symmetry and connected by the hydroxyl groups through pairs of O(3)-H…O(4) hydrogen bond interactions (Fig. 3, O…O distance of 2.736 Å), with O(4)-H that in turn binds the lattice water O(2w). Geometrical parameters for Hydrogen bond are given in Table 2. Moreover the aqua ligand O(1w) acts as H-bond donor towards hydroxyl group O(3) and phenolato oxygen O(1) (O…O distance of 2.688 and 2.825 Å, respectively), of symmetry related complexes giving rise to a 1D array running in the direction of axis *b* of the dimers described above.

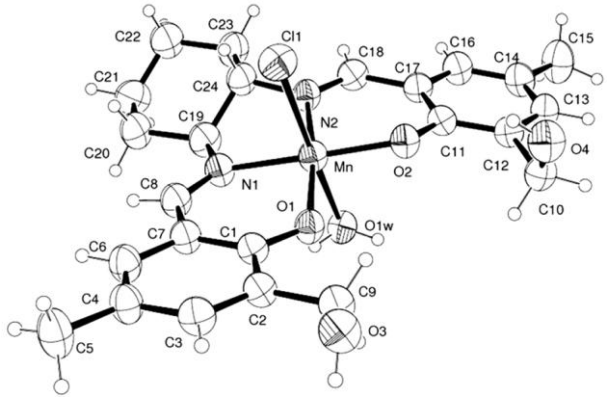


Fig. 1 — ORTEP drawing (ellipsoids at 40% probability) of **1**

Table 1 — Selected coordination bond lengths (Å) and angles (deg)

Bond distances (Å)		Bond angles (Å)			
Mn-O(1)	1.905(2)	O(1)-Mn-O(2)	94.85(9)	O(2)-Mn-Cl(1)	94.81(8)
Mn-O(2)	1.888(2)	O(1)-Mn-N(1)	91.05(10)	N(1)-Mn-N(2)	81.73(11)
Mn-N(1)	1.993(3)	O(1)-Mn-N(2)	172.10(11)	N(1)-Mn-O(1w)	90.93(11)
Mn-N(2)	1.979(3)	O(1)-Mn-O(1w)	90.50(10)	N(1)-Mn-Cl(1)	89.34(10)
Mn-O(1w)	2.258(2)	O(1)-Mn-Cl(1)	92.22(8)	N(2)-Mn-O(1w)	86.42(11)
Mn-Cl(1)	2.5572(14)	O(2)-Mn-N(1)	172.64(10)	N(2)-Mn-Cl(1)	90.92(9)
		O(2)-Mn-N(2)	92.12(11)	O(1w)-Mn-Cl(1)	177.26(7)
		(2)-Mn-O(1w)	84.65(10)		

Catecholase activity and Kinetic study

All of the mononuclear Mn^{III} complexes show a significant catalytic activity towards 3,5-di-*tert*-butylcatechol (3,5-DTBC). The substrate 3,5-DTBC with bulky substituents on the ring has a low quinone-catechol reduction potential which makes it easily oxidizable to the corresponding *o*-quinone, 3,5-di-*tert*-butylquinone. Moreover it is highly stable and shows maximum absorption at 401 nm in methanol. Kinetic experiments were performed in order to test the ability of complexes **1**-**4** to oxidize the substrate 3,5-DTBC to 3,5-DTBQ aerobically and all of them were observed to be potential catalysts in methanol medium. Fig. 4 shows the spectral changes for complex **1** as representative of the four on reaction with substrate 3,5-DTBC for 2 h course of reaction. The spectral changes for other complexes were given in Supporting Data.

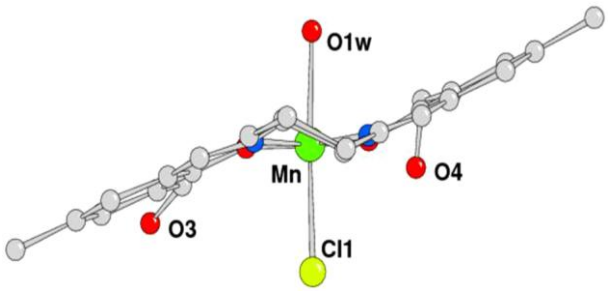


Fig. 2 — Side view of the complex showing the disposition assumed by the phenolato rings with respect to the equatorial coordination plane

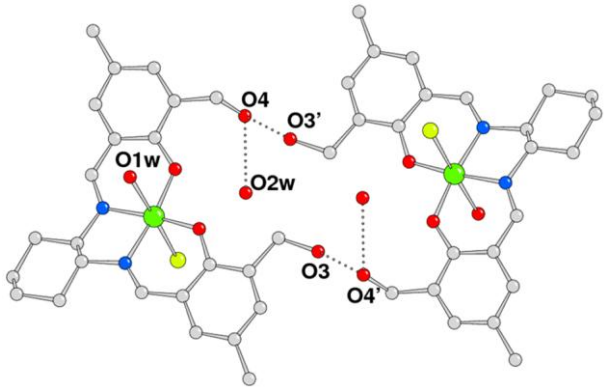


Fig. 3 — Crystal packing showing pair of complexes connected by H-bonds

The kinetics for the oxidation of 3,5-DTBC induced by **1**-**4** were determined by the initial rates method monitoring the increase of the product 3,5-DTBC at around 405 nm. The concentration of 3,5-DTBC was always kept at least 10 times larger than that of the Mn^{III} complex to maintain a pseudo-first-order condition. All kinetic experiments were conducted at 25 °C by using a thermostat. Initially, a series of solutions of the substrate 3,5-DTBC at different concentrations (0.001–0.05 mol.dm^{-3}) were prepared from a concentrated stock solution in MeOH medium. In each run, 2 mL of the substrate solution was poured in a 1 cm quartz cell and kept in the spectrophotometer to equilibrate the temperature at 25 °C. To this 0.04 mL of 0.005 mol dm^{-3} solution of Mn^{III} complexes were quickly added and mixed thoroughly to get an ultimate complex concentration of 1 x 10^{-4} mol dm^{-3}. By applying *GraFit32* program for enzymatic kinetics, the values of K_m and V_{max} are calculated. Fig. 5 shows the rate vs concentration plot obtained for complex **1** and the inset shows the

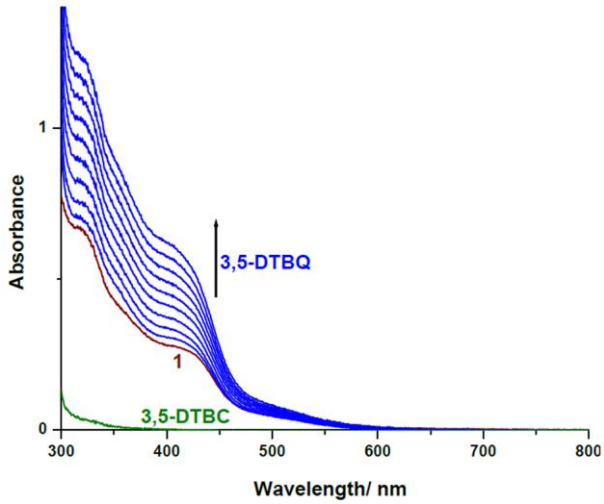


Fig. 4 — UV-visible spectra of 3,5-DTBC in MeOH (1 × 10^{-2} M), of complex **1** (1 × 10^{-4} M) and its changes upon addition of 100-fold 3,5-DTBC observed at intervals of 10 min

Table 2 — Hydrogen bond geometrical parameters

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A	
O3-H3	0.838	2.003	145.67	2.736	O4	-x,-y+1,-z+2
O4-H4	0.817	1.901	172.65	2.713	O2w	
O1w-H1w	0.847	1.842	177.18	2.688	O3	x+1,y,z
O1w-H2w	0.810	2.110	147.26	2.825	O1	-x+1,-y+1,-z+2
O2w-H3w	0.850	2.436	157.94	3.240	Cl1	-x,-y+2,-z+2
O2w-H4w	0.845	2.433	171.40	3.272	Cl1	

Lineweaver-Burk plot. Data for complexes **2, 3** and **4** are given in Supporting Data.

The initial rates method shows a first-order dependence on lower complex concentration. Since complexes **1-4** showed saturation kinetics at higher DTBC concentrations, a treatment based on Michaelis-Menten model seemed appropriate to be applied. All the experiments were performed three times, and Fig. 6 shows the Lineweaver-Burk plots (double reciprocal plot) for complexes **1-4** in methanol medium. The Lineweaver-Burk plots allow to evaluate kinetic parameters of different complexes, such as maximum velocity (V_{max}), Michaelis binding constant (K_M), rate constant for the dissociation of substrate (i.e., turnover number, k_{cat}), and the data are summarized in Table 3. From this data it is clear that the catalytic efficiency (on the basis of k_{cat} value) of the complexes follows the trends, **1**>**2**>**3**>**4**.

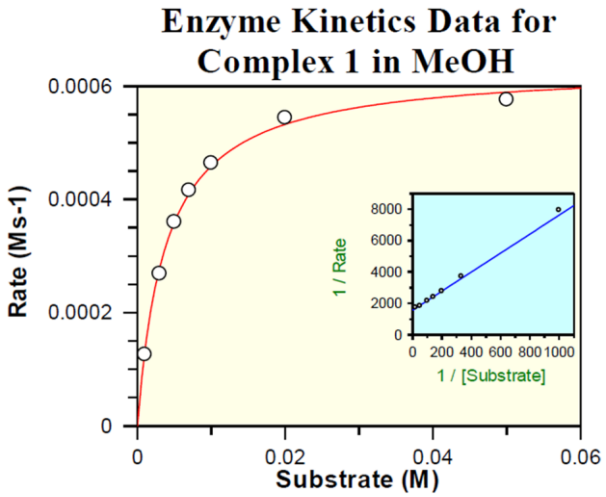


Fig. 5 — Dependence of initial rate on the concentration of the substrate for **1**

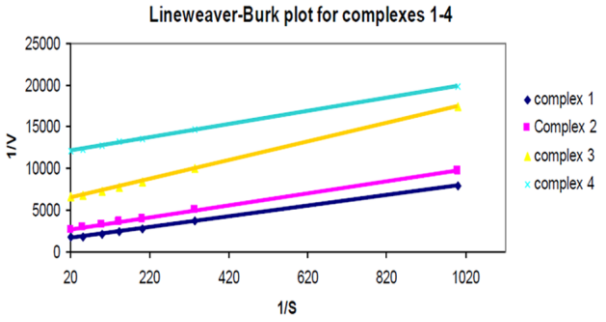


Fig. 6 — The Lineweaver-Burk plots (double reciprocal plot) for the complexes **1-4** in methanol medium

Effect of ligand backbone on catecholase activity

Kinetic parameters reported in Table 3 clearly indicate that the catalytic activities of the complexes were controlled by their structural properties. In fact, k_{cat} values changes appreciably on changing the imine portion of the ligand back-bone in L^1 -L^4. Substrate 3,5-DTBC undergoes oxidation to 3,5-DTBQ by a two electron transfer process in presence of aerial oxygen. Since in all the complexes the manganese ion exists in +3 oxidation state, it is rational to consider that in the catalytic process 3,5-DTBC is converted to 3,5-DTBQ with simultaneous reduction of Mn^{III} to Mn^{II}. The gradual decrease in inductive (+I) effect from L^1 to L^4 may stabilise the Mn^{II} intermediate and a steady increase in the k_{cat} values would be expected. But the experimental results indicate that complex **1** has highest efficiency followed by **2**, **3** and **4**, which may be rather attributed to the steric effect exerted by the alkyl bridge connecting the imino nitrogens in the L^1-L^4 system. The insertion of bulky alkyl group into the imine arm causes disruption of the equatorial moiety from planarity driving the substrate more efficiently towards the metal centre for interaction. The cyclohexyl substituent disrupts the planarity to the highest extent followed by ligand systems L^2, L^3 and L^4. Thus, the metal centre in complex **1** will be more exposed to the substrate for its interaction leading to the highest catalytic efficiency. This type of observation is also reported earlier by our group[37] It is also noted that on changing the aldehyde from 2,6-difomyl-4-methyl phenol[37] to 2-hydroxy-3-hydroxymethyl-5-methylbenzaldehyde the catalytic efficiency almost increased to 1.5 times.

Table 3 — Kinetic Parameters for **1-4** in MeOH medium

Complex	V_{max} (Ms^{-1})	K_M (M)	k_{cat} (h^{-1})
1	$0.0006 \pm 1.03 \times 10^{-5}$	$0.0038 \pm 2 \times 10^{-4}$	2.16×10^4
2	$0.0004 \pm 1.90 \times 10^{-6}$	$0.0029 \pm 5.21 \times 10^{-5}$	1.44×10^4
3	$0.0002 \pm 1.68 \times 10^{-6}$	$0.0017 \pm 8.55 \times 10^{-5}$	7.2×10^3
4	$0.000084 \pm 2.83 \times 10^{-7}$	$0.0007 \pm 1.67 \times 10^{-5}$	3.02×10^3

Table 4 — Epoxidation of (*E*)-stilbene and styrene catalyzed by complexes **1**–**4** in DCM and MeCN

Catalyst	Solvent	Time (h)	Oxidant PhIO		Time (h)	Oxidant NaOCl	
			Epoxide yield (%)			Epoxide yield (%)	
			(*E*)-Stilbene	Styrene		(*E*)-Stilbene	Styrene
1	DCM	2	78	60	3	33	56
2	DCM	2	72	56	3	28	53
3	DCM	2	67	52	3	21	49
4	DCM	2	63	49	3	19	46
1	MeCN	2	86	72	3	37	65
2	MeCN	2	83	68	3	31	61
3	MeCN	2	78	66	3	24	57
4	MeCN	2	75	58	3	23	55

Epoxidation activity study

The catalytic activity of all the complexes in presence of iodosylbenzene (PhIO) on substrate *E*-stilbene/styrene was measured in acetonitrile (MeCN) and dichloromethane (DCM) medium at room temperature. Freshly prepared PhIO (0.300 mmol) was added to the reaction mixture containing 0.300 mmol of olefin and 0.01 mmol of Mn^{III} complex (catalyst) in 5 mL freshly distilled MeCN/ DCM. The suspension was stirred vigorously for 2 h and the crude product obtained is separated through column chromatography and characterised through ^{1}H-NMR. When the oxidant was sodium hypochlorite, the solution was buffered at pH 11.3 with NaH_2PO_4 and NaOH and the reaction temperature maintained at 0 °C. To the buffered solution of the oxidant, 0.04 mmol of Mn^{III} complex (catalyst) and 10 mmol of olefin (*E*-stilbene /styrene) in 10 mL of MeCN/ DCM were added and stirred for 3 h. The product was isolated through partition chromatography followed by flash chromatography[21(b)].

Complexes **1-4** generate a brown coloured solution (in both solvents) which is intensified upon oxidant (PhIO or NaOCl) addition. When olefin (*E*-stilbene/ styrene) is added to it, the colour starts fading and after completion of reaction the solution regains its colour, almost identical to the pure complex solution. Data in Table 4 reports the percentage of epoxide yield and the time required to get the maximum yield on substrate (*E*)-stilbene and styrene either in MeCN or DCM medium and by using using PhIO and NaOCl as oxidant. All the complexes **1-4** oxidise (*E*)-stilbene much effectively than styrene and the catalytic efficiency increases in the following order **4** < **3** < **2** < **1**, either in DCM and MeCN medium: Moreover it is evident that NaOCl acts as a better terminal oxidant for styrene oxidation as we reported earlier[36]. The data in Table 4 also suggest that MeCN provides better medium (than DCM) for epoxidation in terms of product yield regardless of the oxidant, catalyst or substrate used. Moreover PhIO was found to be a far better source of oxygen than NaOCl.

Effect of ligand backbone

The data listed above clearly indicates that epoxide yield varies by tuning the steric factor of the ligand back-bone, and the introduction of bulky substituents in the imine moiety of the ligand improves the epoxide yield. Oxidation with PhIO proceeds via Mn(V)=O species formation so it is logical to think that substituent with electron releasing group or having inductive (+I) effect can increase the stability of the higher oxidation state and thus formation of the product. On the other hand, presence of bulky groups on the ligand would force the Mn=O bond to bend away from the imine side, thereby facilitating the approach of the olefin from the hydroxymethyl portion of the ligand which also reinforces the product formation. This is actually found to be the case as the epoxide yield increases on going from complex **4** to **1**. When NaOCl is used as terminal oxidant the oxidation occurs with involvement of Mn(III)-O-Cl species. Here also the diimine bridge substituent has a pronounced effect on the catalytic efficiencies as discussed above in case of PhIO, and the catalytic activity of the complexes follows the same trend.

Conclusions

Four new mononuclear manganese(III) complexes of salen-type Schiff-base ligands have been synthesised, characterised and their catalytic efficiency has been studied during the oxidation of 3,5-DTBC in MeOH medium aerobically and in the epoxidation of *(E)*-stilbene /styrene in DCM/MeCN medium in presence of PhIO and NaOCl as terminal oxidant. The structural differences of the ligand system in four

complexes observed to regulate the efficiency of the catecholase activity and epoxidation. The steric and electronic effects of the substituents present on the back-bone of the salen-type ligand work parallel to improve the epoxidation yield and therefore complex **1** exhibits the highest efficiency during epoxidation of olefins. On the contrary, steric effect prevails over the electronic effect during catechol oxidation and consequently complex **1,** again shows the highest activity to catalyze the oxidation. In epoxidation reaction MeCN acts as a better solvent than DCM and PhIO seems to be better oxidant than NaOCl. Epoxidation by the two different terminal oxidants proceed via different intermediate which are being advocated by several groups including us[36] has been verified here once again.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(02)169-176_ SupplData.pdf.

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