

Mono- and bi-metallic Mn(III) complexes of macroacyclic salen type ligands: Syntheses, characterization and studies of their catalytic activity

Tanmay Chattopadhyay^a, Samimul Islam^b, Munirathinam Nethaji^{c,*},
Adinath Majee^b, Debasis Das^{a,*}

^a Department of Chemistry, University of Calcutta, 92, A.P.C. Road, Kolkata 700009, India

^b Department of Chemistry, Visva-Bharati University, Santiniketan 731235, India

^c Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Received 3 March 2006; received in revised form 23 November 2006; accepted 29 November 2006

Available online 15 December 2006

Abstract

Complex **1**, a six-coordinated Mn(III) species of a macroacyclic salen type ligand L [L = *N,N'*-cyclohexanebis(3-formyl-5-methylsalicylaldimine)] having two axial positions occupied by water molecules with chloride as counter anion has been synthesized and characterized by X-ray single crystal structure analysis. Structural analysis reveals that it is the N₂O₂ site, and not the O₄ site, of L that acts as the potential ligating site to accommodate Mn(III) ion. In order to put second metal close to the Mn(III) center the two formyl groups of L were condensed with aniline to generate another O₂N₂ site and subsequent reaction with MCl_x produced a series of bimetallic complexes MnML'_xCl_x·yH₂O [M = Zn(II), Cu(II), Ni(II), Co(II), Fe(III) and Mn(III); x = 3 or 4 depending on the oxidation state of M; L' = condensation product of L with aniline; y = 2 or 3]. The bimetallic complexes have been characterized by elemental analyses, UV–vis and IR spectroscopic, magnetic susceptibilities and thermogravimetric analyses. The catalytic property of the complexes for epoxidation of alkenes has been investigated in the presence of two terminal oxidants PhIO and NaOCl, with two solvents CH₃CN and CH₂Cl₂. As alkenes styrene and (*E*)-stilbene have been chosen for investigation. The study suggests the possibility of atleast another active epoxidizing species, most probably (salen)Mn(III)OCl, in addition to the discrete Mn(V)=O(salen) species in epoxidation of olefins depending upon whether NaOCl or PhIO is used as terminal oxidants. Complex **1** is observed to exhibit the highest efficiency to catalyze the epoxidation of both the substrates irrespective of the terminal oxidant and solvent used, whereas the bimetallic complexes exhibit moderate to poor activity. The study has also established that as solvent CH₃CN and as terminal oxidant PhIO are the better options for epoxidation of both styrene and (*E*)-stilbene. The UV–vis spectroscopic studies imply that the detrimental effect of the second metal present in the close vicinity of Mn(III) center on the catalytic efficiency of Mn(III) is a consequence of the slow rate of formation of the active intermediate Mn(V)=O species as well as the gradual decomposition of the binuclear complexes in the presence of PhIO.

© 2006 Published by Elsevier B.V.

Keywords: Macroacyclic ligands; Mn(III) complexes; Epoxidation of alkenes

1. Introduction

Metal catalyzed oxidations of organic substrates are of immense importance from synthetic as well as biochemical points of view. Several metal(salen) complexes have been investigated as epoxidation catalysts and as model systems of various metalloproteins e.g. cytochrome P-450. Amongst them Mn(III)(salen) complexes are the most promising. The choice

of (salen) ligand system is unique not only for its features in common with the porphyrin system with respect to electronic structure but also for its desirable characteristic of being readily subject to systematic modification of its electronic and steric factors as per requirements. Role of steric and electronic factors exerted by the substituents present on the backbone of the (salen) ligands, the influence of different solvents like dichloromethane, acetonitrile, etc. and the effectiveness of the terminal oxidants like PhIO, peroxide, NaOCl, etc. on the epoxidation yield and especially on the enantiomeric excess have been studied by several groups [1–15]. In spite of monumental works the mechanism for the Mn(III)(salen)-catalyzed epoxidation of

* Corresponding authors. Tel.: +91 33 24837031; fax: +91 33 23519755.
E-mail address: dasdebasis2001@yahoo.com (D. Das).

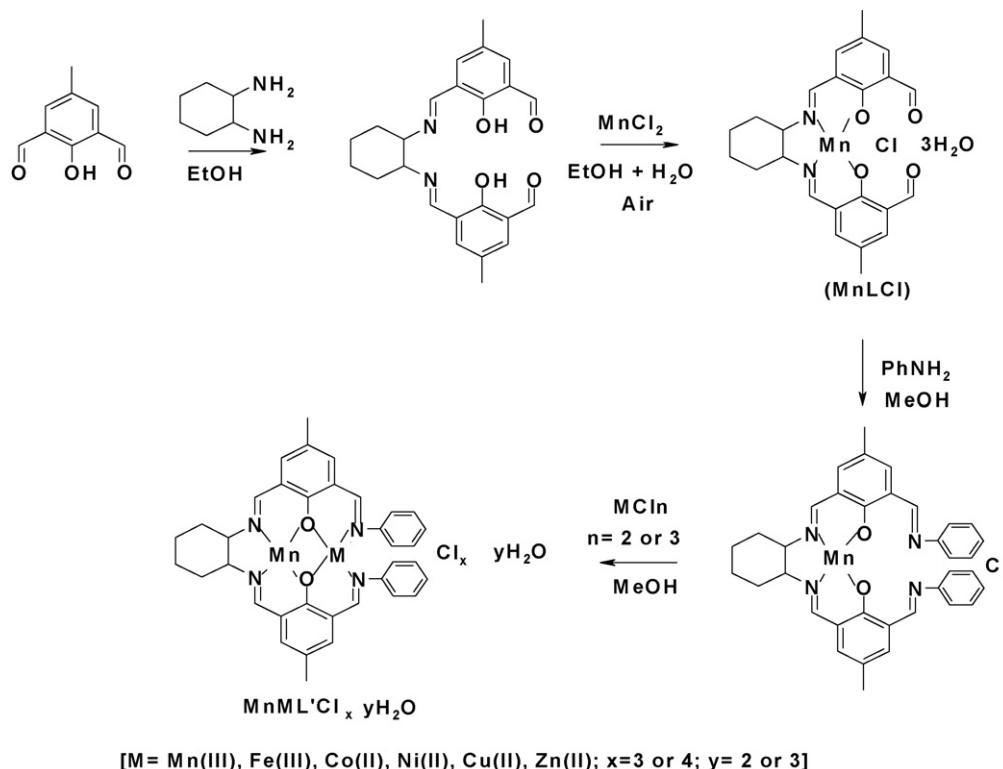
olefins is a topic of great controversy. However, the general mechanism of cytochrome P-450 catalyzed oxo transfer may be considered as the guideline for the mechanistic pathway through which the Mn(III)(salen) catalyzed epoxidation of olefins may proceed in the presence of terminal oxidant like PhIO [16]. Nature has designed several bimetallic metalloproteins to carry out various biochemical reactions. The role of the second metal in many cases is functional but in some cases only structural. Surprisingly, reports on the effect of second metals in the close vicinity of the Mn(III) center of Mn(III)(salen) complexes on the catalytic efficiency of Mn(III)(salen) species are very scanty [17,18].

Our aims are to investigate and to rationalize the effect of the second metal present in close proximity to the Mn(III) center in Mn(III)(salen) complexes on their catalytic activity as epoxidation catalysts using two common terminal oxidants PhIO and NaOCl with two of the most commonly used solvents dichloromethane and acetonitrile, to verify the possibility of the existence of more than one active intermediates in Mn(III)(salen) catalyzed epoxidation of alkenes. Accordingly we have designed “salen” ligand in such a way so that mononuclear Mn(III)(salen) complex may be utilized to synthesize bimetallic complexes and we are reporting herein synthesis of bimetallic Mn(III) complexes based on monomanganese complex of *N,N'*-cyclohexanebis(3-formyl-5-methylsalicylaldehyde) (L) and their catalytic activity as epoxidation catalysts of alkenes to understand the influence of the second metal as well as the solvent and oxygen donor effects on the catalytic efficiency of the Mn(III) center.

2. Results and discussion

2.1. Synthesis procedure and characterization

Synthesis of *N,N'*-ethylenebis(3-formyl-5-methylsalicylaldehyde) (L1) and its Ni(II) and Cu(II) complexes was first reported by Okawa and Kida [19]. In 1981, Gagne et al. reported Ni(II) and Cu(II) complexes of *N,N'*-propylenebis(3-formyl-5-methylsalicylaldehyde) (L2) [20]. Those ligand systems are interesting since they may be utilized as compartmental ligands with N₂O₂ and O₄ binding sites to synthesize bimetallic complexes. The complexes of L1 and L2 were characterized by elemental analyses, magnetic moment, IR and UV–vis spectroscopic studies and it has been proposed that the metal ions preferentially bind to the N₂O₂ site instead of O₄ site of the ligands. This proposition was established by X-ray single crystal structure analysis of Mn(III)(L1)Cl complexes by Das and Cheng in 2000 and it is to be noted that even in the presence of large excess of metal ion always mononuclear metal complex was isolated [17]. Synthesis of *N,N'*-cyclohexanebis(3-formyl-5-methylsalicylaldehyde) (L) and its metal complexes have also been reported in the same year, albeit with different anion from what we are reporting here and furthermore catalytic activity of Mn(III) species in that ligand system has not been studied [21]. Therefore, we prepared the ligand L and its monomanganese complex with chloride as counter anion and characterized it structurally by the single crystal X-ray diffraction method (*vide infra*). This time also we failed to prepare bimetallic complexes containing Mn(III) from the monometallic species and thus



Scheme 1. Synthetic out-line of macroacyclic salen type ligands and their mono- and bi-metallic Mn(III) complexes.

Table 1
Effective magnetic moments of the complexes 1–7 at 300 K

Complex	μ_{eff}/μ_B	$\mu_{\text{spin only}}^a/\mu_B$	M: S ^b
1	4.79	4.90	–
2	4.78	4.90	Zn(II): 0
3	5.09	5.20	Cu(II): 1/2
4	5.61	5.66	Ni(II): 1
5	6.16	6.24	Co(II): 3/2
6	7.48	7.68	Fe(III): 5/2
7	6.78	6.93	Mn(II): 2

^a Calculated based on the assumption that Mn(III) is in a high spin state in all the complex.

^b The metal ion and the spin state of second metal in complexes 2–7 used to calculate $\mu_{\text{spin only}}$.

proved that O₄ site of those macrocyclic salen-type ligands may not be used as a binding site to accommodate the second metal in that compartment. Just like the previous case [17] we overcome this difficulty by condensing the formyl groups with aniline to create another O₂N₂ site for the accommodation of the second metal in Mn(III)L system (Scheme 1). The six bimetallic Mn(III)ML/Cl_x·yH₂O complexes (M = Zn(II), x = 3, y = 2; M = Cu(II), x = 3, y = 2; M = Ni(II), x = 3, y = 3; M = Co(II), x = 3, y = 2; M = Fe(III), x = 4, y = 2; M = Mn(III), x = 4, y = 3) were synthesized by the reactions of Mn(III)L(H₂O)₃Cl with aniline and various metal chlorides (Scheme 1).

The complex 1 exhibits characteristic IR bands at 1662, 1623 and 1548 cm⁻¹ assigned to C=O, C=N and skeletal vibrations [4(a),4(h),5(a),17]. In bimetallic complexes the 1662 cm⁻¹ band is observed to be absent, whereas the other two bands remain, suggesting the complete condensation of the formyl groups of L with aniline. Table 1 represents the effective magnetic moments of the complexes at 300 K along with the expected spin only values. The effective magnetic moment of complex 1 suggests that Mn(III) is present in the complex with the high spin d⁴ configuration. In the case of binuclear complexes the room temperature effective magnetic moments are slightly lower than their corresponding spin only values, but it is not possible to comment on the magnetic interactions between the metal centers from room temperature magnetic measurements alone. However, it is evident from the data that both Mn(III) and the second metal ion are in their high spin state. Here it is to be noted that the diamagnetic corrections due to four extra (CH₂) groups present in L compared to L1 contribute only at three decimal place and therefore the observed μ_{eff}/μ_B values reported in Table 1 coincide exactly with the magnetic moments obtained for the complexes of L1 studied earlier [17]. The water content in the complexes has been verified by appropriate weight losses in their thermogravimetric (TG) analyses. These weight losses and their corresponding temperatures are noted in Section 3.

2.1.1. Description of structure of complex 1

The structure of complex MnLCl·4H₂O·(1/2)CH₃CN has been depicted in Fig. 1; selected bond lengths and angles are given in Table 2. Mn(III) in this complex is six-coordinated and the geometry can be best described as slightly distorted elongated octahedral. The two phenolic O atoms and the two

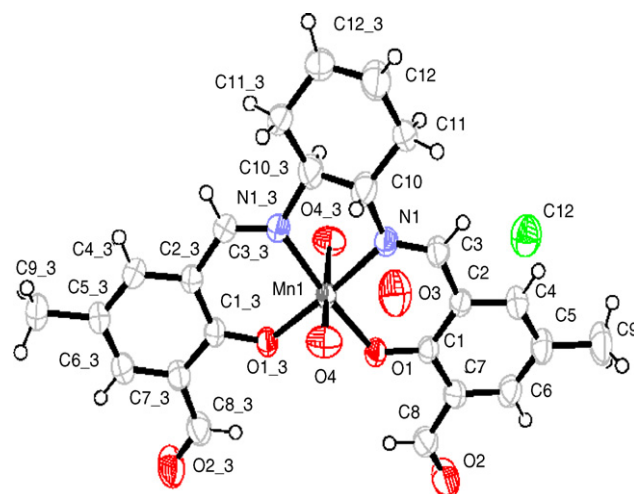


Fig. 1. ORTEP [28] view of complex 1·(1/2)CH₃CN with atom numbering scheme (CH₃CN and H₂O molecules of crystallization have not been shown for clarity).

imine N atoms of Schiff-base constitute the basal plane and two O atoms of two water molecules are occupying the axial positions. The Mn–O (phenolic O) and Mn–N distances of 1.881 (4) and 1.986 (4) Å, respectively, are comparable to those previously reported for Mn(III)(salen) derivatives with or without the presence of formyl groups [1,2,4(a),17,21]. The Mn–O (water) distance of 2.247 (4) Å is also consistent with the corresponding values of similar systems [2,21]. The longer axial distances are responsible for the elongated octahedral geometry of the complex. Fig. 2 represents the packing diagram of the

Table 2
Selected bond lengths (Å) and angles (°) for complex 1·(1/2)CH₃CN

Mn1–O1	1.881(4)
Mn1–O4	2.247(4)
Mn1–N1	1.986(4)
C7–C8	1.461(6)
O1–C1	1.314(5)
O2–C8	1.201(6)
N1–C3	1.275(5)
C10–C11	1.504(7)
N1–C10	1.486(6)
C1–C2	1.421(5)
C1–C7	1.416(6)
C11–C12	1.505(7)
O1–Mn1–O4	93.63(12)
O1–Mn1–N1	92.79(13)
O1–Mn1–O1.a	91.69(13)
O1–Mn1–O4.a	91.68(12)
O1–Mn1–N1.a	175.09(13)
O4–Mn1–N1	86.02(12)
O1.a–Mn1–O4	91.68(12)
O4–Mn1–O4.a	172.37(11)
O4–Mn1–N1.a	88.26(12)
O1.a–Mn1–N1	175.09(13)
O4.a–Mn1–N1	88.26(12)
N1–Mn1–N1.a	82.82(13)
O1.a–Mn1–O4.a	93.63(12)
O1.a–Mn1–N1.a	92.79(13)

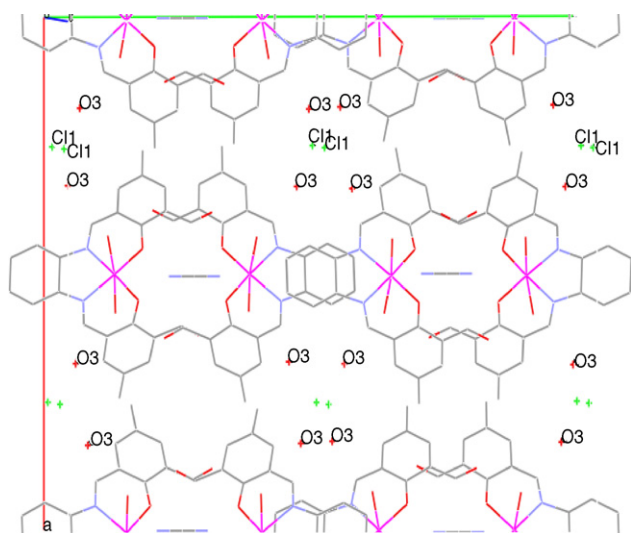


Fig. 2. Packing diagram of unit cell showing 16 isolated water molecules and eight Mn(III)(salen) molecules in the unit cell.

complex, there are 16 isolated water molecules in the unit cell, each unit cell comprises of eight Mn(III)(salen) species and thus each Mn(III)(salen) molecule shares on an average two isolated water molecules. The complex also contains half molecule of acetonitrile of crystallization which is different from that found for the species described in Section 3 and this results from different crystallization conditions. It is noteworthy that the present result also verified once again that the formyl groups of this kind of compartmental ligands do not participate in coordination with metal atom and the proposition of N₂O₂ site as the coordination site in CuL1, CuL2, NiL1 and NiL2 complexes [19,20]. The acetonitrile group is sitting on the special position and the middle carbon is sitting on a two-fold special position and the carbon and nitrogen (end ones) on it is flipping between two positions. But they could be assigned as neither nitrogen nor carbon.

2.2. Epoxidation of alkenes

Complexes **1–7** are highly soluble in CH₃CN. Complex **1** is less soluble in CH₂Cl₂, whereas all bimetallic complexes are highly soluble in that solvent. All the complexes in both of those solvents produce a brown color solution after dissolution. The color is intensified on addition of the terminal oxidants. When substrates are added the color starts fading and when complete consumption of the substrates takes place, the intensity of the color turns back nearly to the original intensity, indicating the catalyst regeneration. Epoxidation reactions are carried out at room temperature.

2.2.1. Epoxidation with sodium hypochlorite

Tables 3 and 4 represent the maximum isolated yield (%), conversion (%) and time required to obtain the maximum yield for styrene and (*E*)-stilbene epoxidation, respectively, using NaOCl as terminal oxidant in the presence of two solvents CH₂Cl₂ and CH₃CN. The data of Table 3 reveal that in CH₂Cl₂, the isolated yield of styrene epoxide ranges from 9% to 57%,

Table 3
Epoxidation of styrene catalyzed by complexes **1–7** in CH₂Cl₂ or CH₃CN using NaOCl as terminal oxidant

Catalyst	Time (h)	Solvent	Conversion (%)	Epoxide yield (%) ^a
1	2	CH ₂ Cl ₂	65	57
	2	CH ₃ CN	72	66
2	3	CH ₂ Cl ₂	40	33
	3	CH ₃ CN	48	42
3	3	CH ₂ Cl ₂	15	9
	3	CH ₃ CN	23	17
4	3	CH ₂ Cl ₂	39	32
	3	CH ₃ CN	46	39
5	3	CH ₂ Cl ₂	49	41
	3	CH ₃ CN	53	47
6	3	CH ₂ Cl ₂	25	19
	3	CH ₃ CN	33	27
7	3	CH ₂ Cl ₂	51	43
	3	CH ₃ CN	58	49

^a Isolated yield based on olefin.

whereas slightly better yield (17–66%) is obtained when CH₃CN is used as solvent. From the data it is also clear that complex **1** exhibits the highest efficiency in both the solvents. The efficiency of the binuclear catalysts in the styrene epoxidation follows the following trend: **7** > **5** > **4** ~ **2** > **6** > **3**. However, Table 4 shows that very low conversion and epoxide yields are obtained on (*E*)-stilbene epoxidation even when complex **1** is used as catalyst irrespective of the solvents used and that virtually no epoxidation are observed when complexes **2**, **3**, **4** and **6** are used as catalyst. Thus, NaOCl is not functioning as a good terminal oxidant in the case of (*E*)-stilbene epoxidation.

Table 4
Epoxidation of (*E*)-stilbene catalyzed by complexes **1–7** in CH₂Cl₂ or CH₃CN using NaOCl as terminal oxidant

Catalyst	Time (h)	Solvent	Conversion (%)	Epoxide yield (%) ^a
1	3	CH ₂ Cl ₂	20	16
	3	CH ₃ CN	25	23
2	3	CH ₂ Cl ₂	b	b
	3	CH ₃ CN	b	b
3	3	CH ₂ Cl ₂	b	b
	3	CH ₃ CN	b	b
4	3	CH ₂ Cl ₂	b	b
	3	CH ₃ CN	b	b
5	3	CH ₂ Cl ₂	10	7
	3	CH ₃ CN	11	9
6	3	CH ₂ Cl ₂	b	b
	3	CH ₃ CN	b	b
7	3	CH ₂ Cl ₂	10	7
	3	CH ₃ CN	13	12

^a Isolated yield based on olefin.

^b No conversion/yield was obtained.

Table 5
Epoxidation of styrene catalyzed by complexes **1–7** in CH₂Cl₂ or CH₃CN using PhIO as terminal oxidant

Catalyst	Time (h)	Solvent	Conversion (%)	Epoxide yield (%) ^a
1	2	CH ₂ Cl ₂	61	65
	2	CH ₃ CN	84	79
2	3	CH ₂ Cl ₂	44	36
	3	CH ₃ CN	54	52
3	3	CH ₂ Cl ₂	19	16
	3	CH ₃ CN	28	26
4	3	CH ₂ Cl ₂	42	39
	3	CH ₃ CN	56	53
5	3	CH ₂ Cl ₂	58	55
	3	CH ₃ CN	62	59
6	3	CH ₂ Cl ₂	29	27
	3	CH ₃ CN	39	37
7	3	CH ₂ Cl ₂	61	59
	3	CH ₃ CN	69	66

^a Isolated yield based on olefin.

2.2.2. Epoxidation with PhIO

Tables 5 and 6 show the maximum isolated yield (%) and conversion (%) for styrene and (*E*)-stilbene epoxidation, respectively, using PhIO as terminal oxidants in the presence of two solvents CH₂Cl₂ and CH₃CN. On comparing Tables 3 and 5 it may be stated that (i) on changing the terminal oxidant from NaOCl to PhIO much improvement in the epoxide yield for styrene epoxidation is observed; (ii) solvent effect becomes prominent (the isolated yield of styrene epoxide ranges from 16% to 65% in CH₂Cl₂ and 26% to 79% in CH₃CN). From Tables 4 and 6 it becomes evident that dramatic improvement in isolated yield, conversion and even time required obtaining maximum yields have taken place in (*E*)-stilbene epoxidation

Table 6
Epoxidation of (*E*)-stilbene catalyzed by complexes **1–7** in CH₂Cl₂ or CH₃CN using PhIO as terminal oxidant

Catalyst	Time (h)	Solvent	Conversion (%)	Epoxide yield (%) ^a
1	1	CH ₂ Cl ₂	81	79
	1	CH ₃ CN	89	87
2	1	CH ₂ Cl ₂	52	49
	1	CH ₃ CN	59	58
3	1	CH ₂ Cl ₂	26	23
	1	CH ₃ CN	32	31
4	1	CH ₂ Cl ₂	51	49
	1	CH ₃ CN	61	60
5	1	CH ₂ Cl ₂	71	70
	1	CH ₃ CN	77	75
6	1	CH ₂ Cl ₂	39	37
	1	CH ₃ CN	44	43
7	1	CH ₂ Cl ₂	69	67
	1	CH ₃ CN	77	76

^a Isolated yield based on olefin.

on changing the terminal oxidant from NaOCl to PhIO. Here also the solvent effect is very much prominent. Complex **1** is observed to be a very good catalyst for the epoxidation of both the substrates and catalytic activity of the binuclear complexes follows the trend: **7** > **5** > **4** ~ **2** > **6** > **3**.

2.2.3. Effect of solvent

CH₃CN is a better solvent than CH₂Cl₂ for epoxidation of both the substrates, styrene and (*E*)-stilbene irrespective of the catalyst used. The slight improvement in epoxidation yield of styrene with sodium hypochlorite as the oxygen source on changing the solvent from CH₂Cl₂ to CH₃CN is most probably related to higher solubility of the catalysts in CH₃CN. When PhIO is used as oxygen source in addition to the solubility effect the minimization of the formation of benzaldehyde and other chlorinated products in styrene epoxidation in CH₃CN are also to be taken in account to explain the better efficiency of CH₃CN as solvent for the epoxidation of styrene [7,9,15].

2.2.4. Effect of terminal oxidant

PhIO is observed to be a far better oxygen source than NaOCl irrespective of the substrates, solvents or catalysts used. Interestingly, epoxidation of (*E*)-stilbene with NaOCl as terminal oxidant does not work well. It is generally accepted that Mn(III)–(salen) catalyzed epoxidations proceed with formation of Mn(V)=O species as the actual oxidant [4–6]. If Mn(V)=O species were the only oxidant in the epoxidation of olefins, irrespective of which oxygen donor is used to produce the species, the percentage of (*E*)-stilbene oxide should be at least comparable for a particular catalyst. But this is not the case in our present study. The divergence can only be explained if we consider the formation of at least another oxidant in Mn(III)(salen) catalyzed epoxidations depending on the oxygen source. The involvement of two different active intermediates: (i) [L–O–Mn(III)(salen)X] and (ii) [O=Mn(V)(salen)X] in Mn(III)(salen) catalyzed epoxidation of olefins have recently been proposed by several research groups [8,9,13,15]. It is also established that with NaOCl as the oxygen source the epoxidation proceeds with the formation of active intermediate [L–O–Mn(III)(salen)X] where the leaving group L (here Cl) transfers the oxygen to the alkene by a concerted step. It is now reasonable to consider that due to much greater steric effect exerted by (*E*)-stilbene compared to styrene the transition intermediate formed by (*E*)-stilbene and [L–O–Mn(III)(salen)X] is too unstable to generate epoxide in appreciable amount and thus we have observed very poor yield in epoxidation of (*E*)-stilbene when NaOCl was used as oxygen source.

2.2.5. Epoxidation kinetics using (*E*)-stilbene as substrate, PhIO as terminal oxidant and CH₃CN as solvent

Since our complexes act as better catalysts in epoxidation of (*E*)-stilbene in CH₃CN using PhIO as oxygen source compared to their activity in the presence of NaOCl as terminal oxidant and CH₂Cl₂ as solvent we have studied in detail epoxidation kinetics using (*E*)-stilbene as substrate, PhIO as terminal oxidant and CH₃CN as solvent. Fig. 3(A) and (B) represent the amounts of PhI and epoxide formed in epoxidation of (*E*)-

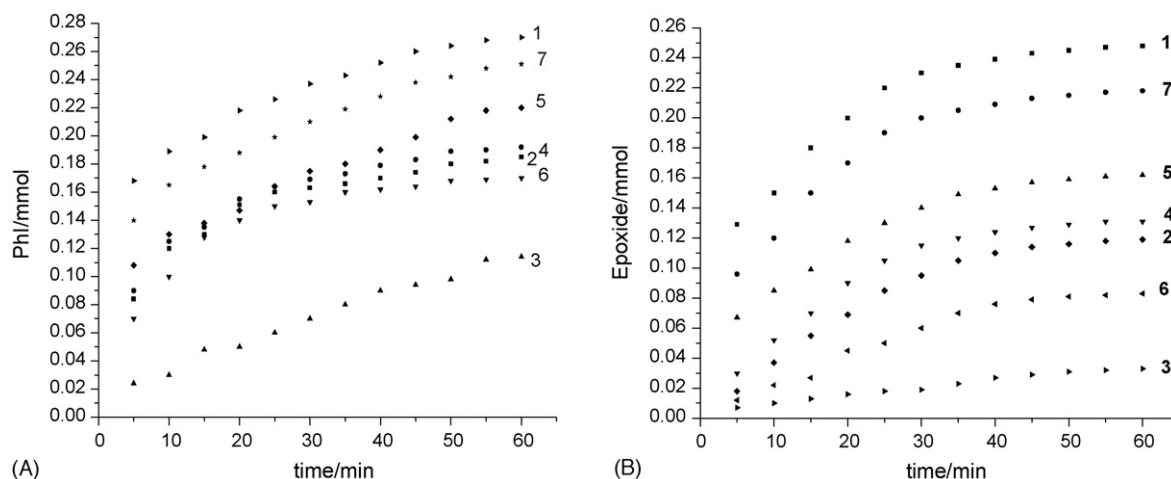


Fig. 3. (A) PhI formation as a function of time in the epoxidation of (*E*)-stilbene with PhIO catalyzed by complexes **1–7** and (B) epoxidation formation as a function of time for the epoxidation of (*E*)-stilbene with PhIO catalyzed by complexes **1–7**. [0.300 mmol of alkene, 1.00×10^{-2} mmol of catalyst and 0.300 mmol of PhIO in 5 mL dry acetonitrile at 25 °C.]

stilbene as a function of time catalyzed by complexes **1–7**, respectively. Within 5 min 0.168 mmol of PhI and 0.129 mmol of *trans*-stilbene oxide were formed by complex **1** catalysis, whereas those amounts were in the range of 0.024–0.140 mmol and of 0.007–0.096 mmol, respectively when the binuclear complexes **2–7** were used as catalysts. From the figures, it is clear that initially both PhI and epoxide formation are rapid, except for complex **3** catalyzed reactions and that after 30 min the rates slowed down in all cases. From Fig. 3(A) and (B) it is evident that complex **1** is the most efficient catalyst in producing *trans*-stilbene oxide and that the order of efficiency for binuclear complexes is $7 > 5 > 4 \sim 2 > 6 > 3$. This observation is entirely consistent with the earlier report [17]. The above experimental results reveal that the presence of a second metal in close proximity to the Mn(III) centers as in complexes **2–7** reduces the catalytic activity of the Mn(III) centers.

There may be several possible explanations for poor activity of Mn(III) center in the presence of second metal in its close vicinity. First, PhIO may undergo decomposition in bimetallic complex catalyzed reactions to produce some unwanted products instead of forming PhI and Mn(V)=O species, the species supposed to be the reactive intermediate in the catalytic cycle of alkenes epoxidation. Second, the formation of Mn(V)=O intermediate may be slowed down or its formation may be hindered in the presence of the second metal in close proximity to Mn(III) center. Third, the oxygen atom transfer from Mn(V)=O to alkenes may be slowed down in the presence of the second metal close to Mn(III) center. The first possibility is not very important in our case since our study of the reactions of the catalysts **1–7** with PhIO (0.010 mmol of catalyst and 0.300 mmol of PhIO in 5 mL dry acetonitrile) in the absence of any substrate show that complex **1** produces 0.138 mmol of PhI and that the binuclear complexes yield 0.05–0.10 mmol of PhI after 1 h reaction, being consistent with the PhI formation for catalysts **1–7** as shown in Fig. 3(A). Here it is noteworthy that in a blank experiment (no catalyst) no PhI was detected in the reaction media. Since the order of effectiveness of catalysts **2–7** does

not correlate with the charge of the second metal ion the third possibility may not be very crucial. It may be assumed that the presence of second metal may affect the coordination environment, both sterically and electronically, of the reactive Mn(III) center or Mn(V)=O intermediate and therefore the second possibility is most probably the vital one for poor catalytic activity of the binuclear species. We have not been able to synthesize the single crystals of any binuclear species till date to get better understanding of this point at this moment.

In order to determine the nature of the complexes **1–7** in the catalytic cycle we studied the UV–vis spectral changes for the complexes in the presence of PhIO (1.00×10^{-3} mmol complex in 5 mL dry acetonitrile was treated with 0.300 mmol of PhIO). The results for complexes **5** (as the representative of the binuclear complexes **2–7** since all of them exhibit similar changes in their UV–vis spectra) and **1** are shown in Fig. 4(A) and (B), respectively. Fig. 4 shows spectra before addition of PhIO (solid line) after 1 h reaction with PhIO (short dash line) and after 1 day of the reaction (dash line). After 1 h both complexes **1** and **5** produce similar spectra, which are totally different from their original patterns. After 1 day the spectrum obtained from the binuclear complex shows some decomposition and fresh addition of PhIO and alkene yielded no epoxidation as is evident from GC analysis, indicating that the binuclear complexes lose their catalytic activity most probably due to the formation of decomposed inactive species after 1 day. On the other hand, after 1 day the spectrum produced by complex **1** does not show any decomposition although this spectrum is not similar to the original spectrum of complex **1**. Addition of fresh PhIO and alkene and subsequent GC analysis after 1 h shows the formation of epoxide with nearly of the same yield as shown in Table 4. Now it may be inferred that complex **1** after 1-day reaction does not back to its original geometry but to a species which retains the catalytic activity. We may rationalize the fact by considering that six-coordinated complex **1** in the first step of catalytic cycle loses one-coordinated water molecule to form a five-coordinated species, **1a** (Scheme 2). This five-coordinated species **1a** actually reacts with PhIO to produce

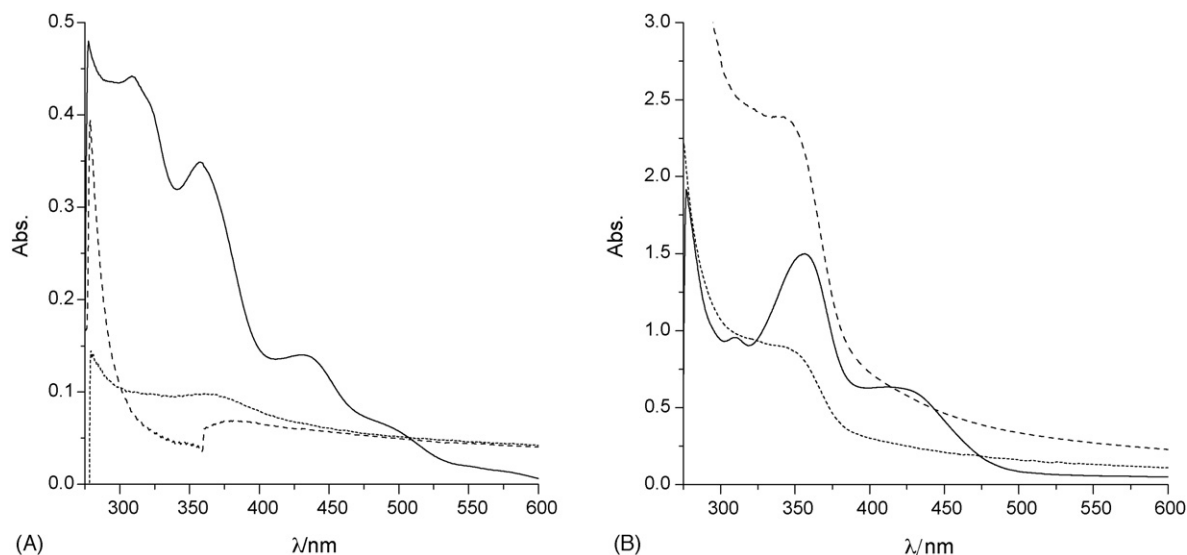
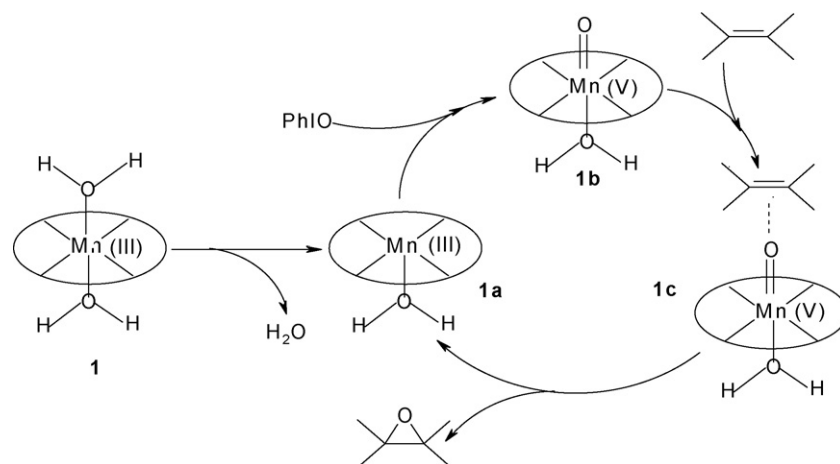


Fig. 4. UV-vis spectral pattern of complex **5** (A) and complex **1** (B): 2.00×10^{-3} M solution of complex in dry acetonitrile at 25°C (solid line); after 1 h reaction with PhIO (0.300 mmol) (sample diluted by five-fold) (short dash line) and after 1 day of the reaction (sample diluted five-fold) (dash line).



Scheme 2. Probable mechanistic pathway of complex **1** catalyzed epoxidation of alkenes in the presence of PhIO as terminal oxidant.

the reactive Mn(V)=O species (**1b**) and now olefin is coordinated with **1b** to generate **1c** which in turn transfers the oxo-group to the olefin to produce epoxide with subsequent regeneration of **1a** and thus one catalytic cycle is completed. Complex **1a** again participates in catalysis and formation of epoxide continued. Therefore, the UV-vis spectrum obtained after 1 day does not match with the original UV-vis spectral pattern of complex **1**.

From the UV-vis spectral study it may be inferred that binuclear complexes lose their catalytic activity due to the formation of some inactive decomposed species. Complex **1** does not revert to its original geometry after 1 day of reaction and at this point complex **1** is remarkably different from other Mn(III)(salen) species used as epoxidation catalysts which are reported to be reconverted to their original geometry at the end of catalytic reactions [1–16]. The five-coordinated species **1a** which is actually the active form of the catalyst in the catalytic cycle is regenerated after the end of catalytic reaction and the catalytic activity of this species is retained beyond 15 cycles.

3. Experimental

3.1. Materials

All chemicals were obtained from commercial sources and used as received. Solvents were dried according to standard procedure and distilled prior to use.

3.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded at 27°C using a Shimadzu FTIR-8400S spectrometer where KBr was used as medium. Electronic spectra ($800\text{--}200\text{ nm}$) were obtained at 27°C using a Shimadzu UV-3101PC spectrometer where methanol was used as a medium as well as a reference. The ^1H NMR spectra were recorded on a Bruker AC300 spectrometer. The magnetic susceptibilities were measured at 27°C

using an EG and G PAR 155 vibrating sample magnetometer, where $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a reference material; diamagnetic corrections were made using Pascal's constants [22]. Thermal analyses (TG–DTA) were carried out on a Shimadzu DT-30 thermal analyzer in flowing dinitrogen (flow rate: $30 \text{ cm}^3 \text{ min}^{-1}$). GC analysis was performed on an Ashco Gas Chromatograph Neon-II instrument with a flame ionization detector.

3.3. Synthesis of the complexes

2,6-Diformyl-4-methylphenol was prepared according to the literature method [20]. The Schiff base *N,N'*-cyclohexenebis(3-formyl-5-methylsalicylaldehyde) (L) was synthesized by following a procedure similar to that for preparing *N,N'*-ethylenebis(3-formyl-5-methylsalicylaldehyde) reported earlier [19].

All the complexes have been synthesized by adopting the procedures similar to those described earlier [17].

3.3.1. $\text{MnCl}_4 \cdot 4\text{H}_2\text{O}$ (1)

Yield: 85% (with respect to L). Anal. calcd. for $\text{MnCl}_4 \cdot 4\text{H}_2\text{O}$: C, 50.84; H, 5.65; N, 4.94. Found: C, 50.81; H, 5.57; N, 4.92. IR: $\nu(\text{C}=\text{O})$ 1662 cm^{-1} ; $\nu(\text{C}=\text{N})$ 1623 cm^{-1} ; $\nu(\text{H}_2\text{O})$ 3406 cm^{-1} ; $\nu(\text{skeletal vibration})$ 1548 cm^{-1} . UV (MeOH)/nm: 411 (sh, $\epsilon = 7500$), 356 ($\epsilon = 15,000$). TG analysis: 1.134 mg weight loss (12.89% of 11.46 mg complex: expected weight loss 12.71%) at 137°C .

3.3.2. $\text{MnZnL}'\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (2)

Yield: 68%. Anal. calcd. for $\text{MnZnL}'\text{Cl}_3 \cdot 2\text{H}_2\text{O}$: C, 52.89; H, 4.68; N, 6.85. Found: C, 53.33; H, 4.73; N, 7.1. IR: $\nu(\text{C}=\text{N})$ 1639 cm^{-1} ; $\nu(\text{H}_2\text{O})$ 3404 cm^{-1} ; $\nu(\text{skeletal vibration})$ 1541 cm^{-1} . UV (MeOH)/nm: 421 (sh, $\epsilon = 7000$), 353 ($\epsilon = 13,500$). TG analysis: 0.528 mg weight loss (4.56% of 11.58 mg complex: expected weight loss 4.40%) at 113°C .

3.3.3. $\text{MnCuL}'\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (3)

Yield: 72%. Anal. calcd. for $\text{MnCuL}'\text{Cl}_3 \cdot 2\text{H}_2\text{O}$: C, 53.01; H, 4.69; N, 6.87. Found: C, 52.8; H, 5.01; N, 7.23. IR: $\nu(\text{C}=\text{N})$ 1637 cm^{-1} ; $\nu(\text{H}_2\text{O})$ 3407 cm^{-1} ; $\nu(\text{skeletal vibration})$ 1548 cm^{-1} . UV (MeOH)/nm: 431 (sh, $\epsilon = 4500$), 376 ($\epsilon = 17,200$). TG analysis: 0.583 mg weight loss (4.84% of 12.05 mg complex: expected weight loss 4.41%) at 118°C .

3.3.4. $\text{MnNiL}'\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ (4)

Yield: 75%. Anal. calcd. for $\text{MnNiL}'\text{Cl}_3 \cdot 3\text{H}_2\text{O}$: C, 52.17; H, 4.86; N, 6.76. Found: C, 52.28; H, 5.01; N, 6.92. IR: $\nu(\text{C}=\text{N})$ 1635 cm^{-1} ; $\nu(\text{H}_2\text{O})$ 3406 cm^{-1} ; $\nu(\text{skeletal vibration})$ 1537 cm^{-1} . UV (MeOH)/nm: 401 (sh, $\epsilon = 1500$), 386 ($\epsilon = 18,000$). TG analysis: 0.888 mg weight loss (6.83% of 13.00 mg complex: expected weight loss 6.51%) at 123°C .

3.3.5. $\text{MnCoL}'\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (5)

Yield: 80%. Anal. calcd. for $\text{MnCoL}'\text{Cl}_3 \cdot 2\text{H}_2\text{O}$: C, 53.31; H, 4.72; N, 6.9. Found: C, 53.41; H, 4.81; N, 7.2. IR:

$\nu(\text{C}=\text{N})$ 1637 cm^{-1} ; $\nu(\text{H}_2\text{O})$ 3404 cm^{-1} ; $\nu(\text{skeletal vibration})$ 1541 cm^{-1} . UV (MeOH)/nm: 405 (sh, $\epsilon = 12,500$), 356 ($\epsilon = 19,000$). TG analysis: 0.587 mg weight loss (4.72% of 12.43 mg complex: expected weight loss 4.44%) at 122°C .

3.3.6. $\text{MnFeL}'\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ (6)

Yield: 70%. Anal. calcd. for $\text{MnFeL}'\text{Cl}_4 \cdot 2\text{H}_2\text{O}$: C, 51.27; H, 4.54; N, 6.64. Found: C, 52.1; H, 5.01; N, 7.02. IR: $\nu(\text{C}=\text{N})$ 1630 cm^{-1} ; $\nu(\text{H}_2\text{O})$ 3400 cm^{-1} ; $\nu(\text{skeletal vibration})$ 1542 cm^{-1} . UV (MeOH)/nm: 511 (sh, $\epsilon = 6000$), 366 ($\epsilon = 15,500$). TG analysis: 0.646 mg weight loss (4.91% of 13.15 mg complex: expected weight loss 4.26%) at 127°C .

3.3.7. $\text{MnMnL}'\text{Cl}_4 \cdot 3\text{H}_2\text{O}$ (7)

Yield: 81%. Anal. calcd. for $\text{MnMnL}'\text{Cl}_4 \cdot 3\text{H}_2\text{O}$: C, 52.41; H, 4.88; N, 6.79. Found: C, 52.65; H, 4.91; N, 7.02. IR: $\nu(\text{C}=\text{N})$ 1635 cm^{-1} ; $\nu(\text{H}_2\text{O})$ 3402 cm^{-1} ; $\nu(\text{skeletal vibration})$ 1535 cm^{-1} . UV (MeOH)/nm: 421 (sh, $\epsilon = 10,200$), 381 ($\epsilon = 17,500$). TG analysis: 0.833 mg weight loss (6.68% of 12.47 mg complex: expected weight loss 6.41%) at 132°C .

3.4. Preparation of iodosylbenzene

It was prepared by hydrolysis of the corresponding diacetate with aqueous sodium hydroxide according to the literature method [23]. Freshly prepared PhIO was used in every epoxidation experiment.

3.5. Epoxidation of alkenes catalyzed by complexes 1–7

Styrene and (*E*)-stilbene were purchased from Aldrich and used in epoxidation experiment without further purification. The epoxides were obtained either from Aldrich or prepared by epoxidation of the corresponding alkenes with *m*-chloroperbenzoic acid in methylene chloride to use as standard sample in GC analysis. In a typical experiment, under nitrogen atmosphere, alkene (0.300 mmol) and catalyst (1.00×10^{-2} mmol) were treated with 5 mL dry acetonitrile or dichloromethane. For GC analysis, chlorobenzene or decane (0.300 mmol) was added as an internal standard. A GC analysis was performed by withdrawing aliquots in small portions from the reaction mixture to establish the initial conditions. Afterwards under nitrogen atmosphere iodosylbenzene/NaOCl (0.066 g, 0.300 mmol) was added to the solution. When NaOCl was used as oxidant the solution was buffered to pH 11 using a NaH_2PO_4 –NaOH buffer. The reaction mixture was then periodically sampled by withdrawing aliquots in small portions for GC analysis. Quantification of the product was performed by the internal standard method (decane in CH_2Cl_2 and chlorobenzene in CH_3CN). Blank experiments were performed with each oxidant following the same experimental conditions without using any catalyst. ^1H NMR spectroscopy was used for identification of the product. For ^1H NMR experiments epoxides were prepared following the procedure described by Kochi and co-workers [1] when PhIO was used as oxidant and adopting the procedure reported by Jacobsen et al. [4] when NaOCl was used as oxidant.

Table 7
Crystallographic data and structure refinement details for complex **1**·(1/2)CH₃CN

Empirical formula	C ₂₅ H _{33.5} N _{2.5} O ₈ ClMn
Formula weight	587.43
<i>T</i> (K)	293
Mo K α	0.71073
Crystal system	Orthorhombic
Space group	<i>Ccca</i>
<i>a</i> (Å)	19.652(19)
<i>b</i> (Å)	26.83(3)
<i>c</i> (Å)	10.483(11)
$\alpha = \beta = \gamma$ (°)	90
<i>V</i> (Å ³)	5527(10)
<i>Z</i>	8
<i>D</i> _{calc} (Mg m ⁻³)	1.406
<i>F</i> (000)	2432
μ (mm ⁻¹)	0.625
Crystal size (mm ³)	0.29 × 0.33 × 0.36
θ range (°)	2.3–27.5
Reflection collected	7674
Independent reflection	3179
Reflection observed	2279
Goodness-of-fit on <i>F</i> ²	0.8
<i>R</i> _{int}	0.027
Final <i>R</i> indices [<i>I</i> > 2(<i>I</i>)]	<i>R</i> 1 = 0.0681, <i>wR</i> 2 = 0.1951
Final <i>R</i> indices (all data)	<i>R</i> 1 = 0.0965, <i>wR</i> 2 = 0.2284

$$w = 1/[\sigma^2(F_o^2) + (0.1759P)^2 + 22.5743P], \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

3.6. X-ray data collection and structure determination

Single crystals of complex MnLCl·4H₂O·(1/2)CH₃CN suitable for X-ray diffraction were obtained by slow evaporation of acetonitrile solution of complex **1** (MnLCl·4H₂O) at room temperature. A single crystal suitable for X-ray data collection was mounted on a Bruker SMART CCD diffractometer equipped with a graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation source. The program SMART [24] was used for collecting frames of data, indexing reflection and determination of lattice parameters, SAINT [24] for integration of the intensity of reflections and scaling, and SADABS [25] for absorption correction. Total 7674 reflections were measured and 2279 were assumed observed in the applying condition $I > 2\sigma(I)$. The structure was solved by the direct method using the SHELXS-97 [26] computer program and refined by full-matrix least squares methods on *F*², using the SHELXL-97 [27] program with anisotropic displacement parameters for all non-hydrogen atoms. Selected crystallographic data and refinement details are displayed in Table 7.

4. Conclusion

A six-coordinated Mn(III) complex of a (salen) type ligand L has been synthesized and characterized by X-ray single crystal structural analysis. The structure determination confirms that it is the N₂O₂ site, and not the O₄ site, of L that acts as the potential ligating site to accommodate Mn(III) ion. The mononuclear complex has been utilized after condensing two formyl groups with aniline to prepare binuclear complexes MnMCl_x·yH₂O. The presence of second metals does not alter the high spin state

of Mn(III) in bimetallic complexes **2–7**. In the epoxidation of styrene and (*E*)-stilbene, the monomanganese complex **1** is the most efficient, as solvent CH₃CN is a better choice over CH₂Cl₂, another commonly used solvent for epoxidation reaction, and as terminal oxidant PhIO is the best option, especially for (*E*)-stilbene epoxidation. Our 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. It becomes evident that when NaOCl is used as the oxygen source the epoxidation reaction most probably proceeds through the concerted Lewis-acid activated epoxidation by active intermediate [L–O–Mn(III)(salen)X], whereas in the presence of PhIO as terminal oxidant the epoxidation takes place by active Mn(V)=O(salen) species. This study also reveals that the presence of second metal in close proximity to Mn(III) center exhibits a detrimental effect on the catalytic efficiency of Mn(III) center in the epoxidation of styrene and (*E*)-stilbene. The influence of the second metal follows the order: Cu(II) > Fe(III) > Zn(II) ~ Ni(II) > Co(II) > Mn(III). Complex **1** is actually the catalyst precursor which is converted to the active catalyst during epoxidation of alkenes, complex **1a** which subsequently reacts with the oxygen donor to generate active intermediate Mn(V)=O(salen) or [Cl–O–Mn(III)(salen)X] species and after oxygen transfer to coordinated olefins it is regenerated to retain its catalytic activity beyond 15 cycles. Hence, complex **1** is related to cytochrome P-450 structurally and functionally to some extent. The poor activity of the bimetallic catalysts in epoxidation of (*E*)-stilbene in the presence of PhIO as terminal oxidant with CH₃CN as solvent is most probably due to their decomposition after sometime as well as due to the lower rate of formation of Mn(V)=O(salen) species.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting deposition number 267779.

Acknowledgements

The authors wish to thank the Council of Scientific and Industrial Research, New Delhi (grant to D.D. & A.M.; Project No. 01(1871)/03/EMR-II dated 17/03/2003) for financial support. We (D.D. & A.M.) also thank Department of Science and Technology (DST), New Delhi for providing FTIR and UV–vis–NIR Spectrophotometers and Net working facility through DST–FIST program.

References

- [1] K. Srinivasan, P. Michaud, J.K. Kochi, J. Am. Chem. Soc. 108 (1986) 2309.
- [2] A.R. Oki, D.J. Hodgson, Inorg. Chim. Acta 170 (1990) 65.
- [3] C. Bowers, P.K. Dutta, J. Catal. 122 (1990) 271.

- [4] (a) W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, *J. Am. Chem. Soc.* 112 (1990) 2801;
(b) W. Zhang, E.N. Jacobsen, *J. Org. Chem.* 56 (1991) 2296;
(c) N.H. Lee, E.N. Jacobsen, *Tetrahedron Lett.* 32 (1991) 6533;
(d) Fu.F. H., G.C. Look, W. Zhang, E.N. Jacobsen, C.H. Wong, *J. Org. Chem.* 56 (1991) 6497;
(e) E.N. Jacobsen, W. Zhang, M.L. Guler, *J. Am. Chem. Soc.* 113 (1991) 6703;
(f) J.F. Larrow, E.N. Jacobsen, Y. Gao, Y. Hong, X. Nie, C.M. Zeep, *J. Org. Chem.* 59 (1994) 1993;
(g) N.S. Finney, P.J. Pospisil, S. Chang, M. Palucki, R.G. Konsler, K.B. Hansen, E.N. Jacobsen, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1720;
(h) M. Palucki, N.S. Finney, P.J. Pospisil, M.L. Guler, T. Ishida, E.N. Jacobsen, *J. Am. Chem. Soc.* 120 (1998) 948.
- [5] (a) R. Irie, Y. Ito, T. Katsuki, *Synlett* (1991) 265;
(b) N. Hosoya, R. Irie, T. Katsuki, *Synlett* (1992) 261;
(c) A. Hatayama, N. Hosoya, R. Irie, Y. Ito, T. Katsuki, *Synlett* (1992) 407;
(d) H. Sasaki, R. Irie, T. Katsuki, *Synlett* (1993) 300;
(e) N. Hosoya, A. Hatayama, K. Yanai, H. Fuji, R. Irie, T. Katsuki, *Synlett* (1993) 641;
(f) T. Hamada, R. Irie, T. Katsuki, *Synlett* (1994) 479;
(g) T. Katsuki, *Coord. Chem. Rev.* 140 (1995) 189;
(h) T. Hamada, T. Fukuda, H. Imanishi, T. Katsuki, *Tetrahedron* 52 (1996) 515;
(i) T. Katsuki, *J. Mol. Catal. A* 113 (1996) 87;
(j) R. Irie, T. Hashihayata, T. Katsuki, M. Akita, Y. Moro-Oka, *Chem. Lett.* (1998) 1041;
(k) T. Katsuki, *Curr. Chem. Org.* (2001) 63;
(l) C. Ohta, T. Katsuki, *Tetrahedron Lett.* 42 (2001) 3885;
(m) T. Katsuki, *Adv. Synth. Catal.* 244 (2002) 131.
- [6] (a) C. Linde, M. Arnold, P.O. Norrby, B. Akermark, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1723;
(b) P.O. Norrby, C. Linde, B. Akermark, *J. Am. Chem. Soc.* 117 (1995) 11035;
(c) P. Brandt, P.-O. Norrby, A.M. Daly, D.G. Gilheany, *Chem. Eur. J.* 8 (2002) 4299;
(d) A.M. Daly, D.G. Gilheany, *Tetrahedron: Asymmetry* 14 (2003) 127.
- [7] L. Canali, D.C. Sherrington, *Chem. Soc. Rev.* 28 (1999) 85.
- [8] K.P. Bryliakov, D.E. Babushkin, E.P. Talsi, *J. Mol. Catal. A* 158 (2000) 19.
- [9] W. Adam, K.J. Roschmann, C.R. Saha-Möller, D. Seebach, *J. Am. Chem. Soc.* 124 (2002) 5068.
- [10] M. Bandini, P.G. Cozzi, A. Umani-Ronchi, *J. Chem. Soc., Chem. Commun.* (2002) 919.
- [11] A. Chellamani, S. Harikengaram, *J. Phys. Org. Chem.* 16 (2003) 589.
- [12] I.V. Khavrutskii, D.G. Musaev, K. Morokuma, *Inorg. Chem.* 42 (2003) 2606.
- [13] A.R. Silva, C. Freire, B. de Castro, *New J. Chem.* 28 (2004) 253.
- [14] N.S. Venkataramanan, G. Kuppuraj, S. Rajagopal, *Coord. Chem. Rev.* 249 (2005) 1249.
- [15] J.P. Collman, L. Zeng, J.I. Brauman, *Inorg. Chem.* 43 (2004) 2672.
- [16] J.T. Groves, T.E. Nemo, R.S. Myers, *J. Am. Chem. Soc.* 101 (1979) 1032.
- [17] D. Das, C.P. Cheng, *J. Chem. Soc., Dalton Trans.* (2000) 1081.
- [18] X.-W. Liu, N. Tang, Y.-H. Chang, M.-Y. Tan, *Tetrahedron: Asymmetry* 15 (2004) 1269.
- [19] H. Okawa, S. Kida, *Bull. Chem. Soc. Jpn.* 16 (1972) 1360.
- [20] R.R. Gagne, C.L. Spiro, T.J. Smit, C.A. Hamann, W.R. Thies, A.D. Shiemke, *J. Am. Chem. Soc.* 103 (1981) 4073.
- [21] S.R. Korupoju, N. Mangayarkarasi, S. Ameerunisha, E.J. Valente, P.S. Zacharias, *J. Chem. Soc., Dalton Trans.* (2000) 2845.
- [22] A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, New York, 1968.
- [23] H. Saltzman, J.G. Sharefkin, *Org. Synth. Coll. V* (1973) 658.
- [24] SMART & SAINT Software Reference Manuals, Version 6.22. Bruker AXS Analytic X-Ray Systems Inc., Madison, WI, 2000.
- [25] G.M. Sheldrick, SADABS, Software for Empirical Absorption Correction, University of Gottingen, Germany, 2000.
- [26] G.M. Sheldrick, SHELXS-97, Program for Solution of Crystal Structure, University of Gottingen, Germany, 1997.
- [27] G.M. Sheldrick, SHELXL-97, Program for Solution of Crystal Structure, University of Gottingen, Germany, 1997.
- [28] L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.