

Comparison of the epoxidation of cyclohexene, dicyclopentadiene and 1,5-cyclooctadiene over LDH hosted Fe and Mn sulfonato-salen complexes

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Abstract

Sulfonato-salen metal complexes containing Fe or Mn metal centres have been synthesised and intercalated into Zn/Al layered double hydroxide hosts and used as catalyst for the epoxidation of cyclohexene, dicyclopentadiene and 1,5-cyclooctadiene. Using a combination of pivalaldehyde and molecular oxygen at atmospheric or higher pressures to produce the corresponding peracid as oxidant, cyclohexene gave two oxidation products, cyclohexene oxide and 2-cyclohexen-1-one, whereas, dicyclopentadiene was transformed exclusively into the corresponding mono-epoxide. The relative order of olefin activity correlates with the C=C=C bond angle for both metal centres. The product selectivity was found to be largely independent of the central metal ion suggesting that the local environment around the central metal ion was of greater importance. A possible mechanism-based on the product distribution is suggested.

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1. Introduction

In recent years, there has been a great deal of interest in the catalytic partial oxidation of alkenes to produce epoxides as the latter are a flexible intermediate and precursor to many useful chemical products [1]. Cyclohexene oxide is a valuable organic intermediate, used in the synthesis of products such as chiral pharmaceuticals, pesticides, epoxy paints, rubber promoters and dyestuffs. Cyclopentadiene (CPD) is a by-product in C5 streams from oil refining and exists as its dimer, dicyclopentadiene (DCPD). Epoxides of DCPD have numerous uses including enhancing the yield of polyalkylene polycarbonates [2].

Epoxidation of cyclohexene has been widely investigated using several metal catalysts under both homogeneous [3,4] and heterogeneous [5–7] conditions. The groups of Venturello [8,9] and Ishii [10–12] prepared effective polyoxometalate-based systems for alkene epoxidation using hydrogen peroxide. Although the system offers good catalytic activity in the epoxidation of

cyclohexene, the use of chlorocarbon solvents such as chloroform and 1,2-dichloroethane are disadvantages and catalyst deactivation is a limitation of the system [13]. Unfortunately, use of other non-Venturello–Ishii systems using heteropoly compounds as catalyst and aqueous hydrogen peroxide as oxidant show relatively poor performance in cyclohexene epoxidation [6,14–16].

Although hydrogen peroxide tends to be the oxidant of choice using polyoxometalate-based systems [6,8–12], the combined use of molecular oxygen with isobutyraldehyde has been shown to be effective in cyclohexene oxidation [6]. This extended the work of Mukaiyama and co-workers [17] who reported an important breakthrough in the epoxidation of alkenes by using molecular oxygen in combination with pivalaldehyde as oxidant. We reported recently [18] that a similar oxidant combination was effective in the epoxidation of *R*-(+)-limonene and (–)- α -pinene over Mn–salen type system intercalated into layered double hydroxide (LDH) hosts.

Various metallosalen complexes in the homogeneous phase-based on manganese(III) [19], chromium(III) [20] and nickel(II) [21] salen have been prepared and used for epoxidation of simple olefins, and cyclohexene or cyclooctene. Of these,

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the cationic manganese(III)–salen complexes showed most efficiency as homogeneous catalysts [19]. The 5,5'-(NO₂)₂-salen–manganese(III) cationic complex produced higher yields of epoxide (%) than methyl or OAc substituted systems [19]. The yield of epoxide showed a degree of dependence on the nature of solvent with acetonitrile giving best results when using cyclohexene and cyclooctene as substrates [19].

Heterogenisation of Mn–salen systems using zeolites as hosts have met with mixed success [22,23] whereas intercalation of these systems into layered double hydroxide (LDH) hosts shows promise [18]. These hydrotalcite-based materials are often employed as catalyst in their own right [24,25] and as catalyst precursors [26–28], although studies on the intercalation of transition metal complexes within hydrotalcite layers are less common. Intercalation of a dioxomolybdenum(VI) anion into a Zn/Al layered double hydroxide host showed useful catalytic properties in the air oxidation of thiol and reduction of nitrobenzene [29,30]. We recently reported that sulfonato–salen–Mn^{III} complexes intercalated into Zn/Al layered double hydroxides showed high conversion, selectivity and de in the stereoselective oxidation of *R*-(+)-limonene and α -(-)-pinene using a combination of pivalaldehyde and molecular oxygen or air as oxidant [18,31]. In this paper, we describe the synthesis of a new LDH-based material [Zn_{2.15}Al_{0.84}(OH)_{5.98}][Fe(Cl)salen]_{0.22}[C₆H₅COO]_{0.40}·2H₂O and compare its behaviour with LDH-[Mn(Cl)(L)] {L = sulfonato–salen ligand} [31] as a heterogeneous catalyst in the oxidation of cyclohexene, 1,4-cyclohexadiene and dicyclohexadiene using molecular oxygen in the presence of pivalaldehyde.

2. Experimental

2.1. Preparation of sulfonato–salen ligand, H₂L (1)

The chiral sulfonato–salen ligand was prepared according to our published method [18,31]. Basically (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate from *trans*-diaminocyclohexane (99%, Aldrich) and (*2R,3R*)-(+)-tartaric acid (99.5%, Aldrich), and sodium salicylaldehyde-5-sulfonate from salicylaldehyde (98%, Aldrich) and aniline (99.5%, Aldrich), were prepared. A mixture of 2.97 g of (*R,R*)-1,2-diammonium cyclohexane mono-(+)-tartrate and 3.12 g of potassium carbonate were combined with 20 ml water–ethanol (1:4) into a two necked round-bottomed flask with reflux condenser and an addition funnel. The mixture was heated and stirred with a magnetic stirrer. A solution of sodium salicylaldehyde-5-sulfonate (5.54 g) in 20 ml of water was added drop wise to the above solution through an addition funnel with constant stirring and gentle heating. The resulting mixture was refluxed for 1 h with stirring and cooled to room temperature. The volume was reduced by 50% by rotary-evaporation until a yellow solid was separated, which was filtered off and washed with ethanol. The yellow solid was then recrystallised from water–diethyl ether mixture and dried over silica gel.

2.2. Preparation of LDH-[Mn(Cl)(L)] (2)

The compounds, Na₂[Mn(Cl)(L)] and LDH-[C₆H₅COO] compounds were prepared according to our previously published methods [18,31]. Briefly, an aqueous solution (30 ml) of Mn(O₂CMe)₂·4H₂O (1.72 g) (99+%, Aldrich) was added dropwise while stirring to an aqueous solution (20 ml) of the ligand (1.75 g). Stirring was continued for 1 h and the mixture left to stand for 2 h. The green solid was separated and filtered and washed with cold water and ethanol and dried over silica gel. A saturated aqueous solution of sodium chloride (3 ml) was added to the mixture after the complete addition of ligand and stirring was continued for 1 h and the mixture allowed to stand for 2 h. The green solid was separated and filtered and washed with cold water and ethanol and dried over silica gel. Yield: 97%.

Na₂[Mn(Cl)(L)] (1.71 g) was then dissolved in de-carbonated water and LDH-[C₆H₅COO] (5.0 g) was added to the solution and stirred for 10 h at room temperature under a nitrogen atmosphere. The pale green product was filtered off and washed with water and dried overnight at 333 K.

2.3. Preparation of Na₂[Fe(Cl)(salen)] (3)

30 ml of an aqueous–ethanol solution of FeCl₃·6H₂O (1.89 g) was added drop wise with stirring for 20 min to a hot aqueous solution containing 2.63 g of ligand (1) until a deep red solid separated. It was filtered off and washed with cold water and ethanol. The complex was purified by dissolving in water and precipitated by addition of diethyl ether followed by drying over silica gel. Yield: 88%.

2.4. Preparation of LDH-[Fe(Cl)(L)] (4)

LDH-[Fe(Cl)(L)] was obtained by the partial substitution of intercalated C₆H₅COO anions by the [Fe(Cl)(L)]²⁻. Na₂[Fe(Cl)(L)] (1.72 g) was dissolved in decarbonated water and 5.0 g of LDH-[C₆H₅COO] was added to the solution and stirred for 10 h at room temperature under a nitrogen atmosphere. The red product was filtered off and washed with water and ethanol and dried overnight at 333 K.

2.5. Catalyst characterisation

FTIR spectra of samples as KBr disks were recorded using a Perkin-Elmer 1720X spectrometer while electronic spectra were recorded on a Perkin-Elmer UV/VIS Lambda 16. The X-ray powder diffraction patterns were recorded on a Philips PW 1010 X-ray generator with Cu K α (1.5402) radiation at 1° min⁻¹. Aluminium, zinc, manganese and iron were determined using a UNICAM 939/959 atomic absorption spectrometer.

2.6. Catalytic reaction

Epoxidation of cyclohexene, dicyclopentadiene and 1,5-cyclooctadiene using pivalaldehyde and molecular oxygen at atmospheric pressure was carried out in a twin-necked round-bottomed flask equipped with condenser. In a typical run,

1 mmol of alkene, 2 mmol pivalaldehyde, 10 ml toluene and 0.050 g of catalyst were stirred at room temperature (25 °C) while bubbling molecular oxygen at atmospheric pressure. Catalytic epoxidation of cyclohexene with molecular oxygen at 100 psi was carried out in a stainless steel autoclave fitted with pressure sensor and stirrer and held at constant temperature using an external oil bath.

After the desired period of reaction was complete, the catalyst was filtered off and the selectivity and conversion were measured using a Hewlett Packard GC–MS fitted with CYDEX-B fused silica column using both FID and MS detectors.

2.7. Computational details

The structure of the alkenes employed were calculated using the Gaussian 98 program [32] with the B3LYP/6-31+G** method.

3. Results and discussion

3.1. Synthesis of $[M^{III}-(\text{sulfonato-salen})(\text{Cl})]^{2-}$

The salen ligand **1** reacted instantly with manganese(II) acetate tetrahydrate in aqueous medium to give dianionic manganese(III) $[\text{Mn}(\text{OAc})(\text{L})]^{2-}$ [$\text{L}^{2-} = \text{salen}(\text{sulfonato})$]. The acetyl ligand in $[\text{Mn}(\text{OAc})(\text{L})]^{2-}$ was readily replaced by chloride at room temperature to produce $[\text{Mn}(\text{Cl})(\text{L})]^{2-}$. Iron(III) chloride hexahydrate reacted with ligand (**1**) to produce $[\text{Fe}(\text{Cl})(\text{L})]^{2-}$ in high yield. The compounds produced were water soluble.

3.2. Synthesis of LDH-[M-salen]

The host hydrotalcite-like material, Zn/Al-[C₆H₅COO], was prepared by co-precipitation of a solution of zinc and aluminium nitrates with an aqueous solution of NaOH and benzoic acid [18,31]. The ions $[\text{M}(\text{Cl})(\text{L})]^{2-}$ (where M=Mn or Fe), were intercalated into the Zn(II)/Al(III) layered double hydroxide at room temperature from an aqueous medium by

anion exchange of the benzoate ion. The apparent equilibrium constants for the exchange process at 298 K were 4.61×10^{-2} and 4.68×10^{-2} for the Mn and Fe sulfonato-salen complexes, respectively.

3.3. Characterisation of $[M^{III}(\text{Cl})(\text{L})]^{2-}$ and LDH-[M(Cl)(L)] catalysts

As previously observed in the case of $[\text{Mn}(\text{Cl})(\text{L})]^{2-}$ [31], the FTIR spectrum of $[\text{Fe}(\text{Cl})(\text{L})]^{2-}$ exhibited strong bands at ca. 1112 and 1029 cm⁻¹ (Fig. 1) due to the anti-symmetric and symmetric stretching modes of the SO³⁻ moiety [33], which are slightly perturbed to lower frequencies in comparison with the free ligand (1110 and 1035 cm⁻¹). The complex **3**, also shows bands at 1621 and 1543 cm⁻¹ due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ vibrations, respectively, which are red shifted (11 cm⁻¹) and blue shifted (21 cm⁻¹) with respect to the free ligand (1632 and 1522 cm⁻¹), indicating that the iron(III) is bonded through the two N and O donor atoms of the ligand as a tetradentate ONNO functionality. The FTIR spectrum (Fig. 1b and Table 1) of the catalyst (**4**) shows bands at ca. 1115 and 1034 cm⁻¹, due to the presence of the sulfonato group and at 568 cm⁻¹ due to $\nu(\text{M}-\text{O})$ vibrations which are not present in the spectrum of the LDH-[C₆H₅COO] (Fig. 1c), confirming the presence of the Fe-salen complex within the exchanged layered double hydroxide.

The XRD patterns of LDH-[C₆H₅COO] and LDH-[Fe(Cl)(L)] are shown in Fig. 2. The basal spacing of the latter was increased from 15.22 Å for LDH-[C₆H₅COO] to 20.53 Å as a consequence of intercalation. The gallery height is 15.83 Å, when the thickness (4.7 Å) of the brucite layers is subtracted. It is interesting to note that LDH-[Mn(Cl)(L)] showed a lesser gallery height (14.1 Å) than the equivalent Fe-based material. This increase in the gallery height provides further qualitative evidence of the successful intercalation of the sulphonato Fe-salen complex into the LDH. Elemental analysis (Table 1) for the final catalysts (**4**) is in reasonable agreement with the unit formula $[\text{Zn}_{2.15}\text{Al}_{0.84}(\text{OH})_{5.98}][\text{Fe}(\text{Cl})\text{salen}]_{0.22}[\text{C}_6\text{H}_5\text{COO}]_{0.40} \cdot 2\text{H}_2\text{O}$. The ratio [Al]/(Zn + Al) in **4**, and in the LDH-[C₆H₅COO] are

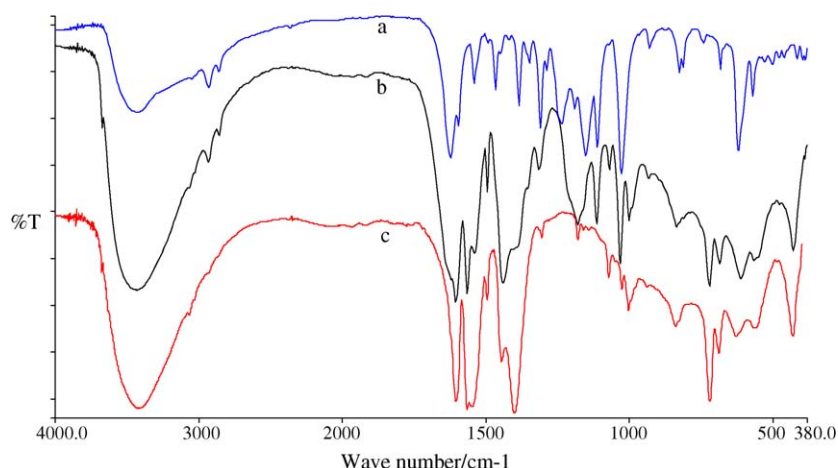


Fig. 1. FTIR spectra of (a) $\text{Na}_2[\text{Fe}(\text{Cl})(\text{L})]$, (b) LDH-[Fe(Cl)(L)] and (c) LDH-[C₆H₅COO].

Table 1
Characterization of catalyst precursors, the LDH-host precursor and hosted metal complexes

Compound	Analytical data ^a (%)							λ_{\max} (nm) ^b	FTIR ^c
	C	H	N	Fe	Co	Zn	Al		
Na ₂ [Fe(Cl)(L)]·2H ₂ O	36.41 (36.84)	3.32 (3.38)	4.36 (4.30)	8.73 (8.57)	–	–	–	575, 400, 280	1621, 1543, 1112, 1029, 572
LDH-[C ₆ H ₅ COO] ^d	–	–	–	–	–	34.61 (34.75)	5.58 (5.67)	227, 234	–
LDH-[Fe(Cl)(L)] ^d	–	–	–	2.63 (2.55)	–	29.62 (29.15)	4.82 (4.70)	540, 370, 242	1115, 1034, 568


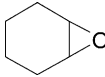
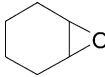
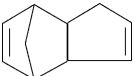
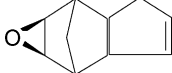
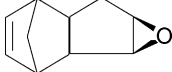

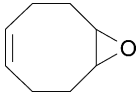
^a Calculated values are shown in parentheses.

^b In Nujol mull.

^c As KBr discs.

^d XRD: $2\theta/\theta$ (d -spacing (Å)) for LDH-[C₆H₅COO]: 5.8 (15.22), 11.3 (7.82), 17.0 (5.21), 22.7 (3.91); for LDH-[Fe(Cl)(L)]: 4.3 (20.53), 8.6 (10.27), 19.9 (4.40).

Table 2
Epoxidation of cyclohexene, dicyclopentadiene and 1,5-cyclooctadiene^a

Alkene	Catalyst	Time (h)	Product	Epoxide selectivity (%)	Yield (%)	TOF ^b (h ⁻¹)	
	LDH-[Mn(Cl)salen] ^c	6.0		74.0	62.2	121.2	
	LDH-[Fe(Cl)salen]	6.0		70.0	61.6	85.2	
	LDH-[Mn(Cl)salen]	6.0		A	81.0	78.6	150.0
				B	19.0	18.4	
	LDH-[Fe(Cl)salen]	6.0		A	80.0	73.6	111.7
				B	20.0	18.4	
	LDH-[Mn(Cl)salen]	12.0		97.0	82.5	62.0	

^a Reaction conditions: ca. 1 mmol substrate, 2 mmol pivalaldehyde, 10 ml toluene, 0.05 g catalyst, 14.5 psi molecular oxygen and 298 K.

^b Turnover frequency is calculated by the expression (mol product)/(mol metal catalyst)/h⁻¹.

^c Reaction condition: temperature 80 °C, time 5 h and 100 psi molecular oxygen: epoxide selectivity 68.0%, epoxide yield 53.0%, TOF (h⁻¹) 153.0.

almost identical, indicating that leaching of Zn^{II} or Al^{III} did not occur during the exchange procedure.

The electronic spectra of free Fe–salen (3) and the LDH hosted Fe compound (4) (in Nujol mull) are shown in Fig. 3. The [Fe(Cl)(L)]²⁻ displays bands at 575, 400 and 280 nm. After

exchange, the LDH hosted compound (4) showed bands at 540, 380 and 242 nm. These absorption bands may be assigned to metal → ligand and ligand → metal charge transfer processes as any d–d transitions would be spin forbidden for the high spin Fe(III) ion. Kessel et al. [34] made similar assignments having observed absorption bands at 463, 402 and 299 nm for Fe (salen) (9,10-phenanthrenequinonato) in benzene.

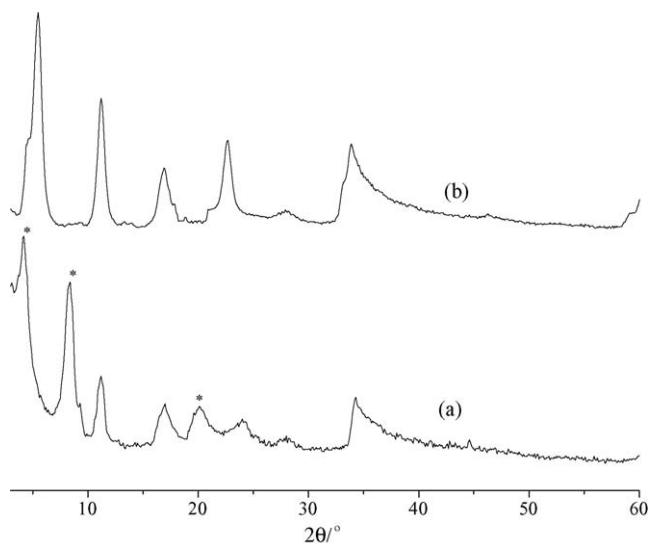


Fig. 2. X-ray powder patterns of (a) LDH-[C₆H₅COO] and (b) LDH-[Fe(Cl)(L)].

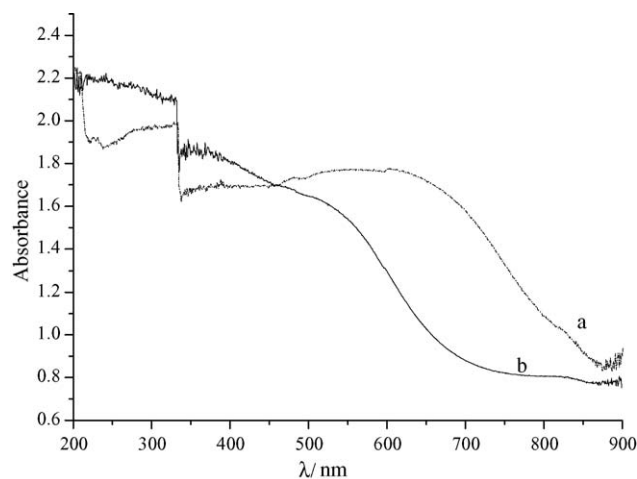
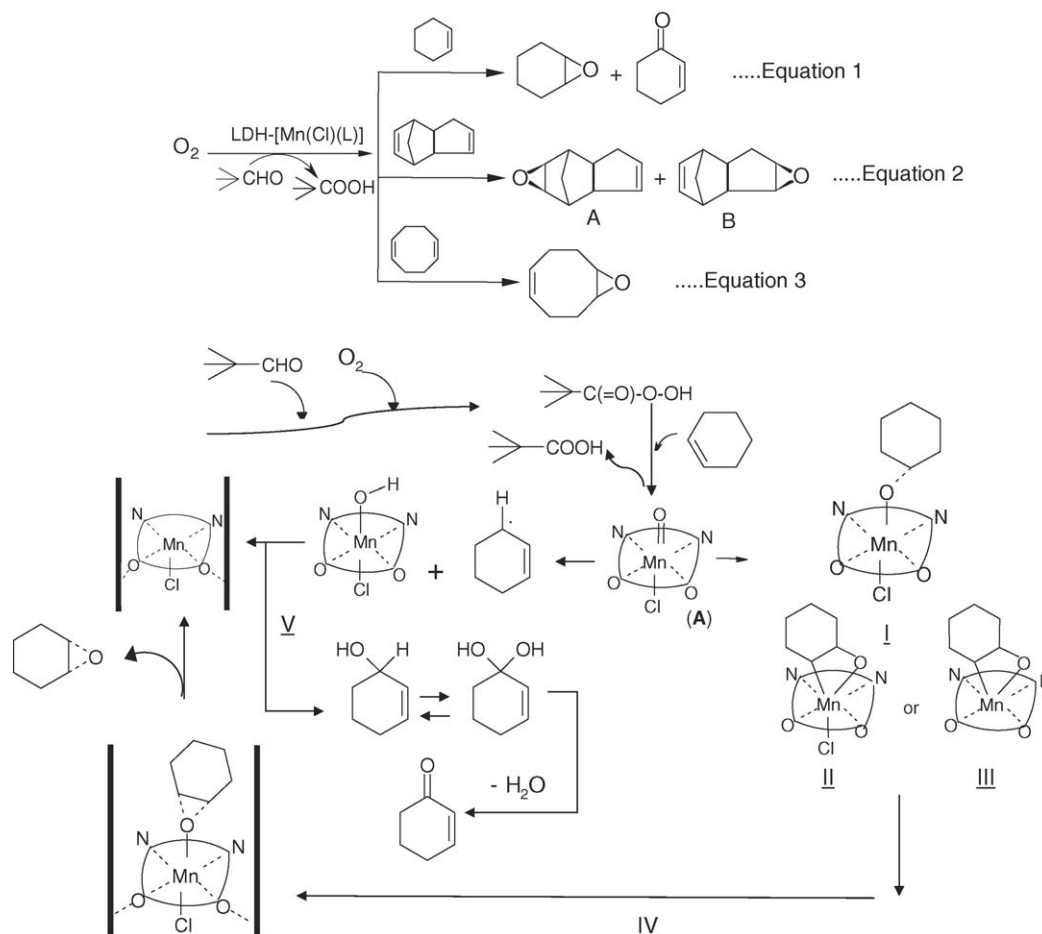


Fig. 3. UV–visible spectra of (a) free chiral sulfonato-iron(III) complex and (b) LDH-[Fe(Cl)(L)] in Nujol mull.



Scheme 1. Proposed reaction mechanism for the oxidation of cyclohexene including intermediate species.

The epoxidation of cyclohexene, dicyclopentadiene and 1,5-cyclooctadiene were studied in the presence of dioxygen and pivaldehyde at room temperature over LDH-[M(Cl)salen] {M = Mn or Fe} catalysts. The reaction schemes are shown in Eqs. (1)–(3) and results are reported in Tables 2–4. Blank test reactions carried out under the same conditions in the presence of LDH-[C₆H₅COO], confirmed that conversion of cyclohexene and dicyclopentadiene were negligible (5.5% for cyclohexene and 4.5% for dicyclopentadiene) in the absence of metal–salen complex. Cyclohexene was converted to give cyclohexene oxide and 2-cyclohexen-1-one (Eq. (1)). At room temperature and at

atmospheric pressure of molecular oxygen, cyclohexene was converted to give ca. 62% epoxide yield over both Mn (2) and Fe (4) systems (Table 2). Selectivity was marginally better for the Mn-based system. The epoxidation of cyclohexene was also carried out using catalyst 2, at 80 °C and 100 psi pressure of molecular oxygen. Under these conditions, the yield to epoxide was 53.0% after 5 h using LDH-[Mn(Cl)salen] as catalyst. The TOF was 153 as opposed to 121 h⁻¹ which had been achieved under milder reaction conditions.

A proposed reaction mechanism for the oxidation of cyclohexene is shown in Scheme 1. The mechanism involves an

Table 3
Performance of reused catalyst in the epoxidation of cyclohexene^a

Catalyst	Run	Conversion (%)	Epoxide selectivity (%)
LDH-[Mn(Cl)(salen)]	1	84.0	74.0
	2	83.0	74.0
	3	83.0	73.0
LDH-[Fe(Cl)(salen)]	1	88.0	70.0
	2	87.0	69.0
	3	86.0	70.0

^a Reaction conditions: ca. 1 mmol substrate, 2 mmol pivaldehyde, 10 ml toluene, 0.05 g catalyst, 14.5 psi molecular oxygen, time 6 h and temperature 298 K.

Table 4
Performance of reused catalyst in the epoxidation of dicyclopentadiene^a

Catalyst	Run	Conversion (%)	Epoxide selectivity, A (%)
LDH-[Mn(Cl)(salen)]	1	97.0	81.0
	2	96.0	81.0
	3	97.0	80.0
LDH-[Fe(Cl)(salen)]	1	92.0	80.0
	2	92.0	79.0
	3	92.0	79.0

^a Reaction conditions: ca. 1 mmol substrate, 2 mmol pivaldehyde, 10 ml toluene, 0.05 g catalyst, 14.5 psi molecular oxygen, temperature 298 K and time 6 h.

initial activation of molecular oxygen over the catalyst which is inserted into the aldehyde to produce the corresponding peracid. Yamada et al. [17] first reported a similar pathway using molecular oxygen in the presence of pivaldehyde over salen–Mn^{III} complexes under homogeneous conditions. They proposed that the reaction of molecular oxygen with the salen–Mn^{III} complex forms a highly reactive acylperoxy salen–Mn species {R₂CO₂–O–Mn^{III}} which was responsible for the direct epoxidation of the alkene. However, very recent studies have suggested that radical pathways may be involved in the oxidation of 1,4-cyclohexadienes using Jacobsen's catalyst which involves attack at labile hydrogen atoms whereas *m*-chloroperoxy-benzoic acid reacts by direct oxidation of the double bond [35]. In the present case, GC–MS analysis revealed only two reaction products i.e., cyclohexene oxide and 2-cyclohexen-1-one during the oxidation of cyclohexene using LDH hosted Mn–salen or Fe–salen catalyst in the presence of molecular oxygen and pivalaldehyde. Further evidence for the role of the LDH hosted metal–salen catalyst beyond merely in situ generation of the 2,2-dimethyl perpropanoic acid will be shown in the selectivity to mono-epoxide isomers from the epoxidation of dicyclopentadiene which differs significantly from the product distribution given by the homogeneous oxidation involving direct use of the peracid (see below). Furthermore, if direct reaction between substrate double bond and peracid were facilitated by an initial protonation of the peracid carbonyl group [36], then this route would be less favourable in the basic environment within the hydrotalcite layers. Using the LDH hosted salen system, we believe that pivaldehyde is firstly converted to the peracid by an oxo-transfer process, and then the in situ generated peracid transfers the oxygen atom to the metal centre to form a higher valent metal oxo species (A). These oxo-metal complexes form an intermediate of the type shown as I–III (Scheme 1) depending on the specific nature of the substrate interaction across the metal–oxygen bond. We propose that in the present LDH system, either species II or III are formed from the oxo-metal complex, by reaction with cyclohexene rather than I. Intermediates II or III would be more likely to induce enantioselectivity within the epoxidised substrate and we have shown this recently using substituted styrenes and cyclic alkenes [37]. Of species II and III, the removal of the labile Cl ligand (III) is not thought to be essential given that axial immobilization of similar Mn–salen complexes via phenoxy groups produced active, stable catalyst for epoxidation of unfunctionalised olefins [38]. This would leave species II as the most likely candidate. In addition to oxo-transfer to the double bond to form the epoxide (pathway IV) the reaction simultaneously forms 2-cyclohexen-1-one via hydrogen atom transfer (pathway V).

Prior to studying dicyclopentadiene, a twin ring system which contains two double bonds for potential oxidation, the epoxidation of a single ring compound containing two double bonds was briefly studied. For this purpose, 1,5-cyclooctadiene epoxidation was attempted over the LDH-[Mn(Cl)salen] system under identical reaction conditions as used for cyclohexene (and dicyclopentadiene—see later). The reaction was purposely left for an extended period of time (12 h) compared to the cyclohexene reaction (6 h) in order to allow the possibility of producing secondary reaction products. Although the reaction rate was less than that for the cyclohexene reaction as deduced by comparing the relative TOF values (Table 2), the extent of reaction (85% conversion) was acceptable for the intended purpose. Results indicate a very high selectivity (97%, 82.5% yield) to the mono-epoxide indicating that the conversion of the double bond to the corresponding oxirane made the molecule less attractive as a substrate than the ring structure containing two double bonds.

The epoxidation of dicyclopentadiene (containing both *endo*- and *exo*-isomers) over LDH-[Mn(Cl)salen] (2) and LDH-[Fe(Cl)salen] (4) using molecular oxygen at atmospheric pressure in combination with pivalaldehyde as oxidant, formed a mixture of mono-epoxides, A and B in accordance with Eq. (2). The yield of epoxides A and B were 78.6% and 18.4%, respectively, over LDH-[Mn(Cl)salen] (2), while a marginally lower value of 73.6% A was obtained over LDH-[Fe(Cl)salen] (4). However, to all extents and purposes, both samples showed very similar behaviour under these chosen conditions and both gave a selectivity ratio of ca. 4:1 as a ratio of mono-epoxides A:B.

The epoxidation of *endo*-dicyclopentadiene using *m*-chloroperoxy-benzoic acid in solution produced a 1.5:1 mixture of epoxides A and B [39]. Similarly, the use of dimethyldioxirane as oxidant led to yields of 35% and 40% of epoxides A and B, respectively, starting from *endo*-dicyclopentadiene [40], suggesting that the use of a heterogeneous catalyst here made a significant difference in terms of selectivity. However, epoxidation of *exo*-dicyclopentadiene produced only epoxide A in 45% yield using dimethyldioxirane [40], suggesting that the high selectivity to mono-epoxide A over the LDH-[Mn(Cl)salen] (2) and LDH-[Fe(Cl)salen] (4) may have resulted from preferential transformation of one of the starting isomers in the mixture. Use of excess dimethyldioxirane yielded bis-epoxide [40] whereas the use of in situ generated peracid here over the LDH-[Mn(Cl)salen] (2) and LDH-[Fe(Cl)salen] (4) heterogeneous catalysts exclusively led to formation of the mono-epoxides (Tables 2 and 4).

To shed light on the factors responsible for product selectivity, cross-sections and selective bond angles were calculated for the three substrate molecules (Table 5, and Fig. 4). In the case of dicyclopentadiene, product A was formed with much higher

Table 5
Calculated cross-sections and selective bond angles

Alkene	Height (Å)	Width (Å)	<C1C2C3	<C2C3C4	<C5C6C7	<C6C7C8
Cyclohexene	4.363	5.026	123.51	123.51	–	–
Dicyclopentadiene	4.327	6.579	112.5	112.9	107.4	107.5
1,5-Cyclooctadiene	4.997	5.224	129.09	120.72	129.08	130.70

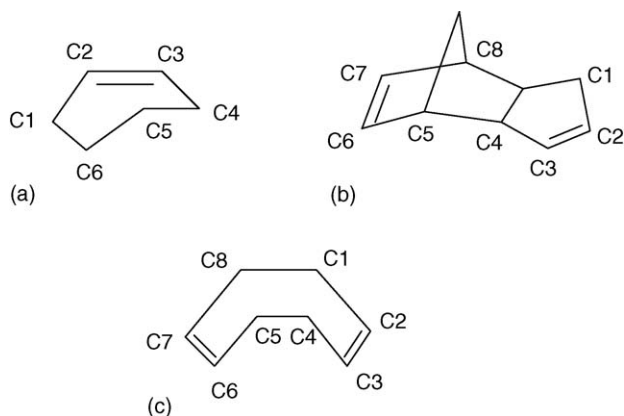


Fig. 4. Lowest-energy geometries of (a) cyclohexene, (b) dicyclopentadiene and (c) 1,5-cyclooctadiene.

selectivity than product **B** over the LDH-[Mn(Cl)salen] (**2**) and LDH-[Fe(Cl)salen] (**4**) which may be due to the greater bond strain of $\langle C5C6C7 \rangle$ than across $\langle C1C2C3 \rangle$ (Table 5).

On comparing TOF using LDH-[Mn(Cl)salen] (**2**) as catalyst (Table 2), the TOF was increased in the sequence: 1,5-cyclooctadiene < cyclohexene < dicyclopentadiene. The calculation of lowest-energy geometries of cyclohexene, dicyclopentadiene and 1,5-cyclooctadiene show that the cross-sectional areas of above substrates is not significantly different suggesting that this is not the factor which discriminates between the molecules in terms of activation. However, the bond angle associated with the double bond varies between each substrate molecule (Table 5 and Scheme 1) and furthermore the order of increasing TOF is in the same order as decreasing bond angle suggesting that angle strain at the double bond favours activation of the olefin and/or facilitates pathway **IV** involving oxygen transfer (Scheme 1). This order was also maintained albeit with lower TOF values for the LDH-[Fe(Cl)salen] (Table 2).

The stability of the catalysts was studied by performing repeated epoxidation reactions under the same conditions as described above. At the end of each reaction cycle, the catalyst was recovered by filtration and washed with toluene, dried and reused. The results are shown in Tables 3 and 4 for catalyst reused up to three times. The conversion (%) and selectivity (%) were almost identical irrespective of the number of cycles. No evidence for leaching of Mn or Fe or decomposition of the catalyst complex was observed during the catalysis reaction and no Mn or Fe could be detected by AA spectroscopic measurement of the liquid reaction mixture after catalytic reaction. The FTIR spectra of the solid catalyst after reuse were identical to the fresh catalyst suggesting no structural modifications had taken place.

4. Conclusions

The sulfonato-salen- M^{III} [$M = Mn$ or Fe] compounds were prepared and successfully intercalated into a Zn/Al-LDH host. The catalysts showed good activity and selectivity in the epoxidation of cyclohexene, dicyclopentadiene and 1,5-cyclooctadiene using dioxygen as oxidant and in the presence of pivaldehyde at room temperature. 1,5-Cyclooctadiene showed

excellent selectivity, nearly 97% to the epoxide. The relative order of activity of the molecules could be related to the strain at the bonds associated with the olefin functionality. This also held true for the case of dicyclopentadiene where two olefin groups are available for reaction. Reaction using 1,5-cyclooctadiene showed that even at high conversion, formation of the di-epoxide was not favourable indicating that once formed, the mono-epoxide was less attractive as a substrate than the di-olefin. Mn complexes proved to be more active than Fe, irrespective of the substrate molecule studied.

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References

- [1] R. Neumann, M. Dahan, *Nature* 388 (1997) 353; C.L. Hill, *Nature* 401 (1999) 436; Y. Ishii, S. Sakaguchi, T. Iwahama, *Adv. Synth. Catal.* 343 (2001) 393.
- [2] H.-N. Sun, US Patent 4,789,727, 1988.
- [3] S.V. Kotov, T.M. Kolev, M.G. Georgieva, *J. Mol. Catal. A: Chem.* 195 (2003) 83; G. Wang, G. Chen, R.L. Luck, Z. Wang, Z. Mu, D.G. Evans, X. Duan, *Inorg. Chim. Acta* 357 (2003) 3223; Y. Ding, Q. Gao, G. Li, H. Zhang, J. Wang, L. Yan, J. Suo, *J. Mol. Catal. A: Chem.* 218 (2004) 161; J. Qi, Y. Li, Z. Zhaou, C. Yeung, A.S.C. Chan, *Adv. Synth. Catal.* 347 (2005) 45.
- [4] K.S. Ravikumar, F. Barbier, J.-P. Begue, D. Bonnet-Delpon, *Tetrahedron* 54 (1998) 7457.
- [5] R. Raja, G. Sankar, J.M. Thomas, *Chem. Commun.* (1999) 829.
- [6] Y. Watanabe, K. Yamamoto, T. Tatsumi, *J. Mol. Catal. A: Chem.* 145 (1999) 281.
- [7] J.M. Fraile, J.I. Garcia, J.A. Mayoral, E. Vispe, *Appl. Catal. A: Gen.* 245 (2003) 363.
- [8] C. Venturello, R. D'Aloisio, J.C.J. Bart, M. Ricci, *J. Mol. Catal.* 32 (1985) 107.
- [9] C. Venturello, R. D'Aloisio, *J. Org. Chem.* 53 (1998) 1553.
- [10] Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* 53 (1998) 3587.
- [11] Y. Matoba, H. Inone, J. Akagi, T. Okabayashi, Y. Ishii, M. Ogawa, *Synth. Commun.* 14 (1984) 865.
- [12] Y. Ishii, M. Ogawa, in: A. Ohno, N. Furukawa (Eds.), *Reviews on Heteroatom Chemistry*, vol. 3, MY U, Tokyo, 1990, p. 121.
- [13] D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, *J. Am. Chem. Soc.* 117 (1995) 681.
- [14] N.I. Kuznetsova, L.I. Kuznetsova, V.A. Likhobolov, *J. Mol. Catal. A: Chem.* 108 (1996) 135.
- [15] E. Gardner, T.J. Pinnavaia, *Appl. Catal. A* 167 (1998) 65.
- [16] N. Mizuno, C. Nozaki, I. Kiyoto, M. Misono, *J. Catal.* 182 (1999) 285.
- [17] Y. Yamada, K. Imagawa, T. Nagata, T. Mukaiyama, *Chem. Lett.* (1992) 2231.
- [18] S. Bhattacharjee, J.A. Anderson, *Catal. Lett.* 95 (2004) 119.
- [19] K. Srinivasan, P. Michaud, J.K. Kochi, *J. Am. Chem. Soc.* 108 (1986) 2309.
- [20] E.G. Samsel, K. Srinivasan, J.K. Kochi, *J. Am. Chem. Soc.* 107 (1985) 7606.
- [21] H. Yoon, C.T. Burrows, *J. Am. Chem. Soc.* 110 (1988) 4087.
- [22] S.B. Ogunwumi, T. Bein, *Chem. Commun.* (1997) 901.
- [23] G. Gbery, A. Zsigmond, K.J. Balkus Jr., *Catal. Lett.* 74 (2001) 77.

- [24] B. Sels, V.D. De, M. Buntinx, F. Pierard, A. Kirsch-De Mesmaeken, P.A. Jacobs, *Nature* 400 (1999) 855.
- [25] B.M. Choudary, M.L. Kantam, A. Rahaman, C.V. Reddy, K.K. Rao, *Angew. Chem. Int. Ed.* 40 (2001) 763.
- [26] B.M. Choudary, N.S. Chowdari, K. Jyothi, M.L. Kantam, *J. Am. Chem. Soc.* 124 (2002) 5341.
- [27] O. Clause, B. Rebours, E. Merlen, F. Trifiro, A. Vaccario, *J. Catal.* 133 (1992) 231.
- [28] H. Schaper, J.J. Berg-Slot, W.H. Stork, *J. Appl. Catal.* 54 (1989) 79.
- [29] A. Cervilla, A. Corma, V. Fornes, E. Llopis, P. Palanca, F. Rey, A. Ribera, *J. Am. Chem. Soc.* 116 (1994) 1595.
- [30] A. Cervilla, A. Corma, V. Fornes, E. Llopis, F. Perez, F. Rey, A. Ribera, *J. Am. Chem. Soc.* 117 (1995) 6781.
- [31] S. Bhattacharjee, T.J. Dines, J.A. Anderson, *J. Catal.* 225 (2004) 398.
- [32] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Mulick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.I. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanaykara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, *Gaussian 98, Revision A.5*, Gaussian Inc., Pittsburgh, PA, 1998.
- [33] N.B. Lin-Vien, W.G. Colhup, J.C. Fateley, Grasselli, *The Hand Book Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, San Diego, 1991.
- [34] S.L. Kessel, R.M. Emberson, P.G. Debrunner, D.N. Hendrickson, *Inorg. Chem.* 19 (1980) 1170.
- [35] U. Engelhardt, T. Linker, *Chem. Commun.* (2005) 1152.
- [36] H. Shi, Z. Zhang, Y. Wang, *J. Mol. Catal.* 238 (2005) 13.
- [37] S. Bhattacharjee, J.A. Anderson, *Adv. Synth. Catal.* 348 (2006) 151–158.
- [38] H. Zhang, S. Xiang, J. Xiao, C. Li, *J. Mol. Catal.* 238 (2005) 175.
- [39] D.R. Paulson, A.S. Murray, E.J. Fornoret, *J. Org. Chem.* 43 (1978) 2010.
- [40] A. Asouti, L.P. Hadjarapoglou, *Tetrahedron Lett.* 41 (2000) 539.