Synthesis, Crystal Structures, and Magnetic and Catalytic Studies on a Linear Trinuclear Mn^{II}₃ Complex

Arpan Dutta,^[a] Surajit Biswas,^[a] Albert Escuer,^[b] Malay Dolai,^[a] Subhadip Ghosh,^[a] and Mahammad Ali^{*[a]}

An almost linear (< Mn-Mn-Mn = 132.25°) trinuclear manganese(II) complex [Mn₃(L)(N₃)₄]·2 H₂O (1) of a decacoordinating N₈O₂ donor ligand, H₂L, was synthesized and structurally characterized by means of single-crystal X-ray crystallography and mass spectrometry. All the Mn^{II} centers are in pseudo-octahedral geometry and wrapped by a single decacoordinating N₈O₂ donor ligand. The central manganese atom (Mn2) is connected to two terminal manganese (Mn1 and Mn3) atoms by two bridging phenolate O atoms and two bridging azide N atoms. Compound 1 is the first example of a linear trinuclear model

Introduction

For quite some time there has been immense interest in the synthesis and study of manganese complexes to develop model compounds for the active sites of manganese-containing enzymes such as superoxide dismutase, catalase, and oxygen-evolving photosystems (PS-II),^[1] which has been further reinforced by the observation of interesting magnetic properties within these polynuclear systems.^[2,3] As a result, many novel polynuclear manganese complexes have been synthesized, some of which have been found to act as single-molecule magnets (SMMs)^[4-7] and behave as models for the manganese core of the oxygen-evolving complexes (OECs) in photosystem II.^[1,8,9] In addition to mononuclear manganese-based superoxide dismutase^[10] and manganese dioxygenase models^[11] as well as dinuclear manganese-based catalase^[12-16] models, tetranuclear manganese clusters were found in the oxygen-evolving PS-II. Efforts to correlate the structural characteristics of these polynuclear manganese cage complexes to their physical and chemical properties have been expanded enormously.^[4-9, 17-24] All these efforts have resulted in isolation of manganese clusters of various nuclearities.

Several linear trinuclear manganese(II) carboxylates such as $[Mn_3(O_2CR_3)_6(N-N)_2]$, in which N–N is 2,2'-bipyridyl (bpy),^[25] 1,10-phenanthroline (phen),^[26] 2-(2-pyridyl)benzimidazole,^[27] or 2,2'-bis(1-methylimidazolyl)phenylmethoxymethane,^[26b]

[a]	A. Dutta, Dr. S. Biswas, M. Dolai, S. Ghosh, Prof. M. Ali
	Department of Chemistry
	Jadavpur University
	Kolkata 700 032 (India)
	E-mail: m_ali2062@yahoo.com
[b]	Prof. A. Escuer
	Departament de Química Inorgànica
	Universitat de Barcelona
	Av. Diagonal 645, 08028 Barcelona (Spain)
	Av. Diagonal 645, 08028 Barcelona (Spain)

to show pronounced epoxidation of olefins by *tert*-butylhydroperoxide (TBHP) with a turnover number (TON) greater than 950. Though epoxidation of olefins by *m*-chloroperbenzoic acid (*m*-CPBA) was found to be complete within 20 minutes of mixing, the conversion was not more than 40% and corresponding alcohols were found to be major products, whereas with H_2O_2 as oxidant there was no visible catalytic epoxidation of olefins. Furthermore, the compound was characterized by temperature-dependent magnetic susceptibility measurements and a total spin ground state of $S_t = 15/2$ was found.

 $RCOO^-$ = benzoate,^[28] and chloroacetate,^[29] have been known for some time. Interestingly, a considerable degree of flexibility in the tricarboxylate-bridged dimetallic unit was notable in such linear trimers with Mn···Mn distances that range between 3.370(3) and 3.716(2) Å,^[26b] which is reflected by the change in magnetic properties even with small structural changes.^[29]

The interesting aspects of Mn^{II}/Mn^{III} or Mn^{III} trinuclear complexes with closed^[1,9,30-32] or linear open structures^[9,33-37] rely on the fact that they can serve as precursors to higher-nuclearity clusters and exhibit intriguing magnetic properties of their own. Most of these trinuclear compounds are symmetrical, with at least two of the three Mn ions being chemically equivalent. Asymmetric linear [Mn^{III}Mn^{III}] and [Mn^{II}Mn^{II}] compounds have been reported but are rare.^[36, 37] Moreover, [Mn^{III}Mn^{III}] and [Mn^{II}Mn^{II}] linear trimers that contain both phenolate and azide linkers have not been reported previously. The extended X-ray absorption fine structure (EXAFS) and ⁵⁵Mn electron nuclear double resonance (ENDOR) data of the S2 (Kock cycle) state along with the multiple electron paramagnetic resonance (EPR) signal suggest the existence of trimer↔monomer models and renewed interest in researching trinuclear Mn complexes as model compounds for OECs.^[38, 39]

Moreover, in the past few years, considerable progress has been made in the field of homogeneously catalyzed epoxidations of unfunctionalized olefins, which is believed to be an important methodology for the preparation of highly functionalized organic compounds. A few systems have been shown to be extremely useful in this field and have reached the stage of synthetic applicability. Again, for industrial purposes, manganese catalysts are preferred since manganese itself is a relatively nontoxic metal. Iron can also be considered,^[40] but so far manganese complexes have proven superior in selective epoxida-

Wiley Online Library



tion of olefins, chiefly because they show fewer side reactions than iron complexes.

The goal of this study was to design new manganese-based epoxidation catalysts with high selectivity towards epoxides. Here we have explored a linear (nearly) trinuclear Mn^{II}₃ complex that was structurally and magnetically characterized and used as a homogeneous catalyst to achieve epoxidation of ole-fins—namely, styrene and cyclooctene—by *tert*-butylhydroper-oxide (TBHP) that display remarkable turnover number (TON) and turnover frequency (TOF) values. Although there has been a report on the epoxidation of olefins catalyzed by a trinuclear manganese(II) complex,^[41] in solution the complex splits into mononuclear species. Therefore our studies constitute the first report on the epoxidation of olefins by *tert*-butylhydroperoxide catalyzed homogeneously by a robust trinuclear manganese(II) complex, which remains intact in solution.

Results and Discussion

The reaction of $Mn(OAc)_2 \cdot 2H_2O$ (3 equiv) with the ligand (1 equiv) and NaN₃ (4 equiv) in MeCN yielded the corresponding trinuclear Mn_3^{II} complex 1, the light brown single crystals of which were obtained by slow evaporation of the solvent.

Single-crystal X-ray diffraction studies revealed that complex 1 is a Mn^{\parallel} trinuclear species that consists of three Mn^{\parallel} ions, a decacoordinating N_8O_2 donor ligand (H_2L) , two bridging EE- N_3^- ions, and two terminal N_3^- ions. It crystallizes in a triclinic system with space group $P\bar{1}$. The structure consists of a discrete $[Mn^{\parallel}_3(L^2)(\mu-N_3)_2(N_3)_2]\cdot 2H_2O$ as a neutral species in which the ligand H_2L is doubly deprotonated. The three Mn^{\parallel} ions are linked almost linearly ($<Mn1-Mn2-Mn3 = 132.25^\circ$) by two phenoxo-O and two EO-azido-N bridges. The central Mn2 atom is coordinated by two bridging phenoxo (O1 and O2) and two ethylenic N (N4 and N5) atoms in the equatorial plane, whereas two N atoms (N12 and N15) from two bridging EO-azide ions occupy the axial positions. The two terminal Mn atoms—

namely, Mn1 and Mn3-are isostructural, and Mn1 is coordinated by two pyridine N atoms (N1 and N3), one tertiary N2 atom that connects two pyridine groups through two intervening methyl groups, and one N atom (N12) from a EO-bridging N_3^- group in the equatorial plane and the axial positions are occupied by an N9 atom from a terminal N₃⁻ group and a phenoxo-O1 atom. Identically, Mn3 is also coordinated by N7, N8 (pyridine), N15 (EO- N_3^-), and N6 (tertiary) in the equatorial plane, as well as O2 (phenoxo) and N18 (terminal azide) in axial positions. A molecular view of complex 1 is shown in Figure 1.







Figure 1. The coordination environment of complex 1. All hydrogen atoms and solvent atoms have been omitted for clarity.

The bond lengths around the central Mn^{II} ion are Mn2– O1(phenoxo) = 2.141(7) Å and Mn2–O2 (phenoxo) = 2.097(6) Å, Mn2–N4(ethylene diamine) = 2.213(7) Å and Mn2–N5 (ethylenediamine) = 2.218(9) Å, and Mn2–N12 = 2.27(1) Å (axial terminal) and Mn2–N15 (axial bridging) = 2.253(9) Å. The bond lengths around the two terminal Mn^{II} atoms fall in the range Mn1–N_x (x=1, 2, and 3) = 2.239(8)–2.30(1) Å and Mn3–N_x (x= 6, 7, and 8) = 2.25(1)–2.300(8) Å. Mn1–N12 ($\eta_{1,1}$ -N₃) = 2.13(1) Å, Mn3–N15 ($\eta_{1,1}$ -N₃) = 2.149(8) Å, and Mn1–O1 = 2.203(6) Å and Mn3–O2 = 2.215(7) Å. For terminal azide ions the bond lengths are Mn1–N9 = 2.15(1) Å and Mn3–N18 = 2.14(1) Å. All the Mn atoms are hexacoordinated in a distorted-octahedral geometry. The selected bond lengths and bond angles are given in



Table 1; these agreed well with the normal reported values in analogous Mn_{3}^{II} complexes.^[36,37] The Mn···Mn internuclear distances fall in the range of 3.373–3.88 Å.

Complex 1 also forms a 2D supramolecular framework (Figure 2) through intermolecular hydrogen-bonding interac-



Figure 2. The 2D supramolecular framework formed through the intermolecular hydrogen-bond interactions as well as π - π stacking of complex 1.

tions (namely, two ethylenic hydrogen atoms with μ^2 -azide groups and monodented azide with phenolic/aromatic –CH···N interactions, C38–H38····N17=2.642 Å, C42–H42···N17=2.524 Å, C22–H22A····N17=2.633 Å, C22–H22B····N20=2.622 Å, C7–H7B····N20=2.666 Å, C4–H4····N20=2.674 Å, C10–H10····N14=2.508 Å, C26–H26····N14=2.557 Å).

Bond valence sum (BVS) calculations

Bond valence sum (BVS)^[42] is a method that is very frequently used to examine the nature of the coordination and oxidation states of the central metal atom by using the crystallographic data in coordination complexes as well as in many biological molecules. The most successful empirical equation is [Eq: (1)]

$$\Sigma s_{ij} = \Sigma \exp[(R_o - R_{ij})/0.37] \tag{1}$$

in which R_o is a parameter characteristic of the bond and R_{ij} is the crystallographically obtained bond lengths. The value of Σ_{Rij} represents the charge on the central metal atom. From the calculations (Table 2) it can be seen that the oxidation state of the manganese is 2.32, 2.31, and 2.29 for Mn1, Mn2, and Mn3, respectively, which unequivocally indicates the +2 oxidation state for the Mn atoms in complex **1**.

Catalytic epoxidation

Olefin epoxidations catalyzed by different transition-metalbased catalysts under homogeneous^[43] and heterogeneous conditions^[44–49] have been thoroughly explored. Stack and coworkers reported a notable catalyst system, $[Mn^{II}{(R,R)}-mcp](CF_3SO_3)_2]$ (mcp = N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-

Table 2. Bond valence sum calculation for Mn atoms in complex 1.								
Bond type (<i>R_{ij}</i>)	R _{ij}	R _o	$R_{o}-R_{ij}$	$\exp[R_{o} - R_{ij}]/0.37$				
Mn1–O1	2.2030	1.79	-0.413	0.328				
Mn1–N1	2.257	1.87	-0.387	0.351				
Mn1–N2	2.302	1.87	-0.432	0.311				
Mn1–N3	2.239	1.87	-0.369	0.369				
Mn1–N9	2.155	1.87	-0.285	0.463				
Mn1–12	2.13	1.87	-0.260	0.495				
total				2.317				
Mn2–01	2.141	1.79	-0.351	0.387				
Mn1–O2	2.097	1.79	-0.307	0.436				
Mn2–N4	2.213	1.87	-0.343	0.396				
Mn2–N5	2.218	1.87	-0.348	0.390				
Mn2–N12	2.267	1.87	-0.397	0.342				
Mn2–N15	2.253	1.87	-0.383	0.355				
total				2.307				
Mn3–O2	2.215	1.79	-0.425	0.317				
Mn3–N6	2.3	1.87	-0.430	0.313				
Mn3–N7	2.249	1.87	-0.379	0.359				
Mn3–N8	2.264	1.87	-0.394	0.345				
Mn3–N15	2.149	1.87	-0.279	0.470				
Mn3–N18 2.138 1.87		1.87	-0.268	0.485				
total				2.289				

CHEMPLUSCHEM

Full Papers

1,2-diaminocyclohexane),^[49] in which the use of peracetic acid significantly expanded the scope of epoxidation of olefin substrates to include terminal and electron-deficient double bonds despite the fact that some sensitive olefins, such as styrene derivatives, are still problematic. Later it was revealed that monomeric manganese catalysts that bear more robust bidentate nitrogen ligands, such as $[Mn^{II}(bipy)_2(CF_3SO_3)_2]$, displayed even higher activities than the initial $[Mn^{II}\{(R,R)-mcp\}(CF_3SO_3)_2]$ system.^[50]

Recently, a series of trinuclear manganese complexes coordinated by a neutral bidentate nitrogen donor ligand, [Mn₃L₂(OAc)₆], were found to exhibit excellent catalytic activity and selectivity in the epoxidation of olefins by peracetic acid under mild conditions.^[41] The highest activity was found with [Mn₃(ppei)₂(OAc)₆] (ppei=2-pyridinal-1-phenylethylimine), which expanded the substrate scope to terminal and electrondeficient double bonds of both aliphatic and aromatic alkenes. The in situ generated complex from a mixture of pyridylimino ligands and manganese acetates also showed undiminished reactivity, thus making this process more convenient. Here, observed conversion was almost negligible with $Mn^{II}(OAc)_{2} \cdot 4H_{2}O$ or $Mn^{III}(OAc)_{3} \cdot 2H_{2}O$ (2 mol%) in the absence of external ligands,^[41] thus pointing out the fact that the oxidation state of the manganese acetate precursors has little effect on the resulting catalytic activities. It was also observed that analogous cyclic trinuclear complexes, [Mn₃(bipy)₂(OAc)₆] and [Mn₃(phen)₂(OAc)₆], displayed excellent activities.^[41] However, the trinuclear complexes [Mn₃(ppei)₂(OAc)₆] dissociate into monomeric species with the formulation of [Mn(ppei)₂(OAc)₂] under the reaction conditions.^[52] The trinuclear to mononuclear conversion is easy here owing to the presence of the bidentate ligand in which the central Mn^{II} is connected to the two terminal Mn^{II} ions simply by acetate bridging. Again, with



 $[Mn_3(ppei)_2(OAc)_6]$, the use of an oxidant other than peracetic acid, such as $H_2O_{2r}^{[41]}$ gave significantly reduced yields of epoxides.

In the present report, we have explored the catalytic epoxidation of two olefins—namely, styrene and cyclooctene—by *tert*-BuOOH in the presence of a catalytic amount of Schiff base complex 1 in MeCN. The main interesting feature of this complex is that in the trinuclear entity the three Mn^{II} ions are entrapped by a single decacoordinating (N₈O₂) ligand along with two bridging and two terminal azide ions to give a rigid structure to the complex. Therefore in solution there is no or negligible possibility of a trinuclear mononuclear equilibrium, as was observed by Chang et al.,^[41] and this is further confirmed by ESI-MS⁺ (*m/z*) studies (1050.2203 for [Mn₃(L)(N₃)₄]⁺).

The results of the catalytic oxidation of styrene and cyclooctene are given in Table 3. Under homogeneous conditions, the

Table 3. Homogeneous catalytic oxidation of olefins by TBHP to epoxides catalyzed by 1 (catalyst concentration: 0.03 mmol).									
Substr.	Reaction time [h]	Conv.	Yield of pr epoxide	od. [%] other	TON				
styrene	3	16	26	74	346				
styrene	6	26	31	69	563				
styrene	9	31	39	61	671				
styrene	12	37	41	59	801				
styrene	24	44	43	57	953				
cyclooctene	3	9	77	23	150				
cyclooctene	6	17	79	21	283				
cyclooctene	9	40	81	19	667				
cyclooctene	12	58	84	16	967				
cyclooctene	24	71	78	22	1183				

styrene oxidation by *tert*-BuOOH gives approximately 43% styrene epoxide selectively with a TON of approximately 950 (Table 3) after 24 h along with a moderate amount of benzaldehyde (ca. 40%) when complex 1 was used as catalyst (Scheme 1). The *tert*-BuOOH oxidation of cyclooctene (Table 3) also proceeds smoothly and shows excellent conversion of approximately 71% in 24 h with good epoxide selectivity (ca. 78%; Figure 3). Nevertheless, cyclooctene oxide was not the sole product of this reaction, and cyclooctane-1,2-diol (ca. 20%) (Scheme 2) was also generated owing to allylic C–H oxidation with a TON of 1136.





CHEMPLUSCHEM Full Papers



Figure 3. Comparison of the conversion of styrene and cyclooctene at different reaction times in the liquid-phase epoxidation catalyzed by 1.



Scheme 2. Synthesis of the proligand. TEA = triethylamine.

The use of Jacobsen catalyst^[51] and the related Katsuki manganese $N_i N'$ -ethylenebis(salicylimine) (salen) catalyst^[52] led to high yields and moderate to excellent enantioselectivities for the oxidation of cis olefins with TONs of 35 to 40 in which iodosylarenes, sodium hypochlorite, molecular oxygen, and so forth were employed as oxidant. Again, a dinuclear manganese complex $[Mn_2(\mu_2-O)(\mu_2-OAc)_2L_2]$ (L = tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) exhibited efficient catalytic oxidation of styrene derivatives by H_2O_2 with a TON of more than 400 without notable catalyst degradation^[53] but it was found to be unsuitable for the epoxidation of electron-deficient olefins. However, high turnover numbers up to 1000 have been reported for the conversion of several alkenes and styrene to the epoxides by the in situ prepared Mn-tmtacn complex using MnSO₄.^[54] After subsequent addition of substrate and oxidant to the reaction mixture, the rate of oxidation remained constant, thus indicating that the catalyst is extremely robust under the oxidation.

Towards this end, the trinuclear complex 1 was found to be superior with respect to TON over the manganese complexes reported so far. In our system (1) the two terminal Mn^{II} atoms are axially coordinated by two terminal N_3^- groups, which seem to be labile and facilitate the accommodation of *tert*-butylhydroperoxide (TBHP) as an active intermediate in the catalytic cycle, or the Mn^{II} center can accommodate TBHP to expand its coordination number to 7. Although we have an impression of the existence of the parent compound in solution through ESI-MS⁺ analysis (1050.2203 for [LMn₃(N₃)₄]⁺ (Figure 4), we failed to get the corresponding peak for TBHP-coordinated species, which might be due to highly reactive nature of the intermediate at room temperature. When we used H₂O₂ under identical reaction conditions, the epoxidation was found to be very low, which might be due to decomposi-





Figure 4. HRMS analysis of [Mn₃(L)(N₃)₄] (top) and [Mn₃(L)(N₃)₄(m-CPBA)] (bottom) in MeOH.

tion of the complex, and indeed it occurs as we failed to get any ESI-MS⁺ peaks that correspond to H_2O_2 adducts of the complex. Again, m-Cl-perbenzoic (m-CPBA) acid results an approximately 40% conversion, but the major product is alcohol rather than epoxides. Here this conversion becomes saturated within 20 minutes and upon a further increase of the reaction time there is no improvement in the percentage of substrate conversion. The reason for this limitation might be due to the degradation of the catalyst in the presence of a strong oxidizing agent such as *m*-CPBA, and this is supported by HRMS $ESI-MS^+ = 611.6006$ $[LMn_3(N_3)_4(m-CPBA) + H]^{2+}$ analysis: (Figure 4) of this reaction mixture, whereas no traces of the mother complex were observed, which was found to be present otherwise in other cases.

Magnetic properties

The value of $\chi_{\rm M}T$ product for compound 1 shows a room-temperature value of 13.89 cm³mol⁻¹K, which is in good agreement with the expected value of 13.125 cm³mol⁻¹K for three isolated Mn^{II} cations (Figure 5). Upon cooling, $\chi_{\rm M}T$ increases continuously up to a maximum value of 28.2 cm³mol⁻¹K at

CHEMPLUSCHEM Full Papers

3.75 K. Below this temperature the $\chi_{\rm M}T$ product decreases slightly down to a final value of 26.9 cm³ mol⁻¹ K at 2.0 K.

According to the structural data, which show only minor differences in the Mn-O-Mn and Mn-N-Mn bond angles between Mn1····Mn2 and Mn2····Mn3, the system was modeled according to the scheme shown in Figure 5 as a linear arrangement of three Mn^{II} cations with the analytical equation derived from the Hamiltonian [Eq. (2)]

$$H = -J_1(S_1 \cdot S_2 + S_2 \cdot S_3) - J_2(S_1 \cdot S_3)$$
(2)

and including a z'J' term to take into account the intermolecular interactions. The best-fit parameters were $J_1 = +1.84(1) \text{ cm}^{-1}$, $J_2 = -0.02(1) \text{ cm}^{-1}$, z'J' = -0.39(1), and g = 2.019(1).

As could be expected, the J_2 interaction between the terminal Mn1 and Mn3 cations is negligible, and the $\chi_M T$ decay at low temperature should be attributed to intermolecular interactions, probably hydrogen bonds that involve the azido ligands. The ferromagnetic inter-

action J_1 leads to an unusually large S = 15/2 ground state. The ground state was confirmed by means of the magnetization measurement, which shows a saturated value equivalent to 15 electrons under the maximum applied field of 5 T. As ex-



Figure 5. The $\chi_M T$ product for compound 1. Inset: Magnetization plot measured at 2 K. Solid lines show the best fits following the indicated coupling scheme (see text).



pected, the plot follows a S = 15/2 Brillouin function (Figure 3, inset).

Although, mixed oxo or hydroxo/azide bridges have been widely studied^[55] and usually they promote ferromagnetic coupling, the corresponding alkoxo/azide bridgeshave been scarcely reported to date.^[56] Compound **1** shows an unprecedented phenoxo/azido bridge between Mn^{II} centers, and the ferromagnetic interaction between the spin carriers is consistent with the Mn-O_{phenoxo}-Mn and Mn-N_{azido}-Mn bond angles that lie in the 99.4(5)–103.4(4)° range, which is usually associated with ferromagnetic coupling.^[55]

Conclusion

A dodecadentate N₈O₂ donor ligand, H₂L, was generated in situ, which, upon reacting with manganese(II) acetate in methanol in the presence of azide ion, gives a linear trinuclear manganese(II) complex $[Mn_3(L)(N_3)_4] \cdot 2H_2O$ (1) as a brown rodshaped crystal. The structure determination by means of single-crystal X-ray crystallography reveals that it is a linear trinuclear $\mathsf{Mn}^{{\scriptscriptstyle \|}}$ complex in which all the $\mathsf{Mn}^{{\scriptscriptstyle \|}}$ centers are in pseudo-octahedral geometry. The central manganese atom (Mn2) is connected to two terminal manganese (Mn1 and Mn3) atoms by two bridging phenolate-O atoms and two bridging azide-N atoms with Mn····Mn internuclear distances in the range of 3.37–3.88 Å. Compound 1 is the first example of a linear trinuclear model that showed pronounced epoxidation of olefins by tert-butylhydroperoxide with a TON > 950. Although epoxidation of olefins by m-chloroperbenzoic acid (m-CPBA) was found to be complete within 20 minutes of mixing, the conversion was not more than 40%, and corresponding alcohols were found to be major products, whereas with H₂O₂ as oxidant there was no visible catalytic epoxidation of olefins. HRMS analysis revealed that the catalytic reactions proceed through the formation of $[(Mn_3L)(N_3)_4(m-CPBA)]$ intermediate with an expansion of coordination number. However, we failed to identify such an intermediate for TBHP as oxidant. Furthermore, it was characterized by temperature-dependent magnetic susceptibility measurements, and a total spin ground state of $S_t = 5/2$ was determined, which was found to be involved in ferromagnetic interactions with the neighboring Mn^{II} centers.

Experimental Section

Reagents

2-(Chloromethyl)-6-carbaldehyde-4-methylphenol and 2-[*N*,*N*-bis(2-methylpyridyl)aminomethyl]-6-carbaldehyde-4-methylphenol were prepared by the reported method.^[57] Mn(OAc)₂·4 H₂O (Aldrich), ethylenediamine (Merck, India), benzyl amine (Merck, India), triethyl-amine (Merck, India), bis-picolylamine (Aldrich), and sodium azide (Merck, India) were of reagent grade and used as received. Solvents such as MeCN (Merck India), methanol, ethanol, and other solvents were of reagent grade and were dried using standard methods before use.

Physical measurements

Elemental analyses were carried out with a Perkin–Elmer 240 elemental analyzer. ¹H NMR spectra were recorded in CDCl₃ with a Bruker 300 MHz NMR spectrophotometer using tetramethylsilane ($\delta = 0$ ppm) as an internal standard. Electronic spectra were recorded with an Agilent-8453 diode array UV/Vis spectrophotometer. Infrared spectra (400–4000 cm⁻¹) were recorded from KBr pellets with a Nicolet Magna IR 750 series-II FTIR spectrophotometer. Magnetic susceptibility measurements were carried out on polycrystalline samples using a Quantum Design MPMS-5 SQUID susceptometer working in the range 2–300 K under magnetic fields of 0.3 T (300–30 K) and 0.03 T (30–2 K) to avoid saturation effects. Diamagnetic corrections were estimated from Pascal tables.

Catalytic studies

The catalytic epoxidation reactions were carried out in the liquid phase in a batch reactor at approximately 55 °C. During our studies, a 50 mL two-necked, round-bottomed flask equipped with a water condenser that contained alkene (65 mmol in the case of styrene and 50 mmol in that of cyclooctene) in acetonitrile (MeCN; 10 mL) solvent and catalyst (0.03 mmol) was kept in a preheated oil bath. TBHP (2 mL) was then added to the mixture and it was magnetically stirred continuously for 24 h. TBHP (0.5 mL) was added intermittently at a time interval of 60 min. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by means of gas chromatography.

Synthesis of proligand 2-[N,N-bis(2-methylpyridyl)aminomethyl]-6-carbaldehyde-4-methylphenol (HL)

2-Chloromethyl-6-carbaldehyde-4-methylphenol (1.515 g, 8.2 mmol) was dissolved in dry THF (15 mL) in a round-bottomed flask. Bis-picolylamine (1.630 g, 8.2 mmol) and triethylamine (Et₃N) (1.659 g, 16.4 mmol) were dissolved in dry THF (10 mL), and this mixture was added dropwise to the 2-chloromethyl-6-carbaldehyde-4-methylphenol solution. Instant precipitation of Et₃NHCl was observed, and the solution turned bright yellow (Scheme 2). After 24 h of stirring, the precipitate Et₃NHCl was removed by filtration. Solvent (THF) was removed under reduced pressure to obtain an oily product, which, upon storage in the refrigerator for a couple of days, yielded a light-yellow crystalline solid. The solid product was then filtered and washed with cold ether. Yield: 78 %. ¹H NMR (CDCl₃, 300 MHz): $\delta = 2.27$ (s, 3 H; Me), 3.80, 3.85 (s, 2 H; Ar-CH₂-N), 3.94 (s, 4H; N-CH₂-py); 7.16-7.68 (8H; pyridine H), 7.40 and 7.37 (2H; aromatic H), 10.39 (s, 1H; OH), 11.48 ppm (s, 1H; CHO).

Synthesis of complex $[Mn_3(L)(N_3)_4] \cdot 2 H_2O(1)$

2-[*N*,*N*-Bis(2-methylpyridyl)aminomethyl]-6-carbaldehyde-4-methylphenol (0.347 g, 1.00 mmol) and ethylenediamine (0.03 g, 0.50 mmol) in methanol (30 mL) were heated to reflux together for 40 min. After cooling to room temperature, manganese(II) acetate tetrahydrate (0.368 g, 1.50 mmol) was added and heated to reflux for 1 h. Sodium azide (0.260 g, 4 mmol) was then added, and the mixture was stirred for another 24 h. The yellow solution turned brown (Scheme 3). It was filtered and kept in a rack. Slow evaporation of methanol gave rod-shaped brown crystals suitable for X-ray studies. Elemental analysis calcd (%) for $C_{44}H_{46}Mn_3N_{20}O_4$ (1083.82): C 48.72, H 4.15, N 25.83; found: C 48.55, H 4.18, N 25.70.



Scheme 3.

X-ray crystallography

Single-crystal X-ray data of complex 1 were collected with a Bruker SMART APEX-II CCD diffractometer using graphite-monochromated $Mo_{\kappa a}$ radiation ($\lambda = 0.71073$ Å). Data collection, reduction, structure solution, and refinement were performed using the Bruker Apex-II suite program at a temperature of 293 K. All available reflections to $2\theta_{\rm max}$ were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus.^[58] Reflections were then corrected for absorption, interframe scaling, and other systematic errors with SADABS.^[58] The structures were solved by direct methods and refined by means of full-matrix least-squares techniques based on F^2 with the SHELX-97 software package.[59] The water molecules O4A and O3---H3A were disordered in their position, and hydrogen atoms could not be fixed on them. All the non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were fixed by HFIX and those that belonged to carbon and nitrogen atoms were placed in their geometrically idealized positions. The molecular view and the other structural representations were drawn by using the DIAMOND-3.2, PLATON-v1.16, and MER-CURY-2.4 software packages. The crystallographic data for 1: $C_{44}H_{45}Mn_3N_{20}O_4$, $M_r = 1082.82$, triclinic, $P\bar{1}$ (no. 2), a = 13.352, b =13.505(5), c = 14.167(5) Å; $\alpha = 98.934(5)$, $\beta = 100.508(5)$, $\gamma =$ 94.085(5)°; V=2468.2(16) Å³, Z=2, $\rho_{\text{calcd}=}$ 1.457 g cm⁻³, $\mu(\text{Mo}_{\text{K}\alpha})$ = 0.820 mm⁻¹, F(000) = 1112; crystal size: $0.20 \times 0.25 \times 0.30$ mm³, T =293 K, Mo_{Ka} radiation $\lambda = 0.71069$ Å, $\theta_{min}/\theta_{max} = 1.6/25.0^{\circ}$, data set: -15:15; -15:15; -16:16; total reflections: 24883, unique reflections: 8707, R(int) = 0.055, observed reflections $[I > 2\sigma(I)]$: 6060; N_{ref} N_{par}: 8707, 644; *R*, *wR*2, *S*: 0.1199, 0.2885, 1.09.

Acknowledgements

Financial support from CSIR (grant no. 02(2490)/11/EMR-II) is gratefully acknowledged. The DST-FIST Departmental Programme is also acknowledged for providing SCXD facilities.

Keywords: epoxidation · magnetic properties · manganese · mass spectrometry · X-ray diffraction

- S. Mukhopadhyay, S. K. Mandal, S. Bhaduri, W. H. Armstrong, *Chem. Rev.* 2004, 104, 3981.
- [2] B. Zhou, R. Tao, S. Q. Shen, J. Q. Liang, Phys. Rev. A 2002, 66, 010301.

- [3] a) D. Gatteschi, R. Sessoli, Angew. Chem. Int. Ed. 2003, 42, 268; Angew. Chem. 2003, 115, 278; b) G. E. Kostakis, V. A. Blatov, D. M. Proserpio, Dalton Trans. 2012, 41, 4634.
- [4] R. Sessoli, H. L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, J. Am. Chem. Soc. 1993, 115, 1804.
- [5] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141.
 [6] C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Per-
- lepes, G. Christou, E. K. Brechin, J. Am. Chem. Soc. 2007, 129, 2754.
 [7] a) C. J. Milios, R. Inglis, A. Vinslava, R. Bagai, W. Wernsdorfer, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, J. Am. Chem. Soc. 2007, 129, 12505; b) G. E. Kostakis, A. M. Ako, A. K. Powell, Chem. Soc. Rev. 2010, 39, 2238.
- [8] C. Boskovic, E. K. Brechin, W. E. Streib, K. Folting, J. C. Bollinger, D. N. Hendrickson, G. Christou, J. Am. Chem. Soc. 2002, 124, 3725.
- [9] D. P. Kessissoglou, Coord. Chem. Rev. 1999, 185, 837.
- [10] J. W. Whittaker in *Metal lons in Biological Systems, Vol. 37* (Eds.: A. Sigel, H. Sigel), Marcel Dekker, Inc., New York, Basel, **2000** p. 587.
- [11] L. Que, M. F. Reynolds in *Metal lons in Biological Systems, Vol. 37* (Eds.: A. Sigel, H. Sigel), Marcel Dekker, Inc., New York, Basel, 2000, p. 505.
- [12] W. F. Beyer Jr., I. Fridovich, Biochemistry 1985, 24, 6460.
- [13] Y. Kono, I. Fridovich, J. Biol. Chem. 1983, 258, 6015.
- [14] V. V. Barynin, A. A. Vagin, W. R. Melik-Adamyan, A. I. Grebenko, S. V. Khangulov, A. N. Popov, M. E. Andrianova, B. K. Vainshtein, *Dokl. Akad. Nauk SSSR* **1986**, *288*, 877.
- [15] V. V. Barynin, P. D. Hempstead, A. A. Vagin, S. V. Antonyuk, W. R. Melik-Adamyan, V. S. Lamzin, P. M. Harrison, P. J. Artymiuk, *J. Inorg. Biochem.* 1997, 67, 196.
- [16] G. S. Allgood, J. J. Perry, J. Bacteriol. 1986, 168, 563.
- [17] J. A. Hoshiko, G. Wang, J. W. Ziller, G. T. Yeev, A. F. Heyduk, *Dalton Trans.* 2008, 5712.
- [18] A. Sieber, D. Foguet-Albiol, O. Waldmann, S. T. Ochsenbein, R. Bircher, G. Christou, F. Fernandez-Alonso, H. Mutka, H. U. Güdel, *Inorg. Chem.* 2005, 44, 6771.
- [19] T. C. Stamatatos, D. Foguet-Albiol, K. M. Poole, W. Wernsdorfer, K. A. Abboud, T. A. O'Brien, G. Christou, *Inorg. Chem.* 2009, 48, 9831.
- [20] T. C. Stamatatos, K. M. Poole, K. A. Abboud, W. Wernsdorfer, T. A. O'Brien, G. Christou, *Inorg. Chem.* 2008, 47, 5006.
- [21] C. M. Zaleski, T.-C. Weng, C. Dendrinou-Samara, M. Alexiou, P. Kanakaraki, W.-Y. Hsieh, J. Kamp, J. E. Penner-Hahn, V. L. Pecoraro, D. P. Kessissoglou, *Inorg. Chem.* 2008, 47, 6127.
- [22] R. Bagai, K. A. Abboud, G. Christou, Inorg. Chem. 2008, 47, 621.
- [23] R. Bhula, S. Collier, W. T. Robinson, D. C. Weatherburn, *Inorg. Chem.* 1990, 29, 4027.
- [24] S. Menage, S. E. Vitols, P. Bergerat, E. Codjovi, O. Kahn, J.-J. Girerd, M. Guillot, X. Solans, T. Calvet, *Inorg. Chem.* **1991**, *30*, 2666.
- [25] a) K. Tsuneyoshi, H. Kobayashi, H. Miyamae, Acta Crystallogr. Sect. C 1993, 49, 233; b) R. L. Rardin, P. Poganiuch, A. Bino, D. P. Goldberg, W. B. Tolman, S. Liu, S. J. Lippard, J. Am. Chem. Soc. 1992, 114, 5240.
- [26] V. Tangoulis, D. A. Malamatari, K. Soulti, V. Stergiou, C. P. Raptopoulou, A. Terzis, T. A. Kabanos, D. P. Kessissoglou, *Inorg. Chem.* **1996**, *35*, 4974.
- [27] G. Christou, Acc. Chem. Res. 1989, 22, 328.
 [28] G. Fernández, M. Corbella, J. Mahía, M. A. Maestro, Eur. J. Inorg. Chem. 2002, 2502.
- [29] R. Bhula, G. J. Gainsford, D. C. Weatherburn, J. Am. Chem. Soc. 1988, 110, 7550.
- [30] A. Dimitrakopoulou, V. Psycharis, C. P. Raptopoulou, A. Terzis, V. Tangoulis, D. P. Kessissoglou, *Inorg. Chem.* 2008, 47, 7608.
- [31] C. Lampropoulos, K. A. Abboud, T. C. Stamatatos, G. Christou, Inorg. Chem. 2009, 48, 813.
- [32] D. Maspoch, J. Gomez-Segura, N. Domingo, D. Ruiz-Molina, K. Wurst, C. Rovira, J. Tejada, J. Veciana, *Inorg. Chem.* 2005, 44, 6936.
- [33] P. Sobota, J. Utko, S. Szafert, Z. Janas, T. J. Glowiak, Chem. Soc. Dalton Trans. 1996, 3469.
- [34] J. L. Seela, M. J. Knapp, K. S. Kolack, H.-R. Chang, J. C. Huffman, D. N. Hendrickson, G. Christou, *Inorg. Chem.* 1998, 37, 516.
- [35] G. Aromí, P. Gamez, J. Krzystek, H. Kooijman, A. L. Spek, E. J. MacLean, S. J. Teat, H. Nowell, *Inorg. Chem.* 2007, 46, 2519.
- [36] G. Aromi, P. C. Berzal, P. Gamez, O. Roubeau, H. Kooijman, A. L. Spek,
 W. L. Driessen, J. Reedijk, Angew. Chem. Int. Ed. 2001, 40, 3444; Angew.
 Chem. 2001, 113, 3552.

www.chempluschem.org

1446



- [37] M. Kloskowski, D. Pursche, R.-D. Hoffmann, R. Pöttgen, M. Läge, A. Hammerschmidt, T. Glaser, B. Krebs, Z. Anorg. Allg. Chem. 2007, 633, 106.
- [38] a) K. N. Ferreira, T. N. Iverson, K. Maghlaoui, J. Barber, S. Iwata, *Science* 2004, 303, 1831; b) A. Zouni, H. T. Witt, J. Kern, P. Fromme, N. Krauss, W. Saenger, P. Orth, *Nature* 2001, 409, 739; c) N. Kamiya, J.-R. Shen, *Proc. Natl. Acad. Sci. USA* 2003, 100, 98.
- [39] a) J. M. Peloquin, K. A. Campbell, K. W. Randall, M. A. Evanchik, V. L. Pecoraro, W. H. Armstrong, R. D. Britt, *J. Am. Chem. Soc.* 2000, *122*, 10926;
 b) M. Dolai, A. Amjad, M. Debnath, J. van Tol, E. del Barco, M. Ali, *Inorg. Chem.* 2014, *53*, 5423.
- [40] K. Hasan, N. Brown, C. M. Kozak, Green Chem. 2011, 13, 1230–1237 and the references therein.
- [41] B. Kang, M. Kim, J. Lee, Y. Do, S. Chang, J. Org. Chem. 2006, 71, 6721– 6727.
- [42] N. E. Brese, M. O'Keeffe, Acta Crystallogr. Sect. B 1991, 47, 192-197.
- [43] S. Seelan, A. K. Sinha, D. Srinivas, S. Sivasanker, J. Mol. Catal. A 2000, 157, 163.
- [44] P. Karandikar, M. Agashe, K. Vijayamohanan, A. Chandwadkar, J. Appl. Catal. A: Gen. 2004, 257, 133.
- [45] D. E. De Vos, M. Dams, B. F. Sel, P. A. Jacobs, Chem. Rev. 2002, 102, 3615.
- [46] T. Osako, S. Nagatomo, Y. Tachi, T. Kitagawa, S. Itoh, Angew. Chem. Int. Ed. 2002, 41, 4325; Angew. Chem. 2002, 114, 4501.
- [47] S. T. Prigge, B. A. Eipper, R. E. Mains, L. M. Amzel, Science 2004, 304, 864.
- [48] R. A. Ghiladi, K. R. Hatwell, K. D. Karlin, H. W. Huang, P. Moënne-Loccoz, C. Krebs, B. H. Huynh, L. A. Marzilli, R. J. Cotter, S. Kaderli, A. D. Zuberbühler, J. Am. Chem. Soc. 2001, 123, 6183.
- [49] A. Murphy, A. Pace, T. D. P. Stack, Org. Lett. 2004, 6, 3119.
- [50] B. S. Lane, K. Burgess, J. Am. Chem. Soc. 2001, 123, 2933.

- [51] a) W. Zhang, E. N. Jacobsen, J. Org. Chem. **1991**, 56, 2296; b) J. F. Larrow, E. N. Jacobsen, Y. Gao, Y. Hong, X. Nie, C. M. Zepp, J. Org. Chem. **1994**, 59, 1939.
- [52] a) T. Schwenkreis, A. Berkessel, *Tetrahedron Lett.* **1993**, *34*, 4785; b) A. Berkessel, M. Frauenkron, T. Schwenkreis, A. Steinmetz, G. Baum, D. Fenske, *J. Mol. Catal. A: Chem.* **1996**, *113*, 321.
- [53] V. Chin Quee-Smith, L. DelPizzo, S. H. Jureller, J. L. Kerschner, R. Hage, *Inorg. Chem.* **1996**, *35*, 6461.
- [54] D. E. De Vos, T. Bein, Chem. Commun. 1996, 917.
- [55] A. Escuer, J. Esteban, S. P. Perlepes, T. C. Stamatatos, *Coord. Chem. Rev.* 2014, 275, 87.
- [56] a) S. Brooker, V. McKee, *Chem. Commun.* **1989**, 619; b) G. S. Papaefstathiou, A. Escuer, C. P. Raptopoulou, A. Terzis, S. P. Perlepes, R. Vicente, *Eur. J. Inorg. Chem.* **2001**, 1567; c) L. A. Berben, J. C. Peters, *Inorg. Chem.* **2008**, *47*, 11669; d) E. E. Moushi, T. C. Stamatatos, V. Nastopolos, G. Christou, A. J. Tasiopoulos, *Polyhedron* **2009**, *28*, 3203; e) S. K. Langley, N. F.
 - Chilton, B. Moubaraki, K. S. Murray, Dalton Trans. 2011, 40, 12201.
- [57] E. Lambert, B. Chabut, S. C. Noblat, A. Deronzier, G. Chottard, A. Bousseksou, J. P. Tuchagues, J. Laugier, M. Bardet, J. M. Latour, J. Am. Chem. Soc. 1997, 119, 9424.
- [58] G. M. Sheldrick, SAINT, Version 6.02, SADABS, Version 2.03, Bruker AXS Inc., Madison, Wisconsin (USA), 2002.
- [59] G. M. Sheldrick, SHELXL-97, Crystal Structure Refinement Programme, University of Göttingen, Göttingen (Germany), 1997.

Manuscript received: February 27, 2015 Final Article published: May 20, 2015