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Isolation of a novel intermediate during unsymmetrical to symmetrical rearrangement of a tetradentate Schiff base ligand in a manganese(III) complex: Catalytic activity of the rearranged product towards alkene epoxidation

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ABSTRACT

An attempt for the synthesis of a Mn^{III} complex with unsymmetrical tetradentate Schiff base ligand uspen (1:1:1 condensate of salicylaldehyde, 2,4-pentanedione and 1,2-ethanediamine) resulted in the isolation of a novel complex, $\{[\{Mn(salen)\}\{Mn(uspen)\}(HCOO)]\cdot ClO_4\}_n$ (**1**) as an intermediate species that contains both the unsymmetrical and symmetrical tetradentate ligand uspen and salen (2:1 condensate of salicylaldehyde and 1,2-ethanediamine) respectively. The structure of the complex shows that half of the unsymmetrical Schiff base, uspen rearranged to its symmetrical analogue, salen. A phenoxo bridged dinuclear Mn^{III} complex $[Mn(salen)(sal)]_2\cdot 2H_2O$ (**2**) with only the symmetrical Schiff base was also obtained. Compound **1** that contains both unsymmetrical and symmetrical Schiff base ligands in one molecule is unprecedented and provides an insight into the unsymmetrical to symmetrical rearrangement of tetradentate Schiff base ligand. Complex **2** acts as an efficient catalyst in the alkene ((*E*)-stilbene, styrene) epoxidation reaction in presence of two terminal oxidants PhIO and NaOCl in solvents CH_3CN and CH_2Cl_2 independently and it retains its reactivity with high efficiency for a long time.

1. Introduction

The coordination chemistry of manganese with a diverse range of ligands is an active field of research for decades. This is not only because of the relevance that a number of model manganese complexes have biological significance [1,2], but also due to their fascinating cluster compounds, which exhibit unusual magnetic properties, and the elegant supramolecular arrays that have been discovered [3–11]. In addition to the interest from this inorganic standpoint, there is also considerable interest in the application of manganese complexes in organic synthesis due to their potent catalytic properties, particularly in the asymmetric epoxidation of certain olefins [12–28]. Moreover in nature, the oxygen evolving complexes of photosystem II are believed to be catalysed by a cluster of manganese ions. Manganese(III)–salen type complexes are very well studied because they can be synthesized easily and as because this ligand shows suitable biometric properties that can mimic the structural feature of the active site [29], but the chemistry of Mn^{III} complexes with unsymmetrical tetradentate Schiff base ligands are relatively unexplored [30].

Literature study shows that Mn^{III} complexes containing unsymmetrical tetradentate Schiff base ligands may undergo acid or base catalysed hydrolysis resulting rearranged product of corresponding more stable symmetrical tetradentate Schiff base ligand [31–33]. There are many other factors such as (i) presence of metal ion, (ii) ligand systems, (iii) solvent, etc. that may also cause the rearrangement of the unsymmetrical tetradentate Schiff base ligand to a symmetric one. Therefore, a first step in order to better understand the factors that may govern the hydrolysis of the unsymmetrical ligands and also to establish the reaction pathways, isolation of an intermediate species that form during hydrolysis of the ligand is required. In most of the previous reports, the isolated products were completely rearranged compounds containing symmetrical Schiff base ligands. An intermediate species was isolated only in one case as cocrystals of both symmetrical and unsymmetrical compounds [31]. We are interested in investigating if two such species can be connected by a bridging ligand to obtain a molecular species that contains both of them. For this purpose we have tried with several carboxylate ions keeping in mind their potentials for bridging the metal ions and fortunately succeeded to obtain the desired compound using the formate ion that contains both the unsymmetrical (uspen) and symmetrical tetradentate ligands (salen). To the best of our knowledge, this is the first report of isolation and characterization (structurally) of an intermediate

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product that contains both unsymmetrical and symmetrical Schiff base ligands in one molecule and thus provide a clear evidence into the reaction pathway of unsymmetrical to symmetrical rearrangement of tetradentate Schiff base ligand. We are also able to isolate and characterize a completely rearranged product Mn^{III}–salen. Herein, we report the synthesis, spectral study and structural characterization of these two compounds.

Among the various metal–salen complexes, the manganese(III)–salen complexes are the most promising as catalysts in alkene epoxidation, which is an important reaction in organic synthesis and as model systems of various metallobiosites, e.g. cytochrome P-450 [12–28,34]. The interest in manganese complexes as catalysts for alkene epoxidations comes mainly from the relationship of these catalytic systems to the biologically relevant manganese porphyrins. In the case of manganese porphyrins as epoxidation catalysts different oxygen sources have been used, e.g. iodosylbenzene, sodium hypochlorite, molecular oxygen in the presence of an electron source, alkyl peroxides and hydroperoxides, N-oxides, potassium hydrogen persulfate and oxaziridines [35]. In spite of huge works, the mechanism of Mn^{III}–salen catalyzed epoxidation of olefins is a topic of great controversy. 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, NaOCl, etc. The stereochemistry of the oxygen transfer from the oxomanganese–salen complex to the alkene depends on the electronic environment around the oxomanganese function. Herein, we also describe the catalytic activity of the dinuclear Mn–salen complex towards epoxidation of alkenes.

2. Experimental

2.1. Starting materials

The diamine (1,2-ethanediamine) and triethylamine were dried over potassium hydroxide and distilled prior to use. Pentane-2,4-dione was dried over anhydrous sodium sulphate and distilled; the fraction boiling at 138–139 °C was collected All the other chemicals were of reagent grade and used without further purification. Styrene and (*E*)-stilbene were purchased from Aldrich and used in epoxidation experiment without further purification.

2.2. Preparations

2.2.1. Synthesis of the Schiff-base ligands H_2salen and H_2uspen

The symmetrical di-Schiff-base ligand H_2salen was prepared by reacting 5 mmol methanolic solution (10 cm^3) of salicylaldehyde (0.525 cm^3) and 5 mmol methanolic solution (10 cm^3) of 1,2-ethanediamine (0.308 cm^3) as reported earlier [36]. For the synthesis of H_2uspen, 2,4-pentanedione (1.10 cm^3; 5 mmol) was added dropwise to a 25 cm^3 chloroform solution of 1,2-ethanediamine (0.31 cm^3; 5 mmol). After the completion of addition, the solution was stirred for an additional 3 h and chloroform was evaporated under reduced pressure, yielding a viscous liquid. A 5 cm^3 methanolic solution of salicylaldehyde (1.10 cm^3; 5 mmol) was added to the methanolic solution (5 cm^3) of this viscous liquid in 1:1 molar ratio and refluxed for ca. 2 h. The ligand was isolated and the purity was checked by melting point (130 °C) and NMR spectra as was reported earlier [30].

Ligand (H_2uspen). ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 13.07 (br, 1H, OH(sal)), 8.23 (s, 1H,CH=N), 7.09–7.24 (m, 2H, aromatic), 6.71–6.87 (m, 2H, aromatic), 4.89 (s, 1H, CH), 4.81 (br, 1H, OH(acac)), 3.11 (t, J = 5.4 Hz, 2H,CH_2), 3.01 (t, J = 5.8 Hz, 2H, CH_2), 2.12 (s, 3H, CH_3(N)), 1.91 (s, 3H, CH_3(O)).

2.2.2. Synthesis of $\{[\{Mn(salen)\}\{Mn(uspen)\}(HCOO)]ClO_4\}_n$ (**1**) and $[Mn(salen)(sal)]_2{\cdot}2H_2O$ (**2**)

$Mn(ClO_4)_2{\cdot}6H_2O$ (1.805 g; 5 mmol), dissolved in 10 cm^3 of methanol, was added to a methanolic solution (10 cm^3) of the ligand (H_2uspen) (5 mmol) with constant stirring. After ca. 10 min a methanol solution of formic acid (0.32 g; 5 mmol) was added to it. Triethylamine (2.10 cm^3, 15 mmol) in methanol (5 cm^3) was added dropwise to this solution with constant stirring. After ca. 2 h a dark brown microcrystalline compound was precipitated out. It was filtered. The precipitate was collected and the filtrate was left to stand overnight in open atmosphere. The precipitate was washed with and redissolved in CH_3CN. X-ray quality deep-brown single crystals of compound **1** were obtained by slow evaporation of the acetonitrile solution of this compound.

From the filtrate, a deep-red microcrystalline compound appears after 2 days. The precipitate was filtered and washed with diethyl ether and redissolved in methanol. Layering of the red solution with diethyl ether gave well-formed X-ray-quality deep-red single crystals of **2**.

Complex 1: (Yield: 0.114 g; 15%) *Anal.* Calc. for $C_{31}H_{29}Mn_2N_4O_{10}Cl$ (762.91): C, 48.80; H, 3.83; N, 7.34. Found: C, 48.72; H, 3.87; N, 7.19%. λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (methanol), 603 (447); IR (cm^{-1}): ν(C=N), 1633, ν_{as}(C=O), 1591, ν_s(C=O), 1439, $\nu(ClO_4^-)$, 1089 cm^{-1}.

Complex 2: (Yield: 0.28 g; 60%) *Anal.* Calc. for $C_{46}H_{42}Mn_2N_4O_{10}$ (920.72): C, 60.01; H, 4.60; N, 6.09. Found: C, 60.12; H, 4.57; N, 6.19%. λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (methanol), 608 (464); IR (cm^{-1}): ν(O–H), 3427, ν(C=N), 1630.

2.2.3. Alternative method for the synthesis of complex **2**

Complex **2** has also been synthesized by reacting of H_2salen (1.340 g; 5 mmol) in methanol (10 cm^3) with a methanolic solution (10 cm^3) containing $Mn(ClO_4)_2{\cdot}6H_2O$ (1.805 g; 5 mmol) and salicylaldehyde (0.525 cm^3; 5 mmol) followed by NEt_3 (0.70 cm^3; 5 mmol). (Yield: 1.84 g; 80%).

2.2.4. Preparation of iodosylbenzene

This was prepared by hydrolysis of the corresponding diacetate with aqueous sodium hydroxide as reported in the literature [37]. Freshly prepared PhIO was used in every epoxidation experiment.

2.3. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanol (1200–350 nm) were recorded in a Hitachi U-3501spectrophotometer. The ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AC300 spectrometer.

2.4. Epoxidation of alkenes catalyzed by complex **2**

Under nitrogen atmosphere, alkene (0.300 mmol) and catalyst (1.00×10^{-2} mmol) were treated with 5 cm^3 dry acetonitrile or dichloromethane. 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. ^{1}H NMR spectroscopy was used for identification of the product. For ^{1}H NMR experiments epoxides were prepared following the procedure described by Kochi and co-workers [38] when PhIO was used as oxidant and adopting the procedure reported by Jacobsen et al. [12,19,39–42] when NaOCl was used as oxidant.

Table 1
Crystal data and structure refinement of complexes **1** and **2**.

	1	2
Empirical formula	$C_{31}H_{31}Mn_2N_4O_{10}Cl$	$C_{46}H_{42}Mn_2N_4O_{10}$
Formula weight	764.93	920.72
Space group	Cc	$P2_1/c$
Crystal system	monoclinic	monoclinic
a (Å)	14.915(2)	11∼.676(3)
b (Å)	17.492(3)	14.149(3)
c (Å)	13.718(2)	12.981(3)
α (°)	90	90
β (°)	115.13(2)	104.97(2)
γ (°)	90	90
V (Å^3)	3240.2(10)	2071.7(9)
Z	4	2
Calculated density (g/cm^3)	1.564	1.476
Absorption coefficient (μ) (mm^{-1})	0.925 (Mo Kα)	0.676 (Mo Kα)
F(0 0 0)	1560	952
Crystal size	0.20 × 0.26 × 0.37	0.05 × 0.05 × 0.30
Refinement method	SHELXL-97 on F^2	SHELXL-97 on F^2
Theta range for data collection (°)	1.6, 27.5	1.8–25.5
R_{int}	0.040	0.049
Number of unique data	7426	3787
Number of data with $I > 2\sigma(I)$	4163	3205
R_1, wR_2	0.0452, 0.1335	0.0497, 0.1116

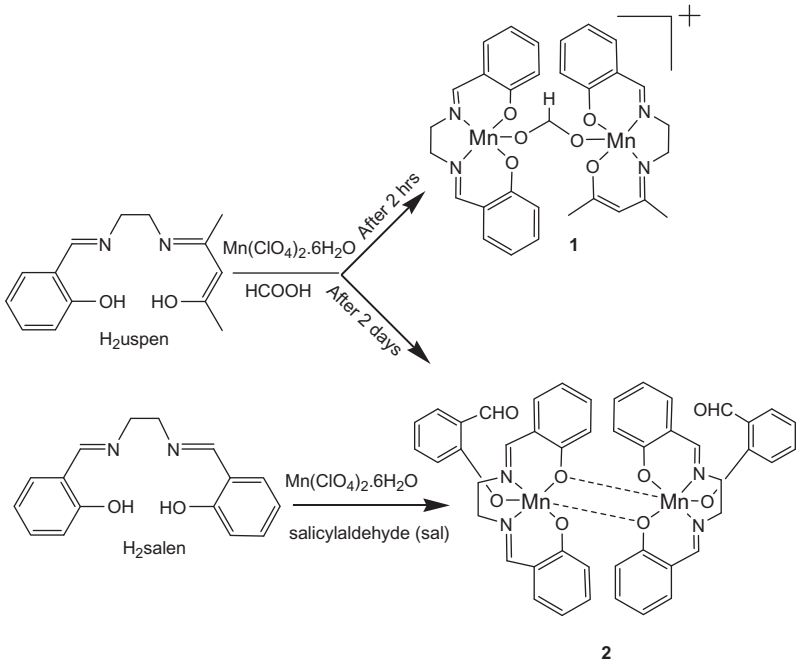
2.5. Crystal data collection and refinement

The data for complex **1** and **2** were collected at room temperature on Bruker AMX Smart 1000 equipped with an area detector diffractometer using graphite monochromated Mo Kα radiation. Semi-empirical absorption corrections were applied using SADABS [43]. The crystal structures of the complexes **1** and **2** were solved by direct method using SHELXS-97 [44] program and refined by using SHELXL-97 [44]. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms, either located from difference electron density maps or placed geometrically, were refined with isotropic thermal parameters. Neutral atom scattering factors were taken from Cromer and Weber [45] and anomalous dispersion effects were included in Fcalc [46]. The crystallographic drawings were made using ORTEP-3 [47]. ADDSYM procedure detects this pseudo centre of symmetry and predicts the structure of **1** to be C2/c. In this structure element, the environments of two Mn atoms are different as two different ligands chelates the Mn sites. Since L1 and L2 are almost similar, the search criteria of check cif detect a pseudo-centre of symmetry. The Mn atoms in the crystal structure seem to be defining a higher symmetry than the actual one which, on the other hand, is not supported by the remainder unit cell contents. Refinement in suggested new space group was checked and the structure solution in the non-centrosymmetric space group Cc is better than the structure solution in the centrosymmetric space group C2/c. Significant crystallographic data are summarized in Table 1.

3. Results and discussion

3.1. Synthesis of the complexes

Addition of methanolic solution of $Mn(ClO_4)_2{\cdot}6H_2O$ to the methanolic solution of H_2uspen followed by formic acid (in methanol) and triethylamine in 1:1:1:3 molar ratio, results in the isolation of complex **1** as microcrystalline solid in ca. 2 h. In this complex, the unsymmetrical Schiff base ligand remains intact around one Mn centre but is rearranged to the symmetrical one (salen) in the other Mn centre (Scheme 1). Upon keeping the filtrate for several days a deep-red microcrystalline solid of complex **2** appears. In this compound, the Schiff base ligand is only the symmetrical salen. These observations, thus clearly suggest that the unsymmetrical Schiff base ligand undergoes rearrangement under the reaction conditions to yield the final product of symmetrical salen ligand, **2** and during the course of this rearrangement reaction an interesting intermediate product containing both symmetrical and unsymmetrical ligands is separated as complex **1**. A CSD search shows 'no hit' for such complexes indicating that the complex is a unique one. Complex **2** has also been synthesized by reacting methanolic solutions of H_2salen, $Mn(ClO_4)_2{\cdot}6H_2O$ and salicylaldehyde in 1:1:1 molar ratio.



Scheme 1. Formation of the complexes.

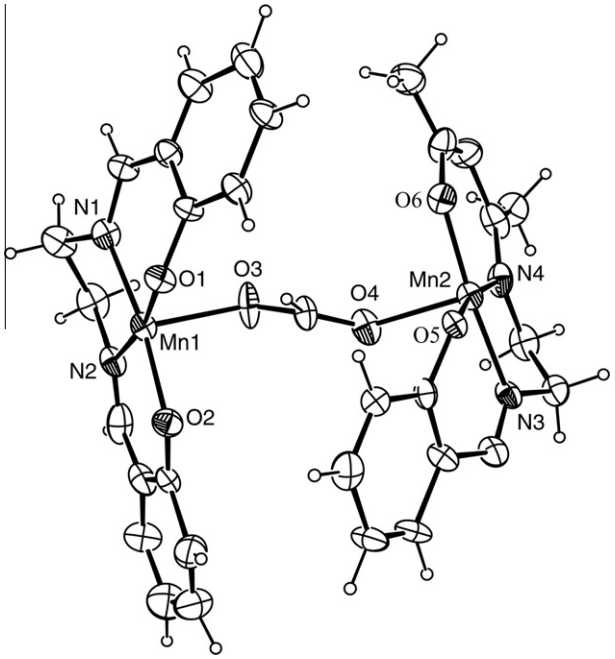


Fig. 1. ORTEP-3 view of the asymmetric unit of **1** with ellipsoids at 50% probability.

Table 2
Selected bond lengths (Å) and bond angles (°) in complex **1**.

Mn1		Mn2	
Mn1–O3	2.091(10)	Mn2–O5	1.932(7)
Mn1–O2	1.906(7)	Mn2–O6	1.866(13)
Mn1–O1	1.876(13)	Mn2–O4	2.125(10)
Mn1–N1	1.982(9)	Mn2–N4	1.955(11)
Mn1–O5′	2.408(8)	Mn2–N3	1.960(15)
Mn1–N2	1.990(15)	Mn2–O2″	2.401(8)
O3–Mn1–O2	95.5(4)	O5–Mn2–O6	95.1(4)
O3–Mn1–O1	94.5(5)	O5–Mn2–O4	95.1(3)
O3–Mn1–N2	92.2(5)	O5–Mn2–N4	169.6(6)
O3–Mn1–N1	91.6(4)	O5–Mn2–N3	88.5(4)
O5′–Mn1–O3	176.1(4)	O5–Mn2–O2″	81.1(3)
O2–Mn1–O1	94.8(4)	O6–Mn2–O4	92.7(5)
O2–Mn1–N2	89.4(4)	O6–Mn2–N4	93.5(6)
O2–Mn1–N1	169.6(5)	O6–Mn2–N3	174.4(4)
O5′–Mn1–O2	81.4(3)	O6–Mn2–O2″	90.8(4)
O1–Mn1–N2	171.7(4)	O4–Mn2–N4	90.2(4)
O1–Mn1–N1	92.2(5)	O4–Mn2–N3	91.3(5)
O5′–Mn1–O1	88.1(4)	O4–Mn2 –O2″	175.1(4)
N2–Mn1–N1	82.7(5)	N4–Mn2–N3	82.5(6)
O5′–Mn1–N2	85.5(4)	O2″–Mn2–N4	93.1(4)
O5′–Mn1–N1	91.1(4)	O2″–Mn2–N3	85.5(4)

Symmetry code ′ = 2 − *x*, 1 − *y*, −*z*.

To have an idea regarding the species distribution in the solutions we recorded the HRMS-ESI after 1 h of mixing the reactants (i.e. before the precipitation of **1** started; solution 1) and found the presence of both Mn(salen)$^+$ (HRMS (ESI): found *m*/*z* M^+ = 299.1924; M_{calc} = 299.00) and Mn(uspen)$^+$ (HRMS (ESI): found *m*/*z* M^+ = 321.1844; M_{calc} = 321.00) moieties (Fig. S1a). The intensity of Mn(uspen)$^+$ peak was much higher than that of Mn(salen)$^+$. In this spectra, a peak of [{Mn(salen){Mn(uspen)}(HCOO)]$^+$ (HRMS (ESI): found *m*/*z* M^+ = 666.3301; M_{calc} = 666.00) (Fig. S1b) was also observed. The HRMS-ESI was again recorded after 4 h of mixing when the precipitation of **1** was completed (solution 2). In this spectra also both Mn(salen)$^+$ and Mn(uspen)$^+$ moieties were present but the intensity ratio was reversed (Fig. S2a). Moreover, the spectra also showed the presence of [Mn(salen)(sal)] (HRMS (ESI): found *m*/*z* (M + Na)$^+$ = 481.4960; M_{calc} = 481.01) fragment (sal = salicylaldehyde) and $Mn(acac)_3$ (acac = acetylacetonate) (HRMS (ESI): found *m*/*z* (M + Na)$^+$ = 375.2571; (M + Na)$^+$ calcd = 375.01) (Fig. S2b) indicating that the hydrolysis of the Schiff base took place during the reaction in agreement with the mechanism proposed by Bermejo et al. [33]. To have greater yield, we also tried to prepare **1** from a 1:1 mixture of H_2uspen and H_2salen but the product was a mixture of **1** and another product which was characterized (elemental analysis) as $[\{Mn(salen)\}_2(HCOO)]ClO_4$ (Supporting information).

3.2. IR and UV–Vis spectra of the complexes

In the IR spectra of complex **1**, the attributions of the IR spectra in the 1300–1650 cm^{-1} region are difficult due to the appearance of several absorption bands from two different Schiff bases and the formate ligands. However, by comparing the IR spectra of the Mn^{III} complexes of the similar type of Schiff base ligands but with other anions (e.g. azide and halides), the moderately strong and sharp band at 1633 cm^{-1}, is assigned to the azomethine ν(C=N) group. The strong band at 1591 cm^{-1}, is likely due to the antisymmetric stretching mode of the carboxylate group and the bands at ν_s(C=O), 1439 cm^{-1} to the symmetric stretching modes of the carboxylates [48]. In this complex, the characteristic strong peaks for stretching vibrations of uncoordinated perchlorate anion have been observed at 1089 cm^{-1} (ν_3) and 948 cm^{-1} (ν_4). For complex **2**, the moderately strong and sharp band at 1630 cm^{-1} is assigned to the azomethine *ν*(C=N) group and a broad band centred at 3427 cm^{-1} is due to the *ν*(OH) of water molecules.

The electronic spectra of the complexes **1** and **2** were recorded in methanol solution. A single absorption band was found at 603 and 608 nm in the visible region for **1** and **2**, respectively, as usually observed in octahedral Mn(III) complexes [49–51].

3.3. Description of the structure of $\{[\{Mn(salen)\}\{Mn(uspen)\}(HCOO)]\cdot ClO_4\}_n$ (**1**)

The molecular structure of complex **1** consists of formate bridged dinuclear units formulated as [{Mn(salen)}{Mn(uspen)}(HCOO)]$^+$ (Fig. 1). The charge is balanced by a non coordinating ClO_4^- anion. Selected bond lengths and angles are summarized in Table 2. The asymmetric unit consists of two independent Mn^{III} atoms, Mn(1) and Mn(2) both presenting a distorted octahedral environment, but the ligand environment is different around the two Mn^{III} centres. Mn(1) is coordinated by two phenoxo oxygen atoms [O(1) and O(2)] and two imine nitrogen atoms [N(1) and N(2)] of deprotonated symmetrical tetradentate Schiff base ligand (salen) in the equatorial site. An oxygen atom O(3) from a formate anion coordinates to one of its axial positions. The same formate ion is coordinated to Mn(2) through the other oxygen atom O(4) to form the *syn-anti* carboxylate bridged dimeic entity. On the other hand, Mn(2) is coordinated by two oxygen atoms O(5) from salicylaldehyde moiety and O(6) from acetylacetone moiety of unsymmetrical tetradentate Schiff base ligand (H_2uspen) and two imine nitrogen atoms N(4) and N(3) from the ligand (H_2uspen), in the equatorial position. The other axial position of Mn(1) and Mn(2) is weakly bonded to a phenoxo oxygen atom O(5′) (′ = *x* − 1/2, -*y* + 1/2, *z* − 1/2) from the unsymmetrical Schiff base ligand (uspen) and O(1″) (″ = *x* + 1/2, −*y* + 1/2, *z* + 1/2) from the symmetrical Schiff base ligand (salen) respectively of neighboring dinuclear units to form a one-dimensional wave-like chain (Fig. 2). The deviations of the four basal donor atoms from their mean plane are within ±0.002 Å and ±0.018 Å around Mn(1) and Mn(2) respectively. The Mn(1) and Mn(2) atoms deviate from the respective mean plane by 0.105(4) and 0.095 (2) Å, respectively towards axial formate. The axial Mn–O bond distances Mn(1)–O(3) 2.091(10) Å and Mn(1)–O(5′) (′ = *x*−1/2, −*y* + 1/2, *z* − 1/2) 2.408(8) Å around

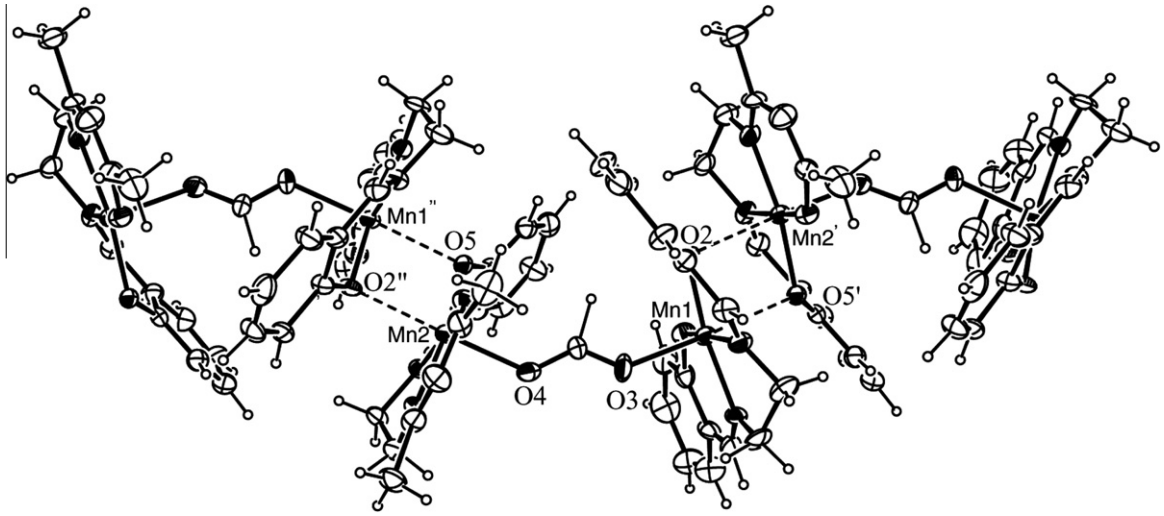


Fig. 2. The polymeric structure of **1**.

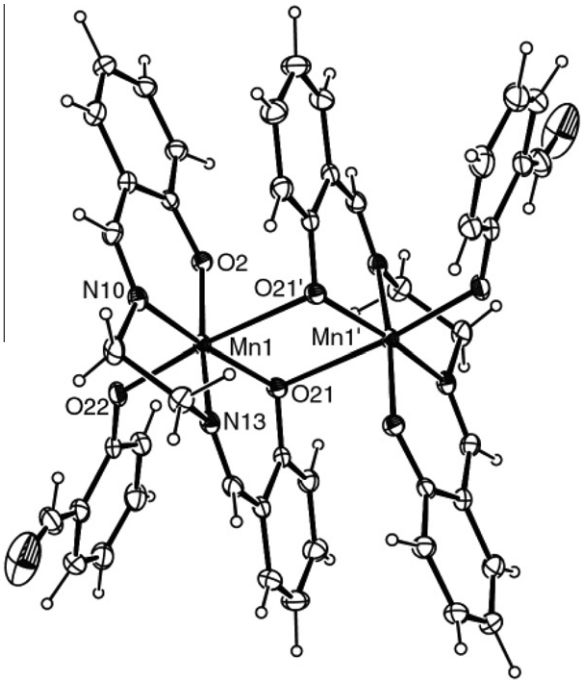


Fig. 3. ORTEP-3 view of the asymmetric unit of **2** with ellipsoids at 50% probability.

Mn(1) and Mn(2)–O(2″) (″ = $x + 1/2$, $-y + 1/2$, $z + 1/2$) 2.401(8) Å and Mn(2)–O(4) 2.125(10) Å are significantly longer than the equatorial bonds as expected for a Jahn–Teller distortion of Mn ions with a +3 oxidation state. The six-member chelate rings around Mn(1) and Mn(2) incorporating the aromatic residue is slightly distorted from planarity towards a boat conformation. At Mn(1) and Mn(2), the five-member chelate rings incorporating the diamine fragment adopts half-chair and envelope conformation, respectively. The six-membered chelate ring around Mn(1) and Mn(2) incorporating aromatic fragment adopts boat and screw-boat conformation, respectively and the six-membered chelate ring around Mn(2) incorporating the acetylacetone fragments is essentially planar with no atoms deviating more than 0.01 Å from their respective mean planes. The complex remains as a one dimensional polymeric chain as shown in Fig. 2.

*3.4. Description of the structure of $[Mn(salen)(sal)]_2 \cdot 2H_2O$ (**2**)*

The crystal structure of complex **2** is composed of a centrosymmetric dinuclear unit $[Mn(salen)(sal)]_2$ as shown in Fig. 3, together with the atomic numbering scheme. Selected bond distances and angles are listed in Table 3. The two Mn^{III} atoms Mn(1) and Mn(1′), have distorted six-coordinate octahedral environment. The phenol functions of the Schiff-base ligand, O(2) and O(21) have been deprotonated during the synthesis and occupy the equatorial plane of the Mn site. The imine nitrogen atoms, N(10) and N(13) also occupy the equatorial site. The deviations of the four basal donor atoms from their mean plane are within ±0.011 Å. The Mn atom deviates from the basal plane by 0.189 Å. The out-of-plane Mn axial positions are occupied by a deprotonated salicylaldehyde molecule and an oxygen atom O(21′) from the neighboring [Mn(salen)] unit involved in the dinuclear complex. The $Mn–O_{phe}$ and $Mn–N_{imi}$ bond distances (Table 3) are in good agreement with those observed for similar compounds in the literature [18]. The axial Mn–O bond distances Mn(1)–O(22) 2.048(2) Å and Mn(1)–O(21′) 2.643(2) Å are significantly longer than the equatorial bonds as expected for a Jahn–Teller distortion of Mn ions with a +3 oxidation state (Table 3). Within the dimer, the two Mn^{III} ions are linked through the phenoxo oxygen atoms O(21) and O(21′); the angle of Mn(1)–O(21)–Mn(1′) is 108.31(8)° and the two Mn^{III} ions are separated by 3.817(5) Å. The six-member chelate ring around Mn(1) incorporating the aromatic residue adopts a boat conformation.

*3.5. Olefin epoxidation catalyzed by complex **2** in presence of terminal oxidants PhIO and NaOCl*

Complex **2** is soluble in both CH_3CN and CH_2Cl_2. Hence, its catalytic activity towards alkene (e.g. (*E*)-stilbene and styrene) epoxidation reaction has been investigated in CH_3CN and CH_2Cl_2 solvents at room temperature.

In both of these solvents, complex **2** produces a brown colour solution after dissolution. The colour is intensified on addition of the terminal oxidants, PhIO. When substrates (alkenes) are added the colour starts fading and on stirring the solution for ca. 3 h when complete consumption of the substrates is assumed, the intensity of the solution again increases to its original value, indicating completion of alkene epoxidation and the catalyst regeneration. The formation of epoxides was confirmed by appearance of the characteristic peak in the ^1H NMR spectroscopy of the resultant products (Figs. S3 and S4 for (*E*)-stilbene epoxide and styrene epoxide, respectively).

Table 3
Selected bond lengths (Å) and bond angles (°) in complex **2**.

Mn(1)–O(2)	1.827(2)
Mn(1)–O(21)	2.047(2)
Mn(1)–O(22)	2.048(2)
Mn(1)–N(10)	2.098(2)
Mn(1)–N(13)	1.961(2)
Mn(1)–O(21′)	2.643(2)
O(2)–Mn(1)–O(21)	88.81(9)
O(2)–Mn(1)–O(22)	95.17(9)
O(2)–Mn(1)–N(10)	97.72(9)
O(2)–Mn(1)–N(13)	168.58(9)
O(2)–Mn(1)–O(21′)	91.89(8)
O(21)–Mn(1)–O(22)	108.62(8)
O(21)–Mn(1)–N(10)	166.75(9)
O(21)–Mn(1)–N(13)	94.50(9)
O(21′)–Mn(1)–O(21)	71.69(7)
O(22)–Mn(1)–N(10)	82.38(9)
O(22)–Mn(1)–N(13)	94.13(9)
O(21′)–Mn(1)–O(22)	172.95(8)
N(10)–Mn(1)–N(13)	76.96(10)
O(21′)–Mn(1)–N(10)	96.47(8)
O(21′)–Mn(1)–N(13)	78.84(8)
Mn(1)–O(21)–Mn(1′)	108.31(8)

Symmetry code ′ = 2 − *x*, 1 − *y*, −*z*.

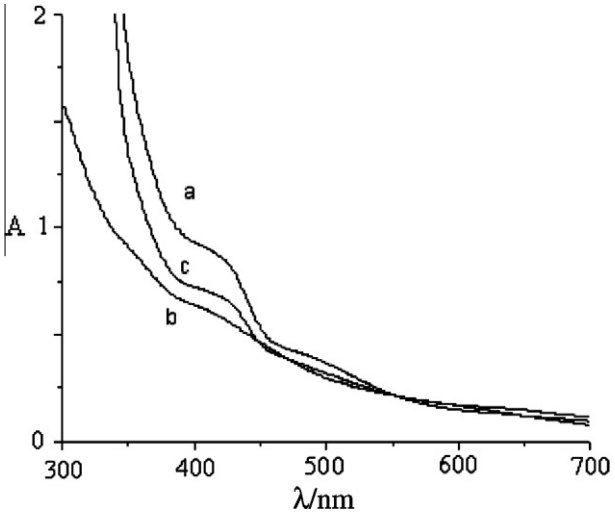


Fig. 4. UV–Vis spectral pattern of complex **2**: (a) 2.00×10^{-3} M solution of complex in dry acetonitrile at 25 °C, (b) after 1 h reaction with PhIO (0.300 mmol) (sample diluted by fivefold) and (c) after 1 day of the reaction (sample diluted fivefold).

Table 4
Yield of epoxides from the reaction of alkenes with PhIO or NaOCl catalysed by complex **2**.

Olefins	Terminal oxidant	Solvent	Isolated yield of epoxides (%)
(*E*)-stilbene	PhIO	CH_3CN	85
		CH_2Cl_2	70
	NaOCl	CH_3CN	60
		CH_2Cl_2	54
Styrene	PhIO	CH_3CN	40
		CH_2Cl_2	35
	NaOCl	CH_3CN	34
		CH_2Cl_2	30

Table 4 shows the maximum isolated yield (%) for (*E*)-stilbene and styrene epoxidation, respectively, using PhIO and NaOCl as terminal oxidants in both CH_2Cl_2 and CH_3CN. On comparing the yield of oxidation it may be stated that (i) PhIO is more efficient as terminal oxidant than NaOCl towards epoxidation of both (*E*)-stilbene and styrene resulting higher epoxide yield; (ii) solvent plays a crucial role in the alkene epoxidation process – the isolated yields of (*E*)-stilbene and styrene epoxide (Table 4) in presence of both terminal oxidants PhIO and NaOCl indicate that CH_3CN is a better solvent than CH_2Cl_2 for epoxidation of both the substrates. The slight improvement in epoxidation yield of alkenes with sodium hypochlorite as the oxygen source on changing the solvent from CH_2Cl_2 to CH_3CN is most probably related to higher solubility of the catalysts in CH_3CN. 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 CH_3CN are also to be taken in account to explain the better efficiency of CH_3CN as solvent for the epoxidation of styrene [52–54].

To examine the nature of the complex **2** in the catalytic process, we studied the UV–Vis spectral changes for complex **2** in the presence of PhIO (1.00×10^{-3} mmol complex in CH_2Cl_2 (5 cm^3) was treated with 0.300 mmol PhIO). The result for the complex has been shown in Fig. 4. It shows spectra before addition of PhIO (a), after 1 h of reaction (b) and after 1 day of reaction (c). PhIO was completely reacted after 1 day in a solution of the complex. After 1 day, complex **2** produced spectrum (c) which is identical to its original one (spectrum (a), Fig. 4) except for the lowering of the intensity. The species which was obtained after 1 day by the reaction of **2** with PhIO, was again treated with fresh PhIO (0.300 mmol) and alkenes. It was found to be as reactive as the initial compound (i.e. complex **2**) and this reactivity was noticed to be retained beyond four cycles.

4. Conclusion

Existence of Mn^{III} complexes with both unsymmetrical (uspen) and symmetrical (salen) tetradentate ligands were proved earlier by isolating them in the form of cocrystals [31]. In the present study, we have shown that these two different species can be joined together through a formate bridge to yield an unprecedented one-dimensional chain of alternating Mn^{III}–salen and Mn^{III}–uspen. It is to be noted that probability of linking two different species by formate is twice as much as that of any one of the similar species considering the equal concentration of Mn^{III}–salen and Mn^{III}–uspen. Therefore, formation of compound **1** is not surprising. The completely rearranged product, which is a phenoxo bridged dinuclear Mn^{III} complex (**2**) acts as an efficient catalyst in the epoxidation of alkenes, e.g. (*E*)-stilbene, styrene, etc and it retains its reactivity with high efficiency for a long time.

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Appendix A. Supplementary material

CCDC 742805 and 742806 contain the supplementary crystallographic data for complexes **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.09.036.

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