New binuclear double-stranded manganese helicates as catalysts for alkene epoxidation†

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New binuclear double-stranded helicates were formed between manganese(II) perchlorate and chiral phenyl- and polyphenyl-bridged oligopyridines; they are active catalysts for alkene epoxidation.

Manganese-catalyzed epoxidation of alkenes are of great current interest and many manganese complexes have been demonstrated to be active catalysts.[1–7] For example, [Mn(MCP)-(CF$_3$SO$_3$)$_2$][2] (MCP = N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-cyclohexane-*trans*-1,2-diamine) and [Mn(bipy)$_2$(CF$_3$SO$_3$)$_2$][3] (bipy = 2,2′-bipyridine) reported by Stack, [Mn(^{H,Me}PyTACN)-(CF$_3$SO$_3$)$_2$][4,5] (^{H,Me}PyTACN = 1-(2-pyridyl)-4,7-dimethyl-1,4,7-triazacyclononane) reported by Costas and [Mn(BQEN)-(CF$_3$SO$_3$)$_2$][6] (BQEN = N,N'-dimethyl-N,N'-bis(8-quinolyl)-ethane-1,2-diamine) reported by Nam are all excellent mononuclear catalysts. We herein report the first use of self-assembled supramolecular manganese helicate as catalysts for epoxidation.[8,9] Supramolecular manganese complexes are expected to be more stable than mononuclear manganese complexes, which are usually labile and easily undergo ligand dissociation catalysis.

Monophenyl- and biphenyl-bridged oligopyridines are known to form supramolecular binuclear metal complexes with metal ions.[10,11] The ligands used in this study, **L1–3**, were developed based on these ligand frameworks and were synthesized by procedures starting from a common bipyridine intermediate **1**.[12] The use of a chiral ketone allows us to form a non-racemic helicate which may have the potential for asymmetric catalysis. **L1** was

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obtained from Pd catalyzed Suzuki coupling between **1** and 1,3-phenyldiboronic acid. Pd catalyzed Suzuki coupling between **1** and 3-chlorophenylboronic acid or 3-bromophenylboronic resulted in chlorophenylbipyridine **2** or bromophenylbipyridine **3**. **L2** was then prepared by Ni(0)-mediated homocoupling of **2**. **L3**, a triphenyl-bridged oligopyridine, was obtained from Pd catalyzed Suzuki coupling of **3** and 1,3-phenyldiboronic acid (Scheme 1).

Reaction of **L** (**L** = **L1–3**) with one equiv. of manganese perchlorate salt in acetonitrile at room temperature afforded the air stable yellow complexes [Mn$_2$(**L**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ in 76–92% yield (Scheme 2). These complexes were characterized by elementary analysis, ESI-MS, and circular dichroism (CD) spectroscopy. The structures of [Mn$_2$(**L2**)$_2$(H$_2$O)(CH$_3$OH)(CH$_3$CN)(ClO$_4$)](ClO$_4$)$_3$ (Fig. 1) and [Mn$_2$(**L3**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ (Fig. 2), have been determined by X-ray crystallography, which show that they have double-stranded helicate structures.‡§
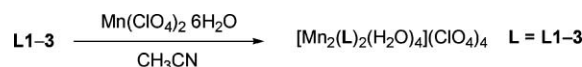
Scheme 2

[Mn$_2$(**L2**)$_2$(H$_2$O)(CH$_3$OH)(CH$_3$CN)(ClO$_4$)](ClO$_4$)$_3$ contains only one diastereomer which is a double-stranded helicate with *P* chirality. In the structure, both manganese centres have a distorted octahedral geometry, and are coordinated to two 2,2′-bipyridine units, one from each **L2** ligand. The other sites are completed by one acetonitrile, one methanol, one water and a perchlorate ion. The Mn–N distances are 2.180–2.369 Å. Its helical structure is achieved by twisting of the interannular C–C bond between the rings; the chelating 2,2′-bipyridine units are slightly nonplanar (16.68°–20.03°). The major helical twists occur between the bipyridine units and the bridged phenyl rings (34.80°–36.85°). The chiral groups are not close to the metal centre with the
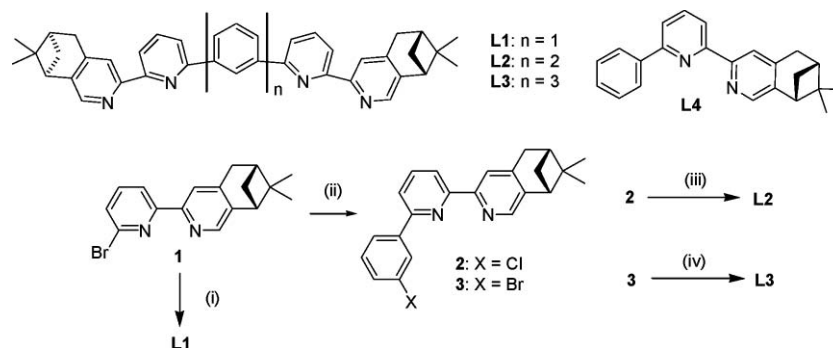
Scheme 1 Reaction conditions: (i) Pd(PPh$_3$)$_4$, 1,3-phenyldiboronic acid, CH$_3$OH, H$_2$O, toluene, NaCO$_3$, 70 °C; (ii) Pd(PPh$_3$)$_4$, 3-chlorophenylboronic acid or 3-bromophenylboronic acid, CH$_3$OH, H$_2$O, toluene, NaCO$_3$, 70 °C; (iii) NiCl$_2$, PPh$_3$, Zn, DMF; (iv) Pd(PPh$_3$)$_4$, 1,3-phenyldiboronic acid, CH$_3$OH, H$_2$O, toluene, NaCO$_3$, 70 °C.
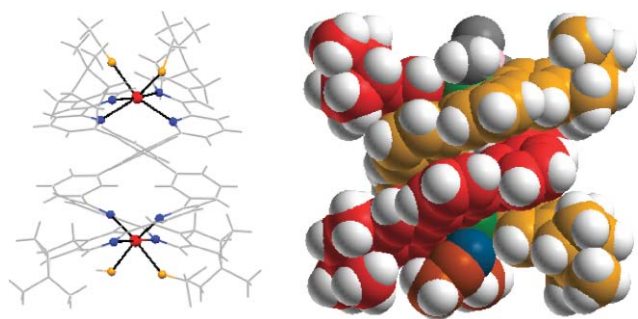
Fig. 1 Crystal structure and space-filling model of [Mn$_2$(**L2**)$_2$(H$_2$O)-(CH$_3$OH)(CH$_3$CN)(ClO$_4$)]$^{3+}$.
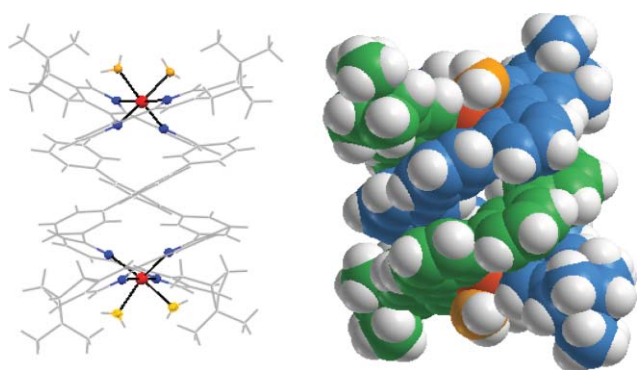
Fig. 2 Crystal structure and space-filling model of [Mn$_2$(**L3**)$_2$(H$_2$O)$_4$]$^{4+}$.

shortest Mn–H distance of 5.682 Å. The helical axis is composed by the two manganese(II) ions with a separation of 7.476 Å. [Mn$_2$(**L3**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$, as shown in Fig. 2, can also establish its double helical structure with the elongated ligand having *P* chirality. Besides coordination to two bipyridine units, the manganese centers complete their sites with water molecules only. The Mn–N distances are 2.199–2.385 Å. In this case, the chelating 2,2′-bipyridine units twist less (13.68°–16.12°). The twisting between the bipyridine units and the bridged phenyl rings (35.82°–43.38°) contribute most of the helical twist. The separation between the two manganeses is now elongated to 9.100 Å.

The helicates show strong CD absorptions at 230–360 nm implying that the helical structures are retained in solution even in coordinating solvents like acetonitrile (Fig. 3). [Mn$_2$(**L1**)$_2$-(H$_2$O)$_4$](ClO$_4$)$_4$ and [Mn$_2$(**L2**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ give a bisignate curve at 240–360 nm while [Mn$_2$(**L3**)$_2$(H$_2$O)$_4$] (ClO$_4$)$_4$ gives no neg-
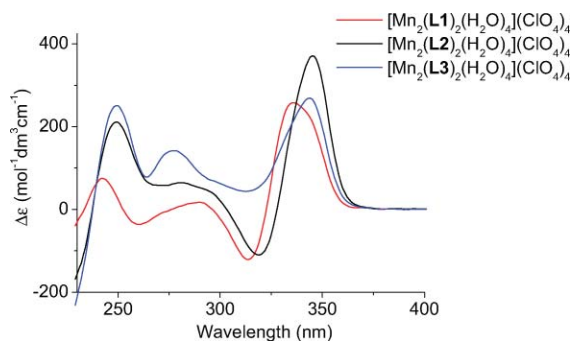
Fig. 3 Circular dichroism spectra of [Mn$_2$(**L**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ in CH$_3$CN.

ative absorption in the same region. These absorptions likely arise from the exciton coupling of the π–π* transition of the ligands.

To gain information about the lability of the helicates, exchange experiments were also carried out. The chiral helicate [Mn$_2$(**L2**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ was allowed to exchange with its achiral analogue, the helicate with ligands having no chiral [4,5]-substituents. Fig. 4 shows the ESI-MS spectra recorded at different time intervals. The parent peak of the "mixed" helicate (*m/z*: 1522) grows gradually with time in the first 60 min. On the other hand, similar experiments with a chiral mononuclear complex [Mn$_2$(**L4**)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ and its achiral analogue, complex with ligands having no chiral [4,5]-substituents, showed the formation of a heteroleptic mononuclear complex (*m/z*: 712) within one minute after mixing (Fig. 5). These results suggest that the helicates exchange at a much slower rate and confirm that the supramolecular structures hold the manganese ions more tightly than the mononuclear analogues.[13,14]
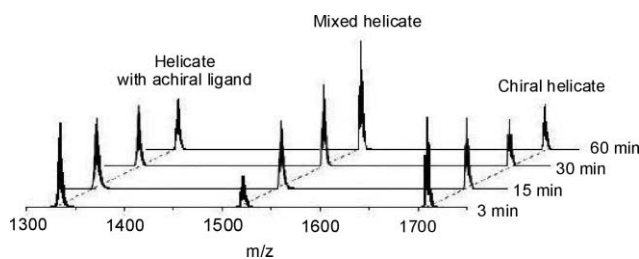

Fig. 4 ESI-MS spectrum showing ligand exchange between the chiral helicate, [Mn$_2$(**L2**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ (*m/z*: 1709.2), and its achiral analogue (*m/z*: 1333.1). Only the parent peaks of the helicates are shown for clearance.

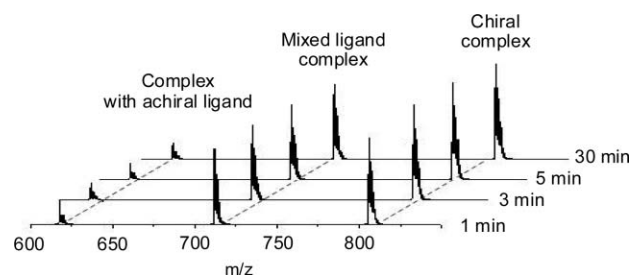**Fig. 5** Ligand exchange between the chiral mononuclear complex, [Mn$_2$(**L4**)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ (*m/z*: 806.3), and its achiral analogue (*m/z*: 618.0). Only the parent peaks are shown for clearance.

The potential of the manganese double stranded helicates in catalysis was first investigated in epoxidation of styrene using the reaction conditions reported by Stack.[3] At room temperature with peracetic acid (PAA) as oxidant, the helicates are all active catalysts. [Mn$_2$(**L1**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ gives 100% conversion of styrene in 6 min with 1 mol% catalyst. Modifying the reaction conditions by decreasing the reaction temperature to 0 °C improves the reaction selectivity (Entry 1) but the reaction is slower. [Mn$_2$(**L1**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ is in general the slightly better catalyst, which completes most reactions in 30 min while [Mn$_2$(**L2**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ and [Mn$_2$(**L3**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ take longer (Entries 9 and 11). Similar to other mononuclear manganese systems, these binuclear manganese helicates catalyze epoxidation of a wide range of olefins selectively. These helicates catalyze challenging aliphatic substrates like cyclooctene and

Table 1 Catalytic epoxidation by manganese complexes[a]

$$\text{alkene} \xrightarrow[\text{CH}_3\text{CN}]{[\text{Mn}_2(\text{L})_2(\text{H}_2\text{O})_4](\text{ClO}_4)_4,\,\text{PAA},\,30\,\text{min},\,0\,^\circ\text{C}} \text{epoxide}$$

Entry	Ligand (**L**)	Substrate	Conversion[b] (%)	Yield[b,c] (%)
1	**L1**		99	81
2			100	92
3[d]			90	>99
4			97	83
5			85	>99
6			100	>99
7			82	90
8			89	88
9[e]	**L2**		100	78
10			90	90
11[e]	**L3**		100	77
12			100	95
13[f]	**L4**		3	66

[a] Reaction condition: alkene (0.05 mmol), [Mn$_2$(**L**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$ (5 × 10^{-4} mmol), PAA (0.1 mmol), CH$_3$CN (0.15 ml) was used as solvent. [b] Determined by GC-FID. [c] GC yield based on conversion. [d] Reactions were carried out at room temperature. [e] Reaction finished in 60 min. [f] Mono-nuclear complex [Mn(**L4**)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ was used.

1-hexene to epoxides with excellent selectively (up to 99%, Entries 2–6). In terms of enantioselectivity, although the catalysts are chiral, unfortunately no asymmetric induction has been observed (<5% ee in all cases). To study how the supramolecular structure affects the catalytic activity of the epoxidation, mononuclear analogy of **L1**, [Mn(**L4**)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$, was also prepared and its catalytic epoxidation investigated. Under the same conditions, this mononuclear complex gives almost no reaction (Entry 13).

In summary, we have presented the first synthesis of chiral supramolecular binuclear manganese double-stranded helicates. The helical structures have been determined by X-ray crystallography. These structures are retained in solution as shown by CD experiments. These supramolecular manganese systems are excellent epoxidation catalysts. Unfortunately no enantioselectivity has been observed so far. Further experiments are underway to modify the systems to achieve more reactive and enantioselective catalysts.

Notes and references

‡ [Mn$_2$(**L1**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$: ESI-MS: m/z 728 [Mn(C$_{40}$H$_{38}$N$_4$)](ClO$_4$)$^+$, 1558 [Mn$_2$(C$_{40}$H$_{38}$N$_4$)$_2$](ClO$_4$)$_3$$^+$; CHN elemental analysis: calc. for Mn$_2$(C$_{40}$H$_{38}$N$_4$)$_2$(H$_2$O)$_4$(ClO$_4$)$_4$·2CH$_3$CN·7H$_2$O·CH$_2$Cl$_2$: C, 50.48; H, 5.28; N, 6.92; Found: C, 50.46, H, 5.31, N, 6.98%. [Mn$_2$(**L2**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$: ESI-MS: 805 [Mn$_2$(C$_{46}$H$_{42}$N$_4$)$_2$](ClO$_4$)$_2$$^{2+}$, 1709 [Mn$_2$(C$_{46}H_{42}N_4$)$_2$](ClO$_4$)$_3$$^+$; CHN elemental analysis: calc. for Mn$_2$(C$_{46}$H$_{42}$N$_4$)$_2$(H$_2$O)$_4$(ClO$_4$)$_4$: C, 58.73; H, 4.93; N, 5.96. Found: C, 58.30, H, 4.93, N, 5.94%. [Mn$_2$(**L3**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$: ESI-MS: 881 [Mn$_2$(C$_{52}$H$_{46}$N$_4$)$_2$](ClO$_4$)$_2$$^{2+}$, 1859 [Mn$_2$(C$_{52}H_{46}N_4$)$_2$](ClO$_4$)$_3$$^+$; CHN elemental analysis: calc. for Mn$_2$(C$_{52}$H$_{46}$N$_4$)$_2$(H$_2$O)$_4$(ClO$_4$)$_4$·5H$_2$O: C, 58.81; H, 5.22; N, 5.28. Found: C, 58.96, H, 5.20, N, 5.47%.

§ *Crystal data* for [Mn$_2$(**L2**)$_2$(H$_2$O)(CH$_3$OH)(CH$_3$CN)(ClO$_4$)] (CH$_3$CN)$_{0.5}$-(C$_4$H$_{10}$O)$_{0.5}$(ClO$_4$)$_3$: C$_{98}$H$_{99.5}$Cl$_4$Mn$_2$N$_{9.5}$O$_{18.5}$, $M = 1958.05$, monoclinic, space group $P2_1$, $a = 16.5520(6)$, $b = 12.3483(4)$, $c = 25.6368(11)$ Å, $V = 5072.2(3)$ Å^3, $Z = 2$, $D_c = 1.282$ Mg m^{-3}, λ(Cu-Kα) = 1.54184 Å, F$_{000}$ = 2040, $T = 143(2)$ K, 69145 reflections measured, 17982 unique, $R_{int} = 0.038$, $R = 0.0789$ ($I > 2\sigma(I)$) and 0.0865 (for all data), w$R_2 = 0.2249$ ($I > 2\sigma(I)$) and 0.2375 (for all data), Flack parameter: 0.020(5). CCDC 775970. *Crystal data* for [Mn$_2$(**L3**)$_2$(H$_2$O)$_4$](ClO$_4$)$_4$(H$_2$O)$_{1.75}$: C$_{104}$H$_{103.5}$Cl$_4$Mn$_2$N$_8$O$_{21.75}$, orthorhombic, space group $P2_12_12_1$, $V = 10173.65(15)$ Å^3, $Z = 4$, $D_c = 1.348$ Mg m^{-3}, λ(Cu-Kα) = 1.54184 Å, F$_{000}$ = 4302, $T = 293(2)$ K, 31704 reflections measured, 16631 unique, $R_{int} = 0.0335$, $R = 0.0612$ ($I > 2\sigma(I)$) and 0.0796 (for all data), w$R_2 = 0.1669$ ($I > 2\sigma(I)$) and 0.1799 (for all data), Flack parameter: 0.009(5). CCDC 775971.

1 For review, see: (a) J.-E. Bäckvall, in *Modern Oxidation Method*, VCH, Weinheim2004, Chapter 2.5; (b) E. N. Jacobsen, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone, G. Wilkinson, L. S. Hegedus, Pergamon, Oxford, 1995, Vol 12, Chapter 11.1.

2 A. Murphy, G. Dubois and T. D. P. Stack, *J. Am. Chem. Soc.*, 2003, **125**, 5250.

3 A. Murphy and T. D. P. Stack, *J. Mol. Catal. A: Chem.*, 2006, **251**, 78.

4 I. Garcia-Bosch, A. Company, X. Fontrodona, X. Ribas and M. Costas, *Org. Lett.*, 2008, **10**, 2095.

5 I. Garcia-Bosch, X. Ribas and M. Costas, *Adv. Synth. Catal.*, 2009, **351**, 348.

6 K. Nehru, S. J. Kim, I. Y. Kim, M. S. Seo, Y. Kim, S.-J. Kim, J. Kim and W. Nam, *Chem. Commun.*, 2007, 4623.

7 J. Rich, M. Rodríguez, I. Romero, L. Vaquer, X. Sala, A. Llobet, M. Corbella, M.-N. Collomb and X. Fontrodona, *Dalton Trans.*, 2009, 8117.

8 For review of polynuclear self-assemble metal complexes, see: (a) M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457; (b) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; (c) J.-M. Lehn, *Supramolecular Chemistry: Concept and perspectives*, VCH, Weinheim, 1995, Chapter 9.

9 (a) For earlier report on use of helicate for catalysis, see: H.-L. Kwong, H.-L. Yeung, W.-S. Lee and W.-T. Wong, *Chem. Commun.*, 2006, 4841; (b) C.-T. Yeung, H.-L. Yeung, C.-S. Tsang and W.-Y. Wong, *Chem. Commun.*, 2007, 5203; (c) H.-L. Yeung, K.-C. Sham, C.-S. Tsang, T.-C. Lau and H.-L. Kwong, *Chem. Commun.*, 2008, 3801.

10 (a) L.-E. Perrett-Aebi, A. von Zelewsky and A. Neels, *New J. Chem.*, 2009, **33**, 462; (b) L.-E. Perret-Aebi, A. von Zelewsky, C. Dietrich-Buchecker and J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2004, **43**, 4482.

11 (a) E. C. Constable, M. J. Hannon, A. J. Edwards and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1994, 2669; (b) E. C. Constable, M. J. Hannon and D. A. Tocher, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 230.

12 M. Düggeli, C. Goujon-Ginglinger, S. R. Ducotterd, D. Mauron, C. Bonte, A. von Zelewsky, H. Steockli-Evans and A. Neels, *Org. Biomol. Chem.*, 2003, **1**, 1894.

13 L. J. Charbonnière, A. F. Williams, U. Frey, A. E. Merbach, P. Kamalaprija and O. Schaad, *J. Am. Chem. Soc.*, 1997, **119**, 2488.

14 M. D. Ward, *Chem. Commun.*, 2009, 4487.