

Synthesis and characterization of novel chiral sulfonato–salen–manganese(III) complex in a zinc–aluminium LDH host

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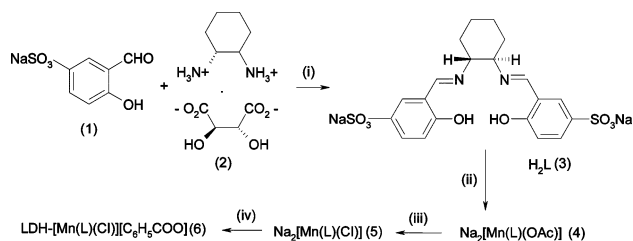
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A novel heterogeneous catalyst, $[\text{Zn}_{2.15}\text{Al}_{0.86}(\text{OH})_{6.02}][\text{Mn}]_{0.19}[\text{C}_6\text{H}_5\text{COO}]_{0.48}\cdot 2\text{H}_2\text{O}$, where $[\text{Mn}] = \text{chiral sulfonato–salen–manganese(III) complex}$, $\text{Na}_2\text{Mn}(\text{C}_2\text{O}_4)_2\cdot 2\text{H}_2\text{O}$, intercalated into $\text{Zn}^{\text{II}}\text{–Al}^{\text{III}}$ layered double hydroxide host, has been synthesized and found to be an effective heterogeneous catalyst for the stereoselective epoxidation of *R*-(+)-limonene using molecular oxygen. The catalyst could be recycled without loss of performance.

Schiff-base ligands derived from salicylaldehyde and chiral amines which are known as Salen ligands and their manganese(III) complexes, developed by Jacobsen,¹ have been widely applied in enantioselective epoxidation under homogeneous and heterogeneous conditions.² Papers dealing with immobilisation of chiral complexes have appeared;^{3,4} however, studies on the intercalation of transition metal complexes into hydroxalite layers are sparse. Corma's group have described the intercalation of a dioxomolybdenum(VI) anion into a Zn(II)–Al(III) layered double hydroxide (LDH) host, which shows useful catalytic properties in the air oxidation of thiols⁵ and reduction of nitrobenzene.⁶ The pillaring of hydroxalite by polyoxometalate anions has also demonstrated that these microporous materials exhibit sufficiently large gallery heights that they may be suitable for the catalytic oxidation of organic compounds,⁷ and also LDH–OsO₄ catalysts displayed good asymmetric dihydroxylation of olefins.⁸ To our knowledge, intercalated systems containing chiral salen–manganese(III) complexes have not been previously reported and in this paper we describe the synthesis of the LDH, $[\text{Zn}_{2.15}\text{Al}_{0.86}(\text{OH})_{6.02}][\text{Mn}]_{0.19}[\text{C}_6\text{H}_5\text{COO}]_{0.48}\cdot 2\text{H}_2\text{O}$ as well as its action as a heterogeneous catalyst in the oxidation of *R*-(+)-limonene using molecular oxygen.

The synthetic route of chiral (sulfonato–salen)–manganese(III) and its LDH compound are shown in Scheme 1. The chiral Schiff base ligand (abbreviated as **3**) was readily prepared as a crystalline yellow solid in 98% yield by refluxing two equivalents of **1** with **2** in a water–ethanol medium. In aqueous solution, the chiral ligand **3** instantly reacts with manganese(II) acetate tetrahydrate to produce dianionic manganese(III) **4** in ~97% yield. The acetyl ligand in **4** is readily replaced by chloride at room temperature to give **5**. The manganese compounds are soluble in water. The host hydroxalite-like material, $\text{ZnAl}[\text{C}_6\text{H}_5\text{COO}]$, was prepared by coprecipitation of a solution of zinc and aluminium nitrates with an aqueous solution of NaOH and benzoic acid.¹⁰ The ion **5** is intercalated into the zinc(II)–aluminium(III) layered double hydroxide at room temperature from an aqueous medium by exchange of the benzoate ion (Scheme 1).



Scheme 1 (i) 11.2 mmol **2**, 22.5 mmol potassium carbonate, 22.0 mmol **1**, water–ethanol and reflux; (ii) 8.0 mmol $\text{Mn}(\text{O}_2\text{CMe})_2\cdot 4\text{H}_2\text{O}$, 7.5 mmol **3**, water; (iii) saturated NaCl; (iv) 5.0 g $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$, 2.5 mmol **5**, water and stirring.

The free Schiff-base ligand exhibits strong bands at 1110 and 1035 cm^{-1} in the IR spectrum due to the anti-symmetric and symmetric stretching modes of the SO_3^- moiety,¹¹ which are slightly displaced to higher frequencies in the Mn(III) complexes†. The modes of metal coordination with the two N and O donor ligands through the phenolic oxygen and azomethine nitrogen of **3** are evidenced from the blue shift (*ca.* 23 cm^{-1}) of $\nu(\text{C}=\text{O})$ and the red shift (*ca.* 12 cm^{-1}) of the $\nu(\text{C}=\text{N})$ vibrations with respect to the free ligand (1522 and 1632 cm^{-1} , respectively).¹² Further support† for this coordination mode is provided by the $\nu(\text{Mn}=\text{O})$ and $\nu(\text{Mn}=\text{N})$ bands at *ca.* 574 and *ca.* 425 cm^{-1} respectively.¹² The IR spectrum of **6** shows bands at 1116 and 1032 cm^{-1} due to the presence of the sulfonato group and at 573 cm^{-1} for $\nu(\text{Mn}=\text{O})$, indicating the presence of the Mn–salen complex in the layered double hydroxide.

The XRD pattern of the exchange material, **6** exhibits four additional peaks compared to the $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$ corresponding to *d*-spacings of 18.78, 10.27, 6.41 and 4.50 Å. The calculated dimension of chloro[*N,N'*-bis(salicylidene)cyclohexanediamine]manganese(III) is 13.0 Å.¹³ The basal spacing increased from 15.22 Å for $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$ to 18.78 Å for **6**. The gallery height of **6** is 14.10 Å when the thickness of brucite layers (4.7 Å) was subtracted. This increase in the gallery height strongly suggests the successful intercalation of **5**. Elemental analysis† for **6** is in reasonable agreement with the unit formula $[\text{Zn}_{2.15}\text{Al}_{0.86}(\text{OH})_{6.02}][\text{Mn}]_{0.19}[\text{C}_6\text{H}_5\text{COO}]_{0.48}\cdot 2\text{H}_2\text{O}$. TGA profiles for the **5** and **6** also provide supporting evidence for the successful incorporation of the complex into the LDH host. The ratio $[\text{Al}/(\text{Zn}+\text{Al})]$ of **6** and $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$ are almost identical, indicating that leaching of either Zn^{II} or Al^{III} did not occur during the exchange procedure.

The electronic spectra (Fig. 1) of the free manganese(III) complex (in Nujol mull) displays bands at 800, 574, 465, 363, 295 and 250 nm. Of these, bands at 800 and 574 nm are due to $^5\text{B}_1 \rightarrow ^5\text{B}_2$, and $^5\text{B}_1 \rightarrow ^5\text{A}_1$ transitions.^{12,14} The UV–Visible spectrum of **6** (in Nujol mull) showed similar features to the free complex, indicating that during intercalation, no change of the manganese(III) co-ordination centre took place. The $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$ shows only two bands: maxima at 277 and 234 nm. The postulated configuration of **5** in the interlayer is shown in Scheme 2.

Recently, salen–metal complexes were occluded *via* the “ship-in-bottle” synthesis approach using X, Y and DAY zeolites, and the materials showed 93% conversion, 70% selectivity and 40% de in the epoxidation of *R*-(+)-limonene, although better results were

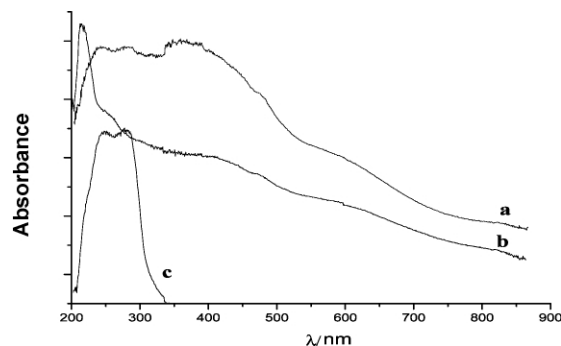
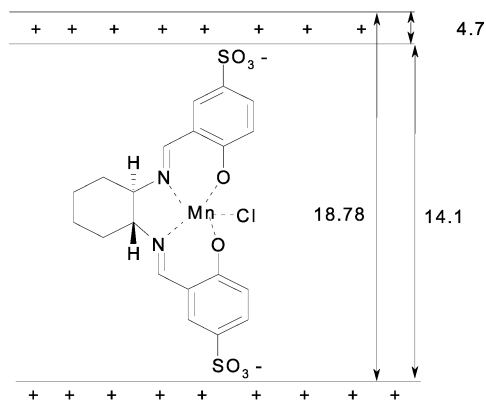


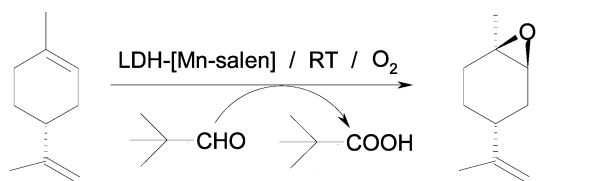
Fig. 1 Electronic spectra of (a) **6**, (b) **5** and (c) $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$.



Scheme 2 Postulated configuration of **5** in the interlayer space.

obtained for the epoxidation of (–)- α -pinene using molecular oxygen.¹⁵ Catalyst **6** was tested for the stereo-selective epoxidation of *R*-(+)-limonene using molecular oxygen at 298 K (Scheme 3), under identical conditions to those reported by Mukaiyama *et al.*¹⁶ for the epoxidation of dihydronaphthalene derivatives.

Using trimethylacetaldehyde and 75 psi molecular oxygen, *R*-(+)-limonene was converted to (+)-*cis*-limonene-1,2-epoxide with 86% selectivity and 34% de (Table 1). Other products formed were the corresponding diepoxide and limonene-1,2-diol. Addition of catalytic amounts of *N*-methylimidazole improved the de to 55% and also slightly increased the selectivity. In both cases, the conversion of *R*-(+)-limonene was 100%. Higher oxygen pressure (150 psi), had little affect on the selectivity or de. The catalyst remained virtually unchanged after three cycles of use (Table 2).



R-(+)-Limonene (+)-*cis*-limonene-1,2-epoxide
Scheme 3 Reaction scheme of epoxidation over intercalated catalyst

Table 1 Epoxidation of *R*-(+)-limonene at different oxygen pressure^a

Oxidant pressure (psi)	Additive	Conversion (%)	Selectivity (%)	De (%)
75	—	100	85.6	33.9
150	—	100	86.1	30.5
75	<i>N</i> -MeI ^b	100	89.0	55.2
150	<i>N</i> -MeI	100	90.7	54.0

^a Reaction conditions: 3.7 mmol *R*-(+)-limonene, 9.2 mmol pivalaldehyde, 0.100 g catalyst, 18.5 ml toluene and molecular oxygen, temperature 298 K and 24 h. ^b *N*-Methylimidazole, 1.78 mmol.

Table 2 Epoxidation of *R*-(+)-limonene over recycled catalyst^a

Run no.	Conversion (%)	Selectivity (%)	De (%)
1	100	89.0	55.2
2	100	87.1	54.8
3	100	90.7	54.0

^a Reaction conditions as Table 1 using 75 psi oxygen pressure.

No leaching of manganese was found by spectroscopic analysis of solution mixture after catalytic reaction. The FTIR spectra of the reused solid catalyst and fresh catalyst were identical.

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Notes and references

† Data: For ligand (**3**): IR (KBr): $\nu(\text{OH})$, 3210; $\nu(\text{CH}=\text{N})$, 1634; $\nu(\text{C}-\text{O})$, 1522, $\nu(\text{SO}_3^-)$, 1110 & 1035 cm^{-1} . Found (%): C, 45.72; H, 3.79; N, 5.36. Calcd (%): $\text{Na}_2\text{C}_{20}\text{H}_{20}\text{N}_2\text{S}_2\text{O}_8$: C, 45.61; H, 3.84; N, 5.32. For **4**: IR: $\nu(\text{C}=\text{N})$, 1623; $\nu(\text{C}-\text{O})$, 1540; $\nu(\text{SO}_3^-)$, 1029 & 1117; $\nu(\text{Mn}-\text{O})$, 573; $\nu(\text{Mn}-\text{N})$, 430 cm^{-1} . UV-Visible: 798, 576, 466, 365, 295, 250. Found (%): C, 38.93; H, 3.76; N, 4.10; Mn, 8.23. Calcd (%): $\text{Na}_2\text{MnC}_{22}\text{H}_{25}\text{N}_2\text{S}_2\text{O}_{12}$: C, 39.17; H, 3.74; N, 4.15; Mn, 8.15. For **5**: IR: $\nu(\text{C}=\text{N})$, 1626; $\nu(\text{C}-\text{O})$, 1545; $\nu(\text{SO}_3^-)$, 1026 & 1118; $\nu(\text{Mn}-\text{O})$, 575; $\nu(\text{Mn}-\text{N})$, 430 cm^{-1} . UV-Visible (Nujol mull): 800, 574, 465, 363, 295, 250. Found: C, 35.25; H, 3.27; N, 3.98; Mn, 8.20. Calcd: $\text{Na}_2\text{MnC}_{20}\text{H}_{22}\text{N}_2\text{S}_2\text{O}_{12}\text{Cl}$: C, 35.16; H, 3.22; N, 4.11; Mn, 8.05. For LDH-[$\text{C}_6\text{H}_5\text{COO}$]: XRD: $2\theta^\circ$ (*d*-spacing, Å): 5.8(15.22), 11.3(7.82), 17.0(5.21), 22.7(3.91). Found: Zn, 34.61; Al, 5.58; H₂O, 8.83. Calcd: LDH-[$\text{C}_6\text{H}_5\text{COO}$]: Zn, 34.75; Al, 5.67; H₂O, 8.91. For **6**: XRD: $2\theta^\circ$ (*d*-spacing, Å): 4.7(18.78), 8.6(10.27), 13.8(6.41), 19.7(4.50). Found (%): Zn, 29.03; Al, 4.69; [Mn], 24.88; H₂O, 7.53. Calcd (%) **6**: Zn, 29.14; Al, 4.81; [Mn], 25.06; H₂O: 7.47. UV-Visible (Nujol mull): 799, 552, 446, 350, 270, 226.

Catalytic reaction: Catalytic epoxidation of *R*-(+)-limonene with molecular oxygen was carried out in a stainless steel autoclave. The reaction products were analysed by GC (FID) and identified using a GC/MS fitted with CYDEX-B fused silica chiral column.

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