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Manganese(II) Complexes of Tetradentate 4N Ligands with Diazepane Backbone for Catalytic Olefin Epoxidation: Effect of Nucleophilicity of Peroxo Complexes On Reactivity

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Abstract

A series of Mn(II) complexes of the types $[Mn^{II}(L)](ClO_4)_2$ **1** - **4** and $[Mn^{II}(L)Cl_2]$ **1a - 4a**, where L = *N*,*N'*-bis(2-pyrid-2-ylmethyl)-1,4-diazepane (**L1**), *N*-(6-methylpyrid-2-ylmethyl)-*N'*-(pyrid-2-ylmethyl)-1,4-diazepane (**L2**), *N*-(1-methyl-1H-imidazol-2-ylmethyl)-*N'*-(pyrid-2-ylmethyl)-1,4-diazepane (**L3**) and *N*-(quinol-2-ylmethyl)-*N'*-(pyrid-2-ylmethyl)-1,4-diazepane (**L4**), has been isolated and characterized both in the solid state and in solution. In the X-ray crystal structure of **4**, Mn(II) adopts a distorted octahedral coordination geometry. The peroxo adducts $[Mn^{III}(O_2)(L)]^+$ have been generated by adding H_2O_2 (30%) and triethylamine to **1 - 4** in CH_3CN solution at -30 °C and characterized by UV-Vis and mass spectral and electrochemical techniques. The role of nucleophilic nature of the peroxo adducts in aldehyde deformylation reaction has been studied by using cyclohexanecarboxaldehyde (CCA) and *para*-substituted benzaldehydes as substrates. The rate constant (k_2) for the deformylation reaction of CCA follows the trend **3b** > **1b** > **2b** > **4b**, which illustrates the dependence of reaction rate upon the Lewis basicity of the ligand donor atoms, as reflected by the Mn^{II}/Mn^{III} redox potential of the complexes. Also, a linear correlation between the rate of deformylation catalysed by **3b** and the substituent constant (σ) has been observed for the deformylation of various *para*-substituted benzaldehydes. The complexes catalyse the epoxidation of *cis*-cyclooctene, cyclohexene and styrene with H_2O_2 as the oxygen source in the presence of acetic acid with high conversion and selectivity, and the product yields are dependent upon the ligand stereoelectronic factors.

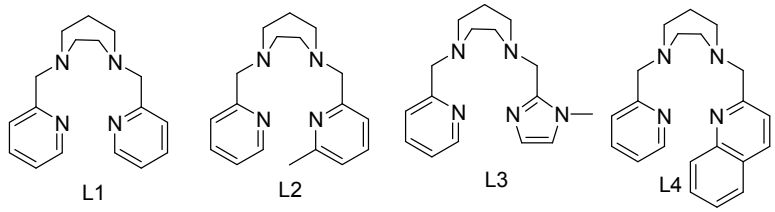
Introduction

Oxidation reactions are one of the very elementary reactions in organic chemistry and are very important in the synthesis of valuable intermediate compounds like epoxides and oxiranes in the preparation of fine chemicals and pharmaceuticals. This has stimulated the designing of efficient regio- and stereoselective catalytic systems for oxidation of organic substrates. Also, the use of several oxygen donors such as molecular oxygen, peroxides, peracids, PhIO and its derivatives, sodium hypochlorite etc have been studied.[1] Several metal-based catalysts have been explored for the oxidation of organic compounds and among them manganese-containing compounds have been attracted considerable attention.[2] Many manganese catalysts have been useful in olefin epoxidation,[3] textile and fabric bleaching[4,5] etc.[6,7] In Nature also manganese containing non-heme metalloenzymes like manganese lipoxygenase (MnLO),[8–10] ribonucleotide reductases,[11] manganese superoxide dismutases (MnSOD),[12–15] catalases,[16] and the oxygen evolving complex in photosystem II.[17,18] are used to catalyse a range of highly regio- and stereoselective oxygenation reactions under mild conditions. Several manganese complexes have been isolated in order to duplicate the oxygenation reactions of natural metalloenzymes.[19]

Several non-heme manganese catalysts have been designed to effect C-H oxidations using H_2O_2 as oxygen source. Mn(II) complexes of 3N ligands like 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) and its derivatives have been proved efficient catalysts for olefin epoxidation.[20] Also, many manganese(II) complexes with tetradentate 4N ligands have been shown to possess higher efficiencies with selectivity lower than their iron(III) analogues.[21] Stack et al.[22a] , Rich et al.[22b] , Sun et. al[23] and Bryliakov et. al[23d] isolated manganese(II) complexes of chiral ligands and showed them to be very fast and efficient epoxidation agents in the presence of peracetic acid. Pfaltz et al. isolated Mn(II) complexes of chiral 4N ligands containing two oxazoline rings and studied them as catalysts for olefin epoxidation.[24] Costas et al. found that Mn(II) complexes of chiral tetradentate 4N ligands with fused pinene rings catalyse epoxidation reactions with modest enantiomeric excess (ee).[25] Very recently, Talsi et al.[26a] and Costas et al.[27] have shown that Mn(II) complexes of 4N ligands containing a bipyrrolidine backbone and pyridyl donors are very effective as catalysts for asymmetric epoxidation of olefins. Also, a number of peroxomanganese(III) complexes of the type $[Mn^{III}(O_2)(L)]^+$ have been isolated,[28-33] and the X-ray structures of several of them have been determined to study the importance of Mn-dioxygen complexes like Mn-superoxo, -peroxo, or -oxo intermediates, which are proposed as intermediates in the catalytic reactions.[34] Thus, the stabilities of Mn^{III}-O_2 adducts of macrocyclic 4N ligands like

13-TMC (1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane) and Me-TPEN (*N*-methyl-*N,N′,N′*-tris(2-pyridylmethyl)ethane-1,2-diamine) have been studied. Very recently, Mn(II) complexes of a few tetradentate diazacycloalkane ligands have been isolated and the geometric and electronic structure of the metal peroxide intermediates has been probed, to throw light on the efficiency of the oxygen transfer step in olefin epoxidation,[35] as influenced by the coordination environment. In this regard, it may be noted that tetrachlorocatecholate adduct of the iron(III) complex of diazepane 4N ligands has been successfully demonstrated as biomimetic models for extradiol-cleaving catechol dioxygenase enzymes and the ligand is bound in a cis-β orientation.[36]

All the above observations clearly underline the importance of exploring the chemistry of Mn-O_2 intermediates of well-defined Mn(II) complexes of 4N ligands with a view to develop novel environmentally benign catalysts for olefin oxidation. So, we are prompted to explore the ligand steric and electronic influences on the reactivity of peroxomanganese complexes. We have successfully isolated Mn(II) complexes of novel tetradentate diaza 4N ligands with one of the terminal donor arms varying from pyridylmethyl (L1) to 6-methyl-pyridylmethyl (L2) to 1-methyl-*1H*-imidazolylmethyl (L3) to quinolinylmethyl arm (L4) (**Scheme 1**) and investigate their reaction with H_2O_2. The single crystal X-ray structure of the complex [Mn(L4)(H_2O)(ClO_4)](ClO_4) **4** contains a readily replaceable water molecule and a perchlorate anion in trans positions, which are convenient for binding of H_2O_2 leading to effect catalytic oxidation reactions. We intend to study the effect of varying Lewis basicity of the novel ligands with unsymmetrical terminal donors on the stability of peroxomanganese(III) intermediates, the nucleophilicity of the peroxo ligand bound to Mn(III) and the catalytic activity of the complexes towards epoxidation of unfunctionalized olefins. The varying Lewis basicity of the ligands, as understood from the redox potential of Mn^{II}/Mn^{III} couple, strongly influences the nucleophilicity of the Mn peroxo species and determines the catalytic activity of the complexes. The Mn(II) complexes exhibit



Scheme 1. Ligands employed in this study

significant catalytic activity towards epoxidation of olefins in high yields (64-84%) by using H_2O_2 as the oxygen source in the presence of CH_3COOH.

Experimental Section

Materials

Pyridine-2-carboxaldehyde, 1-methylimidazole-2-carboxyaldehyde, sodium triacetoxy-borohydride, homopiperazine, cyclohexanecarboxaldehyde (CCA), 4-methylbenzaldehyde, 4-methoxybenzaldehyde, cyclooctene, cyclohexene, styrene, *tert*-butyl hydroperoxide (Aldrich), 6-methylpyridine-2-carboxaldehyde, quinoline-2-carboxaldehyde, 2-picolylchloride hydrochloride (Alfa-Aesar), triethylamine, benzaldehyde, and 4-chlorobenzaldehyde (Merck, India) were used as received. Acetonitrile, dichloromethane, ethylacetate, chloroform, diethylether, and hexane (Merck, India) were used as received.

Synthesis of Ligands

Synthesis of *N*,*N'*-bis(2-pyridylmethyl)-1,4-diazepane (L1)

This was prepared by reductive amination.[36] A mixture of homopiperazine (0.66 g, 6.22 mmol) and pyridine-2-carboxaldehyde (1.41g, 13.2mmol) was used to give L4 as a pale yellow oil, which is used for the complex preparation as such without further purification. Yield: 64%; ^{1}H NMR ($CDCl_3$, 400 MHz) 1.74 (pentet, J = 5.9 Hz, 2H), 2.67 (s, 4H), 2.31 (d, J = 5.8 Hz, 4H), 2.48 (s, 4H), 7.03 (m, 2H), 7.37 (d, 2H), 7.54 (m, 2H), δ 8.43 (m, 2H) ppm.

General Procedure

A common two step procedure was followed for the syntheses of ligands L2, L3 and L4 and the first step in the preparation of *N*-(pyrid-2-ylmethyl)-1,4-diazepane, which were then reacted with corresponding aldehyde in the second step to obtain L2, L3 and L4 respectively.

Synthesis of *N*-(pyrid-2-ylmethyl)-1,4-diazepane

Step 1. A solution of 2-(chloromethyl)pyridine hydrochloride (1.0 g, 6.2 mmol) and triethylamine (2.09 g, 15.0 mmol) in anhydrous ethanol (20 mL) was then added dropwise to the homopiperazine (2.50 g, 25 mmol). The resulting mixture is refluxed for 1 hour and then stirred at room temperature two days. The solvent was then removed under reduced pressure, the residue was redissolved in water (15 mL), and the pH of the resulting solution was adjusted to ca. 10 with anhydrous K_2CO_3. The organic phase that separated from the mixture was concentrated in vacuo and the crude product was purified by column chromatography on

silica gel (CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$, 10:10:1). The free ligand was obtained as colorless oil; Yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) 1.31(m, 2H), 2.45 (s, 4H), 2.31(s, 4H), 3.39 (s, 4H), 7.26 (m, 2H), 6.7 (d, *J* = 8 Hz, H), 7.05 (d, *J* = 7.6 Hz, H), 8.09 (br, s, H) ppm.

Step 2. To the above general procedure was followed, and 6-methyl-pyridine-2-carboxaldehyde, 1-methyl-imidazole-2-carboxyaldehyde and quinoline-2-carboxyaldehyde, was obtained the L2, L3 and L4 respectively as yellow oil.

***N*-(6-methyl-pyrid-2-ylmethyl)-*N'*-(pyrid-2-ylmethyl)-1,4-diazepane(L2)** Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$) 1.78(m, 2H), 2.47 (s, 3H), 2.71(s, 4H), 3.76(s, 4H), 4.74(s, 4H), 3.39 (s, 2H), 7.26 (m, H), 7.44 (m, H), 7.86 (d, H), 8.47 (d, H) ppm.

***N*-(1-methyl-*1H*-imidazol-2-ylmethyl)-*N'*-(pyrid-2-ylmethyl)-1,4-diazepane (L3)** Yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$) 2.71(m, 2H), 3.43 (s, 4H), 3.65(s, 4H), 3.73 (s, 3H), 4.72 (s, 4H), 7.19(s, 2H), 7.58 (m, H), 7.60 (m, H), 8.02 (d, *J* = 6.8 Hz, H), 8.44 (d, *J* = 5.6 Hz, H) ppm.

***N*-(quinoline-2-ylmethyl)-*N'*-(pyrid-2-ylmethyl)-1,4-diazepane (L4)** Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) 1.85(m, 2H), 2.80 (m, 8H), 3.81(s, 4H), 7.10 (t, H), 7.68 (d, H), 7.70(d, H) (s, H), 8.09 (d, H), 7.5 (d, H) ppm.

Synthesis of Mn(II) Complexes

[Mn(L1)(ClO_4)](ClO_4) (1)

The complex [Mn(L1)](ClO_4)$_2$] **1** was prepared by adding $MnCl_2 \cdot 4H_2O$ (0.20 g, 1 mmol) in acetonitrile (5 mL) to a solution of L1 (0.26 g, 1 mmol) in acetonitrile (10 mL), stirred for 30 minutes. The resulting solution was evaporated under vacuum and the solid thus precipitate was dried in vacuo. Recrystallization of the crude solid from MeCN/diethyl ether afforded as nearly colorless crystals. Electrospray ionization mass spectrometry (ESI-MS) was used to explore the solution composition of the purified complexes in MeCN solution. ESI-MS data are as follows: {[Mn(L1)(ClO_4)]$^+$} m/z = 436.26 (calcd 436.07) Yield: 80%; Anal. Calcd for $C_{17}H_{22}N_4Cl_2O_8Mn$: C, 38.08; H, 4.14; N, 10.45; Found. C, 38.43; H, 4.62; N, 10.65%.

[Mn(L1)Cl_2] 1a

The complex [Mn(L1)Cl_2] **1a**, was prepared by adding $MnCl_2 \cdot 4H_2O$ (0.20 g, 1 mmol) in methanol (5 mL) to a solution of L1 (0.26 g, 1 mmol) in methanol (10 mL), stirred for 30 minutes and the obtained colourless precipitate was filtered off and dried in vacuo Pale white crystals suitable for X-ray diffraction were grown from a slow evaporation methanolic solution of the complex. Yield: 76%; Anal. Calcd for $C_{17}H_{22}Cl_2MnN_4$: C, 50.02; H, 5.43; N, 13.72. Found C, 50.02; H, 5.31; N, 13.24%.

[Mn(L2)(ClO_4)](ClO_4) (2)

This complex was prepared in a manner analogous to that described for **1** using L2 instead of L1. Colourless precipitate was filtered off and dried in vacuo. ESI-MS data are as follows: $\{[Mn(L2)(ClO_4)]^+\}$ m/z = 450.27 (calcd 450.09) Yield: 72%; Anal. Calcd for $C_{18}H_{24}N_4Cl_2O_8Mn$: C, 39.29; H, 4.40; N, 10.18 Found. C, 39.45; H, 4.78; N, 10.35%.

[Mn(L2)Cl_2] 2a

This complex was prepared in a manner analogous to that described for **1a** using L2 instead of L1. Yield: 63%; $\{[Mn(L2)Cl]^+\}$ m/z = 386.52 (calcd 386.11); Anal.Calcd for $C_{18}H_{24}Cl_2MnN_4$: C, 51.20; H, 5.73; N, 13.27; Found C, 51.32; H, 5.45; N, 13.58%.

[Mn(L3)(ClO_4)](ClO_4) (3)

This complex was prepared in a manner analogous to that described for **1** using L3 instead of L1. precipitate was filtered off and dried in vacuo. Yield: 68%; ESI-MS data are as follows: $\{[Mn(L3)(ClO_4)]^+\}$ m/z = 439.13 (calcd. 439.06); Yield: 72%; Anal. Calcd for $C_{16}H_{23}N_5Cl_2O_8Mn$: C, 35.64; H, 4.30; N, 12.99; Found. C, 35.45; H, 4.38; N, 12.83%.

[Mn(L3)Cl_2] 3a

This complex was prepared in a manner analogous to that described for **1a** using L3 instead of L1. Yield: 74%; ESI-MS data are as follows: $\{[Mn(L3)Cl]^+\}$ m/z = 375.41 (calcd 375.71); Anal. Calcd for $C_{15}H_{20}Cl_2MnN_5$: C, 45.47; H, 5.09; N, 17.68; Found C, 45.62; H, 5.54; N, 17.72%.

[Mn(L4)(ClO_4)(H_2O)](ClO_4) (4)

This complex was prepared in a manner analogous to that described for **1** using L4 instead of L1. Colourless crystals suitable for X-ray diffraction were grown from re-crystallization of the crude solid from MeCN/diethyl ether afforded (85%) of [Mn(L4)](ClO_4)$_2$ as nearly colorless crystals. Yield: 69%; ESI-MS data are as follows: {[Mn(L4)(ClO_4)]$^+$} m/z = 486.33 (calcd 486.09); Anal. Calcd for $C_{22}H_{27}N_4Cl_2O_8Mn$: C, 43.94; H, 4.53; N, 9.32; Found. C, 43.86; H, 4.29; N, 9.12%.

[Mn(L4)Cl_2] 4a

This complex was prepared in a manner analogous to that described for **1a** using L4 instead of L1. Yield: 71%; ESI-MS data are as follows: {[Mn(L4)Cl]$^+$} m/z = 422.01 (calcd 422.11); Anal. Calcd for $C_{22}H_{27}Cl_2MnN_4$: C, 55.83; H, 5.75; N, 11.84; Found C, 55.62; H, 5.48; N, 11.62%.

In Situ Preparation of Peroxomanganese(III) Complexes

The green peroxomanganese(III) intermediates [$Mn^{III}(O_2)(L)]^+$, where L = L1, L2, L3 and L4 formed by treating an acetonitrile solution of [Mn^{II}(L)(ClO4)](ClO4)] with 5 equiv of H_2O_2 and 0.5 equiv of triethylamine at -30 °C. The formation of the [$Mn^{III}(O_2)(L)]^+$ complexes was evident from the appearance of characteristic bands in the electronic absorption spectra and supported by ESI-MS data (Vide infra).

Physical Measurements

Elemental analyses were performed on a Perkin Elmer Series II CHNS/O analyzer 2400. The electronic spectra were recorded on an Agilent 8453 diode array spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. GC-MS analysis was performed on Agilent GC-MS spectrometer using a HP-5 capillary column. All ligands were purified by using Teledyne Isco Combi Flash R_f flash chromatography. ESI mass spectra of the complexes were recorded with a Thermofinnigan LCQ-6000 Advantage Max ion trap mass spectrometer equipped with an electron spray source by using methanol as solvent. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using a three electrode cell configuration. A platinum sphere, a platinum plate and Ag(s)/Ag+ were used as working, auxiliary, and reference electrodes, respectively. The supporting electrolyte used was NBu_4ClO_4 (TBAP). The

temperature of the electrochemical cell was maintained at 25.0 ± 0.2 °C by a cryocirculator (HAAKE D8 G). By bubbling research grade nitrogen, the solutions were deoxygenated and maintained under nitrogen atmosphere during measurements. The $E_{1/2}$ values were observed under identical conditions for various scan rates. The instruments utilized included an EG & G PAR 273 Potentiostat/Galvanostat to carry out the experiments and to acquire the data. The products were quantified by using Hewlett Packard (HP) 6890 Gas Chromatograph (GC) series equipped with a FID detector and a HP-5 capillary column (30 m × 0.32 mm × 2.5 μm).

Reactivity Studies

The catalytic activity of all the complexes towards cyclooctene, cyclohexene and styrene (**Scheme 4**) epoxidation was examined by treating a solution of $[Mn^{II}(L)](ClO4)_2$ in acetonitrile by using H_2O_2 as oxidant in the presence of AcOH. The catalytic reaction has been carried out at 0 °C to minimize the disproportion of the hydrogen peroxide. The oxygenated products were identified by Agilent GC-MS instrument equipped with 7890A GC system 5975C MSD using a HP-5 capillary column and quantified by GC using Hewlett-Packed HP 6890 series gas chromatograph equipped with an FID detector and a HP-5 capillary column (30 m, 0.32 mm i.d) with the following temperature program: initial temperature, 80 °C, 5 degree min^{-1}; final temperature 250 °C; detector temperature 250 °C.

Crystal Data Collection and Structure Refinement

Single crystal X-ray crystallographic data for complexes **4** were collected on a Bruker SMART Apex diffractometer equipped with a CCD area detector at 100 K with Mo-Kα (λ = 0.71073 Å) radiation. A crystal of suitable size was immersed in paraffin oil and mounted on the tip of a glass fiber and cemented by using epoxy resin. The crystallographic data and experimental parameters of the complexes **4** are listed in **Table 1**. For the data collection SAINT[37] software program was used for frames of data, indexing the reflections, and determination of lattice parameters; SAINT program for integration of the intensity of reflections and scaling. An empirical absorption correction was applied to the collected reflections with SADABS.[38] The structure was solved by direct methods using SHELXTL[39] and was refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 program package.[40] All non-hydrogen atoms were refined anisotropically till convergence was reached for the three complexes. Hydrogen atoms attached to the ligand moieties are

either located from the difference Fourier map or stereochemically fixed. The crystallographic data and details of data collection for **4** is given in **Table 1**.

Results and Discussion

Synthesis and Characterization of Ligands and Complexes

The ligand L1 was prepared according to a known reductive amination procedure by treating two equivalents of pyridine-2-carboxaldehyde with one equivalent of homopiperazine and then using sodium triacetoxyborohydride as reducing agent. The ligands L2 - L4 (**Scheme 1**) were synthesized by a two step procedure involving selective substitution of 2-(chloromethyl)pyridine with homopiperazine in the presence of triethylamine followed by reductive amination with the corresponding aldehyde. The ligands were treated with an equimolar amount of $Mn(ClO_4)_2{\cdot}4H_2O$ in acetonitrile to give mononuclear Mn(II) perchlorate complexes in good yields. All the complexes have been formulated as $[Mn(L)(ClO_4)](ClO_4)$ on the basis of elemental and ESI-MS analyses, which is further supported by the X-ray structures of $[Mn(L1)(CH_3CN)_3](ClO_4)_2$ **1**[33] and $[Mn(L4)(H_2O)(ClO_4)](ClO_4)$ **4**. The electronic absorption spectra of complexes **1 - 4** exhibit no Ligand Field band, which is expected of high-spin Mn(II). In frozen methanol solution all the complexes exhibit well-resolved six-line hyperfine EPR signals centered around g = 2.0 (**Figure S1**), which is consistent with high-spin (S = 5/2) Mn(II) complex species. Conductivity measurements in acetonitrile (Λ_M, 220 - 278 Ω^{-1} cm^2 mol^{-1}) reveal that the complexes behave as 1:2 electrolytes.[41] The mononuclear Mn(II) chloride complexes **1a** – **4a** were obtained in good yields when the ligands were treated with an equimolar amount of $MnCl_2{\cdot}6H_2O$ in methanol. They are formulated as $[Mn(L)Cl_2]$, which is supported by the X-ray crystal structure[42] of $[Mn(L1)Cl_2]$ **1a** and the ESI-MS of the complexes in acetonitrile solution. They behave as 1:1 electrolytes in acetonitrile (Λ_M, 90 - 122 Ω^{-1} cm^2 mol^{-1}).[41] The present tetradentate diaza ligands with selective variation in one of the donor arms is expected to confer a systematic variation in the electronic environment around Mn(II) center.

Description of Molecular Structure of $[Mn(L4)(H_2O)(ClO_4)](ClO_4)$ 4

The X-ray crystal structure of the cation $[Mn(L4)(H_2O)(ClO_4)]^+$ of complex **4** is depicted in **Figure 1** together with atom numbering scheme. The selected bond distances and bond angles are collected in **Table 2**. The complex cation possesses a distorted octahedral coordination geometry constituted by the pyridyl (N1), quinolyl (N4) and two tertiary amine

nitrogen atoms (N2, N3) of the tetradentate ligand L4 and the oxygen atoms of water molecule and perchlorate ion. The linear ligand is coordinated meridionally to Mn(II) with the trans coordination sites occupied by water (O1w) and perchlorate ion (O2) (**Figure 1**). This is in contrast to the cis-α coordination geometry of the related complex $[Mn(bispicen)Cl_2]$[42] and $[Mn(BPMEN)Cl_2]$,[43] where bispicen is *N,N'*-bis(pyrid-2-ylmethyl)-1,2-diaminoethane, BPMEN is *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-1,2-diaminoethane, in which the 4N ligand is cis coordinated to Mn(II) with folded geometry. The bond angles N(1)-Mn(1)-N(4) (142.48 (14)°), N(2)-Mn(1)-N(4) (139.74(14)°) and N(1)-Mn(1)-N(3) (138.99(14)°) and O(1w)-Mn(1)-O(2) (144.30(16)°) deviate markedly from the ideal octahedral bond angle of 180°, indicating that the octahedral coordination geometry is distorted. The Mn-N_{py} (2.220(3) Å) and Mn-N_{amine} (2.272(3), 2.264(4) Å) bond distances of **4** fall in the ranges of those observed in the previously reported linear tetradentate 4N ligand complexes such as $[Mn(bispicen)Cl_2]$[42] (2.324(5), 2.338(6) Å), $[Mn(BPMEN)Cl_2]$,[43] (2.278(2) Å), $[Mn^{II}(L1)(MeCN)_3](ClO_4)_2$ (2.306(9), 2.308(3) Å), $[Mn^{II}(L5)(MeCN)(ClO_4)](ClO_4)$ (2.284(2), 2.284(2) Å), $[Mn^{II}(L6)(MeCN)_2(ClO_4)](ClO_4)$,[33a] (2.262(3), 2.285(3) Å) and $[Mn^{II}(L7)(ClO_4)_2]$,[34b] (2.283(2), 2.284(2) Å), where L5 is *N,N'*-bis(1-pyrid-2-ylmethyl)-1,4-diazepane, L6 is *N,N'*-bis(4-methyl-pyrid-2-ylmethyl)-1,4-diazepane and L7 is *N,N'*-bis(6-methyl-pyrid-2-ylmethyl)-1,4-diazepane. The Mn-N_{amine} bonds are longer than both the Mn-N_{py} and Mn-N_{quin} (2.208(3) Å) bonds, which is expected of the sp^3 and sp^2 hybridizations respectively of the amine and pyridyl/quinolyl nitrogen atoms.[41] The lower basicity of quinolyl nitrogen (pK_a: $(QuinH)^+$: 4.94; $(pyH)^+$, 5.25) and its steric hindrance from the fused ring are expected to render Mn-N_{quin} bond in **4** longer than the Mn-N_{py} bond. In contrast, the observed shorter Mn-N_{quin} bond distance (2.208 Å) in **4** than those observed (2.226(3) 2.254(3) Å) for the corresponding bis(quinolylmethyl) complex $[Mn^{II}(L8)(ClO_4)_2]$,[33c] where L8 is *N,N'*-bis(2-quinol-2-ylmethyl)-1,4-diazepane. This reveals that the quinolyl nitrogen in **4** is bound to Mn(II) more strongly than those in $[Mn^{II}(L8)(ClO_4)_2]$, due to the stronger involvement in π-back bonding of quinolyl nitrogen in the presence of the coordinated pyridyl nitrogen in **4.** Similar to $[Mn^{II}(L7)(ClO_4)_2]$[33b] in which the methyl substituted pyridine sterically hinders the coordination of pyridyl nitrogen leading to Mn-N_{py} bonds longer than in **1**, similarly upon the fusion of a benzene ring to the pyridyl moieties of L1 in **1** to give $[Mn^{II}(L8)(ClO_4)_2]$ leads to Mn-N_{quin} bonds longer. Thus, the sterically hindered quinolyl nitrogen is bonded to Mn(II) conferring a longer Mn-N_{quin} bond. However, the observed shorter Mn-N_{quin} bond in **4,** is due to the presence of

unsymmetrical donor arms leads to confer stronger coordination of quinolyl nitrogen and hence an interesting Mn(II) stereochemistry on **4**.

The meridional coordination of the linear tetradentate ligand L4 in **4** is similar to that of L1 in $[Mn(L1)Cl_2]$[42] with a distorted octahedral coordination geometry and $[Mn^{II}(L1)(MeCN)_3](ClO_4)_2$[33] with a seven-coordinated near pentagonal bipyramidal coordination geometry around Mn(II). Also, the ligand L1 has been predicted[44] to coordinate meridionally to iron(III) in the *in situ* generated complex species $[Fe(L1)(CH_3CN)_3]^{2+}$. On the other hand, interestingly, in the iron(III) tetrachlorocatecholate adduct $[Fe(L1)(cat)]^+$ the sterically encumbered ligand L1 is bound with a cis-β configuration,[36] revealing that the mode of coordination of L1 depends on the nature of the metal ion.

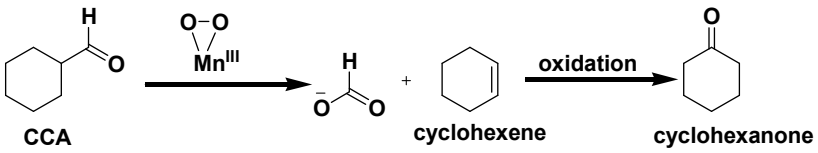
Electrochemical Behaviour

As the electrochemical responses for the perchlorate complexes **1** - **4** were not well-defined, the electrochemical features of the corresponding Mn(II) chloride complexes **1a** – **4a** were investigated in acetonitrile solution by employing cyclic (CV) and differential pulse voltammetry (DPV) on a stationary platinum-sphere electrode. Typical cyclic and differential pulse voltammograms of complex **2a** is depicted in **Figure 2**. The Mn(II)/Mn(III) redox potentials (**Table 3**) follow the trend **3a** < **1a** < **2a** < **4a**, which reflects the changes in electronic environment around Mn(II) along this series upon varying the donor atom. Thus, the replacement of one of the pyridylmethyl arms of **1a** by a *N*-methylimidazolylmethyl arm to obtain **3a**, the Mn(II)/Mn(III) redox potential decreases ($E_{1/2}$: **1a**: 0.444, **3a**: 0.424 V), illustrating that the strongly σ-bonding of imidazolyl nitrogen (pK_a: $(pyH)^+$: 5.25, $(imidazoleH)^+$: 7.01) enhances the electron density on Mn(II) center rendering the oxidation of Mn(II) to Mn(III) more facile. On the other hand, the incorporation of a methyl group on 6-position of one of the pyridyl rings in **1a** to get **2a**, the Mn(II)/Mn(III) redox potential increases ($E_{1/2}$, 0.546 V), revealing that the sterically hindering methyl group weakens the coordination of the pyridyl nitrogen atom, decreases the electron density on Mn(II), and renders the oxidation of Mn(II) to Mn(III) difficult. Similarly, the replacement of one of the pyridylmethyl arms in **1a** by a quinolylmethyl arm to obtain **4a** ($E_{1/2}$, 0.559 V), the electron density around Mn(II) decreases as quinolyl nitrogen is involved in stronger π-back bonding. Similar observations have been made earlier for iron(III) complexes of 3N ligands with *N*-alkyl substituents[45] and Ni(II) complexes of 4N ligands with (benz)imidazolyl/quinolyl/pyridyl nitrogen donors.[46]

Spectral Characterization and Reactivity of $[Mn^{III}(O_2)(L)]^+$ Intermediates

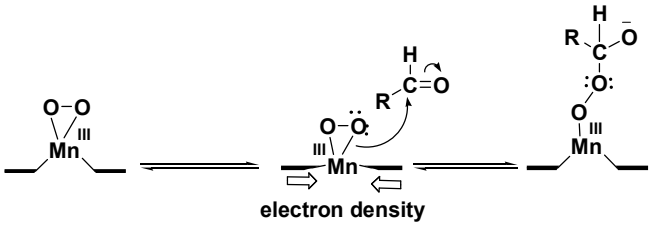
The absorption spectra of acetonitrile solution of complexes $[Mn^{II}(L1\text{-}L4)](ClO_4)_2$ **1** - **4** are featureless at wavelengths above 300 nm, because the d - d transitions for high-spin Mn(II) centers are all spin-forbidden, and no charge transfer (CT) transitions involving the pyridine and amine ligands is expected in the visible region. Upon treatment of acetonitrile solutions of the Mn(II) complexes with 5 equivalents of H_2O_2 and 0.5 equivalent of triethylamine at -30 °C, green coloured solutions, which exhibit absorption bands in the visible region, are obtained. The prominent band in the range 430 – 445 nm (ε, 148 – 214 M^{-1} cm^{-1}) and a broader less intense band in the range 590 - 612 nm (ε, 39 – 42 M^{-1} cm^{-1}) are characteristic of peroxomanganese intermediate species $[Mn^{III}(O_2)(L1\text{-}L4)]^+$ **1b - 4b** (**Figure 3**, **Table 4**). These spectral features resemble those of the structurally well-characterised peroxomanganese complexes $[Mn^{III}(O_2)(TMC)]^+$, $[Mn^{III}(O_2)(13\text{-}TMC)]^+$ and $[Mn^{III}(O_2)(Tp^{iPr})(L)]^+$, which display an intense absorption band at less than 460 nm and a broader band in the range 560 - 590 nm,[28] both originating from d – d transitions. The position of the high energy band depends upon the nature of the heterocyclic nitrogen donor atom. Thus the high energy band for the complex **3a** with imidazolyl donor is higher than those for complexes with pyridyl (**1a**, **2a**) and quinolyl (**4a**) donors. Also, the position of the band for **4a** with quinolyl and pyridyl donors is the average of those for peroxomanganese complexes of $[Mn^{II}(L1)(MeCN)_3](ClO_4)_2$[33a] and $[Mn^{II}(L8)(ClO_4)_2]$.[33c] Mass spectrometry experiments on the above green colored solutions at -30 °C reveal major ion peaks consistent with the intermediate peroxomanganese(III) species $[Mn^{III}(O_2)(L1\text{-}L4)]^+$ **1b - 4b** (**Figure 4**, **Table 5**). As the species **1b - 4b** are stable at -30 °C for several hours, the half-life period ($t_{1/2}$) of the complexes were determined by following the gradual decay of the high energy band in the range 432 - 445 nm at 0 °C. The $t_{1/2}$ of the complex species follows the trend, **3b** > **1b** > **2b** > **4b** **(Figure 5, Table 5)**, and a plot of $t_{1/2}$ versus redox potential of Mn(II)/Mn(III) couple is linear (**Figure 6**); this illustrates that the highest stability of the peroxo species $[Mn^{III}(O_2)(L3)]^+$ **3b** is due to increase in electron density on Mn(III) center by the strongly σ-bonding imidazole donor.

The nucleophilic character of the peroxo complex species was investigated using aldehyde deformylation reaction[33] (**Scheme 2**). An excess (40 equiv.) of cyclohexanecarboxaldehyde (CCA) was added to the green acetonitrile solutions of $[Mn^{III}(O_2)(L1\text{-}L4)]^+$ at -30 °C and the disappearance of the high energy visible band, which



Scheme 2. Schematic representation for the aldehyde deformylation reaction of CCA

corresponds to the decay of the peroxo intermediates, is followed. By plotting the pseudo-first order rate constants (k_{obs}) as a function of CCA concentration, a second-order rate constant (k_2) is determined. The variation in rate constant (k_2) follows the order, **3b** > **1b** > **2b** > **4b (Table 5**), illustrating that the nucleophilicity of $[Mn^{III}(O_2)(L)]^+$ intermediate is higher for **3b** with imidazole nitrogen donor (cf. above). The value of k_{obs} (0.19 min^{-1}) for **3b** is higher than those for **2b** and **4b** (**Table 4**, **Figure 7**) revealing that the σ-bonding imidazole donor in the peroxo complex $[Mn^{III}(O_2)(L3)]^+$ increases the electron density around Mn(III), enhancing the nucleophilic character of the bound peroxo group (**Scheme 3**). Similar observation has been made by Nam *et. al.,* for the axial ligand effect on the structurally well-characterised peroxomanganese complexes $[Mn^{III}(O_2)(TMC)]^+$, which react with *para*-substituted benzaldehydes[28b] by nucleophilic attack of bound peroxo ligand.



Scheme 3. Schematic representation for the conversion of side-on to end-on fashion on increasing electron density

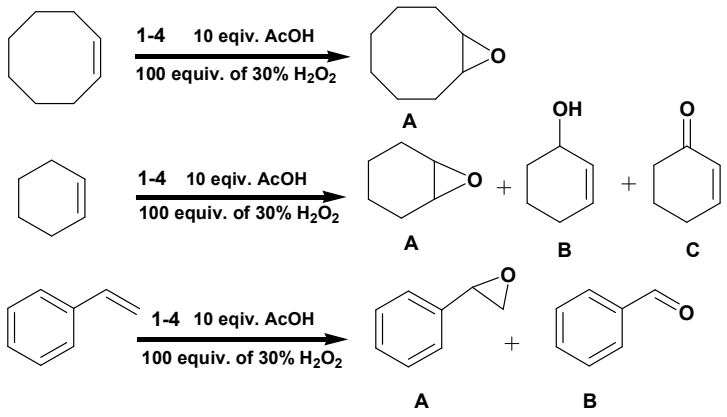
The aldehyde deformylation reaction involves nucleophilic attack of the Mn(III)-bound peroxo ligand on the carbonyl carbon. In order to further understand the nucleophilic nature of this deformylation reaction the relatively more stable $[Mn^{III}(O_2)(L3)]^+$ species **3b** (cf. above) was selected for further study with *para*-substituted benzaldehydes as substrates. The value of k_{obs} for **3b** follows the trend Cl > H > Me > OMe, illustrating that the electron-withdrawing *para* substituents on the benzaldehydes render the nucleophillic attack of Mn(III) peroxo species facile. Indeed, a plot of values of log k_{obs} versus Hammett substituent

constants (σ_p) for **3b** is linear (**Figure 7**), and the ρ value of 2.14 is higher than that previously reported (ρ, 1.25)[33] for Mn(II) complexes of linear tetradentate diaza ligands with similar donor atoms.

Catalytic Properties

The catalytic activity of complexes **1 - 4** towards olefin epoxidation was investigated by using H_2O_2 as the oxygen source in the presence of CH_3COOH at 0 °C in acetonitrile solution. All the reactions were performed at least thrice, and the average amounts of products obtained are reported. In these reactions typically 1 equiv. of the complex, 100 equiv. of H_2O_2, 1000 equiv. of both the olefin substrate and decane (internal standard) were mixed in acetonitrile. The solution was stirred for 1h at 0 °C and then passed through a neutral silica column (**Scheme 4**). The resulting solution was directly analyzed by GC and GC-MS. The yields of products reported are based on the oxidant used and determined by comparison of peak area with those of known authentic samples. The influence of solvent on epoxidation was explored by carrying out the reactions in different solvents like methanol, dichloromethane and acetonitrile and, as expected,[47] the highest activity (results are not shown here) is achieved in acetonitrile as solvent. Maximum conversions were observed when 10 equiv. of CH_3COOH was used. Also, when control experiments were performed for all the complexes at 0 ºC by using 10 equiv. CH_3COOH and 100 equiv. of H_2O_2 in the absence of the additive in acetonitrile solvent and the products analysed, no picolinic acid formation was detected. So it is evident that the pyridyl moieties of **1 - 4** do not undergo any oxidative degradation under the present reaction conditions.

The epoxidation of *cis*-cyclooctene catalysed by **1 - 4** in acetonitrile solvent in the presence of CH_3COOH proceeds with both efficient conversion (64-86%) and selectivity (100%) for *cis*-epoxide. The yield of *cis*-cycloocteneoxide follows the trend **3 > 1 > 2 > 4** (**Table 6**), which reveals that the ligand donor atom type determines the epoxide yield. The epoxidation of cyclohexene has been also studied in acetonitrile solvent with **1- 4** as catalysts using H_2O_2 in the presence of CH_3COOH in acetonitrile solvent at 0 °C. The major product observed is cyclohexene oxide (E, 48.0 - 63.7%, **Table 6**), apart from the allylic oxidation product like 2-cyclohexen-1-ol and 2-cyclohexen-1-one, which is the further oxidised product of the former involving an oxidative dehydrogenation pathway catalysed by the complexes, and the epoxide selectivity ranges from 54.4 to 66.4% (**Table 6**). The yield of cyclohexene oxide follows the trend **3 > 1 > 2 > 4**, which is the same as that observed for cyclooctene.

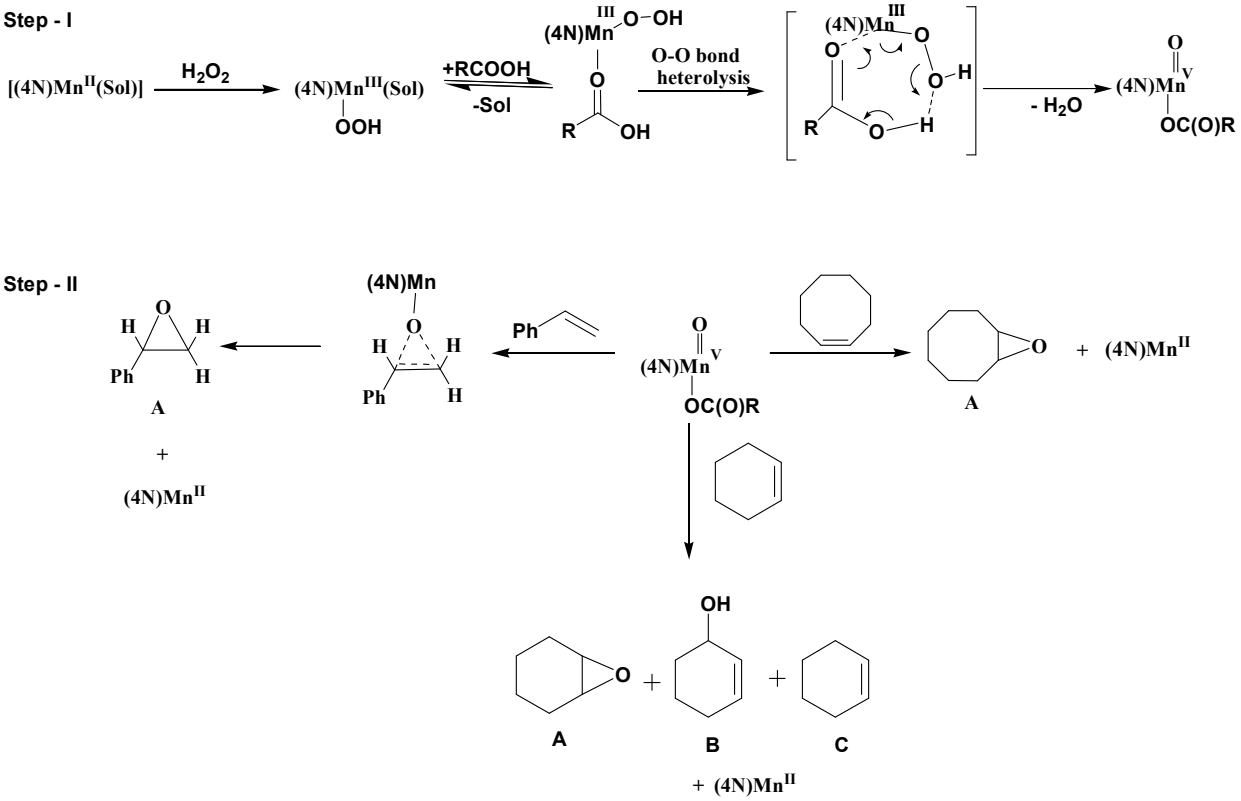


Scheme 4. Epoxidation of alkenes by Mn(II) complexes

The reaction of styrene using **1** - **4** with H_2O_2 in the presence of CH_3COOH in acetonitrile solvent at 0 °C has been also investigated under the same reaction conditions described above for cyclooctene and cyclohexene. In addition to major amounts of styrene oxide (46.8-67.5%; **Table 6**), benzaldehyde (22.7-33.9%) is also obtained as a side product. The yield of styrene oxide follows the trend **3 > 1 > 2 > 4**, which is the same as that observed above for cyclooctene and cyclohexene **(Scheme 5)**.

The same trend in the epoxide yield observed for all the olefins is illustrated by invoking the hydroperoxo complex species $[Mn^{III}(L)(OOH)]^{2+}$ formed by the interaction of the catalyst with H_2O_2, which is likely to epoxidize the alkene directly by exchanging its sixth ligand (solvent) with CH_3COOH leading to the formation of reactive $(4N)Mn^{V}=O$ complex species.[21,26] The addition of CH_3COOH to the reaction mixture plays a vital role on heterolysis of O-O bond in $[(L)Mn^{III}(OOH)(CH_3COOH)]$ intermediate, which is similar to the recent report by Browne and Que co-workers on carboxylic acid-assisted mechanism (**Scheme 5**).[26b,48] However, attempts to spectroscopically detect the $[(L)Mn^{III}(OOH)(CH_3COOH)]$ adduct species and the high-valent manganese-oxo intermediate at low-temperature (-40 °C) were unsuccessful. The proposed mechanism illustrates the dependence of epoxide yields of all the olefins on the ligand donor environment of the complexes. Thus for complex **3** imidazole coordination enhances the electron density on the manganese center (cf. above) resulting in the facile formation of the high-valent manganese-oxo species $(4N)Mn^{V}=O$ and hence the epoxide yield. Also, the in-cage electronic rearrangement in $[(L)Mn^{III}(OOH)(CH_3COOH)]$, which plays a key role in O-O

bond heterolysis is facilitated by a more Lewis basic ligand. The π-back bonding quinolyl donor (**4**) and the sterically hindering 6-methyl substituent on the pyridyl ring (**2**) would lead



Scheme 5. Proposed mechanisms for epoxidation of cyclooctene, cyclohexene and styrene by using Mn(II) complexes and H_2O_2 in the presence of CH_3COOH in acetonitrile solvent at 0 °C

to decreased epoxide yield. Thus the catalytic activity of the manganese complexes is tuned by the ligand electronic as well as steric factors imposed on the metal center. The formation of increased allylic oxidation products and decreased epoxide for cyclohexene oxidation is illustrated by invoking the facile abstraction of allylic proton by the intermediate species $(4N)Mn^{V}=O$, followed by in-cage electron-transfer to form the allylic alcohol product.[42,49] The amount of benzaldehyde detected for styrene in the presence of $Mn(ClO_4)_2 \cdot 6H_2O$ in acetonitrile falls in the range for complexes **1** – **4**, suggesting that Fenton-type decomposition of H_2O_2 by solvated Mn(II) ions formed by dissociation of the labile complexes in acetonitrile solvent leads to benzaldehyde formation.

Conclusions

The mononuclear Mn(II) complexes of linear tetradentate 4N ligands with sterically demanding diazacycloalkane backbone and selective variation of one of the arms have been

isolated and characterized both in the solid state and in solution. In the molecular structure of **4** Mn(II) adopts a distorted octahedral coordination geometry in which the 4N ligand is meridionally coordinated. The manganese peroxo adducts generated by adding H_2O_2 to the parent complexes in acetonitrile solution have been characterized by UV-Vis and mass spectral techniques. The nucleophilic nature of the peroxo adducts $[Mn^{III}(O_2)(L)]^+$ has been studied by using aldehyde deformylation reaction with cyclohexanecarboxaldehyde (CCA) and *para*-substituted benzaldehydes as substrates. A linear correlation between the rate of deformylation catalysed by one of the peroxomanganese species and the substituent constant (σ) has been observed for *para*-substituted benzaldehydes. The epoxidation of *cis*-cyclooctene, cyclohexene and styrene catalysed by the complexes with H_2O_2 as the oxygen source proceeds with high conversion and selectivity. Both the epoxide yield and selectivity change upon varying one of the two terminal ligand arms. The present study reveals that an efficient and robust Mn(II) catalytic system for olefin epoxidation can be designed by using 4N ligands with high Lewis basicity and low steric demand.

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Appendix A. Supplementary Material

CCDC reference 927923 for the crystal structure of **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Bioinspired Manganese(II) Complexes of Tetradentate 4N Ligands for Catalytic Olefin Epoxidation: Effect of Nucleophilicity of Peroxo Complexes On Reactivity

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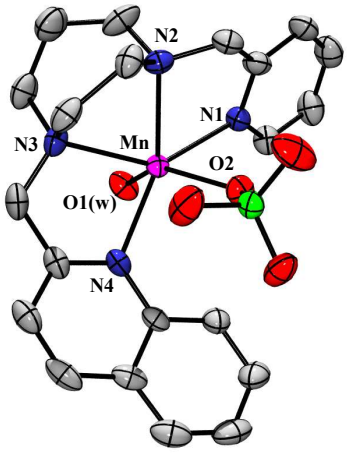
Graphical Abstract

A series of mononuclear Mn(II) complexes of linear 4N diazacycloalkane ligands as catalysts for alkene epoxidation using H_2O_2 as oxidant. The steric and electronic factors of Mn(II) complexes are tuned upon variation of one of the terminal arms of ligand donors. Lewis acidity of the Mn(II) center governs the nucleophilicity of peroxomanganese intermediates on reactivity. The epoxide product yield and selectivity increase upon increasing the Lewis acidity of metal center.



$[Mn(L4)(H_2O)(ClO_4)]^+$

Highlights

Mn(II) complexes of linear diazacycloalkane 4N ligands has been prepared. The complex **4** adopts distorted octahedral coordination geometry. Complexes screened for selective epoxidation of alkenes. Correlation of Lewis acidity of Mn(II) centre and stability of the highvalent peroxomanganese intermediate species.