This article is published as part of the Dalton Transactions themed issue entitled:

Self-Assembly in Inorganic Chemistry

Guest Editors Paul Kruger and Thorri Gunnlaugsson

Published in issue 45, 2011 of Dalton Transactions



Image reproduced with permission of Mark Ogden

Articles in the issue include:

PERSPECTIVE:

Metal ion directed self-assembly of sensors for ions, molecules and biomolecules Jim A. Thomas Dalton Trans., 2011, DOI: 10.1039/C1DT10876J

ARTICLES:

Self-assembly between dicarboxylate ions and a binuclear europium complex: formation of stable adducts and heterometallic lanthanide complexes James A. Tilney, Thomas Just Sørensen, Benjamin P. Burton-Pye and Stephen Faulkner Dalton Trans., 2011, DOI: 10.1039/C1DT11103E

Structural and metallo selectivity in the assembly of [2 × 2] grid-type metallosupramolecular species: Mechanisms and kinetic control Artur R. Stefankiewicz, Jack Harrowfield, Augustin Madalan, Kari Rissanen, Alexandre N. Sobolev and Jean-Marie Lehn Dalton Trans., 2011, DOI: 10.1039/C1DT11226K

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research <u>www.rsc.org/dalton</u>

Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 12060

COMMUNICATION

Metallo-macrocycles with labile coordination sites through self assembly: Binuclear phenyl bridged bisbipyridine manganese complexes[†]

Kiu-Chor Sham, Guoli Zheng, Yinyan Li, Shek-Man Yiu and Hoi-Lun Kwong*

Received 23rd August 2011, Accepted 26th September 2011 DOI: 10.1039/c1dt11589h

Self assembly of phenyl bridged bisbipyridines with manganese perchlorate gave structurally different metallomacrocycles having *cis*-labile coordination sites which can catalyse olefin epoxidation with peracetic acid in good yield.

The chemistry of metallo-macrocycles has been of great interest. Various interesting architectures, for examples triangles, squares, rectangles, polygons, circle, *etc.*, have been synthesised¹⁻⁶ and the applications of them in molecular recognition, molecular machinery and catalysis have been investigated.^{7–14} Metallo-macrocycles can be constructed by metal complex formation using cyclic ligands^{15,16} or self assembly of suitable metal ions or metal complexes with ditopic ligands.^{17–19} Attempts have been made to functionalise the macrocycles by incorporating coordinatively unsaturated metal complexes into the macrocycles^{20–24} and it will be of interest if metallo-macrocycles inherently having labile coordination sites can be synthesised.

Bipyridine, an important binding motif in supramolecular chemistry, has been used in different supramolecular architectures including metallo-macrocycles²⁵⁻²⁷ and phenyl-bridged oligopyridines are known to form supramolecular architectures with metal ions.^{28,29} Herein, we report the synthesis of two manganese macrocycles with labile coordination sites and their application in catalytic epoxidation.

As shown in Scheme 1, phenyl-bridged bisbipyridine ligands L1 and L2 were synthesised through Pd catalysed Suzuki coupling of 1,3-phenyldiboronic acid with an achiral and a chiral bromo-bipyridine respectively.³⁰ Both ligands have a phenyl linker connecting two bipyridine units at the 5'-position. Stirring of L with one equivalent of manganese perchlorate salt in acetonitrile at room temperature gave a clear bright yellow solution. Air stable yellow complexes 1 and 2, from L1 and L2 respectively, were obtained by filtration of the precipitates after addition of diethyl ether and they were purified and then characterised by CHN elemental analysis[‡] and ESI-MS. In the mass spectra, peaks corresponded to singly charged species [Mn₂(L)₂(ClO₄)₃]⁺ were observed for both 1 and 2 suggesting the formation of bimetallic species.



Scheme 1 Reaction conditions: (i) BuLi, THF, -50 °C, 30 min; ZnCl₂, 0 °C, 2 h; 2,5-dibromopyridine, Pd(PPh₃)₄, 10 h (ii) Pd(PPh₃)₄, 1,3-phenyldiboronic acid, CH₃OH, H₂O, toluene, NaCO₃, 70 °C; (iii) AcOH, NH₄OAc, 100 °C(rv) Pd(PPh₃)₄, 1,3-phenyldiboronic acid, CH₃OH, H₂O, toluene, NaCO₃, 70 °C.

Crystallisation by diffusion of diisopropyl ether into an acetonitrile solution of 1 and diffusion of diethyl ether into a mixture of methanol and dichloromethane solution of 2 both gave single crystals that were suitable for X-ray crystal structural analysis.§ Complex 1, of formula $[Mn_2(L1)_2(H_2O)_4](ClO_4)_4$, crystallised in the monoclinic space group C2/c as a racemic mixture. Fig. 1 shows the ORTEP plot of one of its enantiomers, the *P*-1 form. The most significant feature of the structure is that it is a helical metallo-macrocycle having two labile manganese centres. Both centres are coordinated to two bipyridine units, one from each L1, with the remaining sites completed by water



Fig. 1 The ORTEP plot of cation of P-1 showing partial atom labeling. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, solvent molecules and counterions are omitted for clarity.

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR. E-mail: bhhoik@cityu.edu.hk; Fax: 852 2788 4706; Tel: 852 2788 7304

[†] Electronic supplementary information (ESI) available: Fig. 1S, and detail experimental procedures. CCDC reference numbers 829526 and 829527. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11589h

molecules. One of the water molecules is trans to the terminal pyridine with Mn–O distances 2.170(4) and 2.175(4) Å, and the other one is trans to the pyridine in the middle with Mn-O distances 2.140(4) and 2.167(4) Å. The manganese centres have distorted octahedral geometry with angles O1-Mn1-O2 and O3-Mn2-O4 equal to 83.1(2)° and 84.1(2)° respectively. The Mn-N distances are in the range 2.232(5)-2.286(5) Å and twisting between the rings of L1 allows L1 to act as a ditopic ligand. The bipyridine units are slightly non-planar [dihedral angle between the two pyridines: $5.9(8)-13.5(8)^{\circ}$ and the major twisting of L1 comes from the twisting between the bridging phenyl ring and bipyridine units [dihedral angle between the phenyl ring and the pyridines: 31.4(9)-46.9(8)°]. Complex 1 has a boat shape structure. The two manganese centres are located on the same side of a pocket with a metal-metal distance (Mn1-Mn2) equal to 9.714(9) Å. Interestingly, a perchlorate anion is captured inside the pocket by hydrogen bonding between the coordinated water molecules and the perchlorate anion (Fig. 2). The shortest distance between the oxygen of the perchlorate anion and hydrogen of coordinating water molecule is 1.926(6) Å.



Fig. 2 Capped stick drawing of the cation of *P*-1 with one of the perchlorate anions. The dotted lines show hydrogen bonding between the hydrogen of water molecules and oxygen of perchlorate.

Complex 2 crystallised in the orthorhombic space group C222(1). The crystal lattice contains two different helical molecules in a 1:1 ratio, M-2 of formula $[Mn_2(L2)_2(H_2O)_2]$ $(ClO_4)_2$ (ClO₄)₂ with both metal centres having Λ configuration and P-2 of formula $[Mn_2(L2)_2(CH_3OH)_2 (ClO_4)_2](ClO_4)_2$ with both metal centres having Δ configuration. Both P-2 and M-2 are metallo-macrocycles with labile coordination sites but their structures are significantly different from the boat shaped 1. They can be described as elliptical structures with manganese centres located at the two focuses of the ellipse. The labile coordination sites of the manganese centres, cached inside the cavity, are trans to terminal pyridines and point towards each other. Fig. 3 shows the ORTEP plots of *M*-2 as an example. It has a two fold symmetry with its C_2 axis perpendicular to the metal axis. The Mn–Mn distance is 7.884(3) Å. The angle O1–Mn1–O2 is 95.55(6)° and the Mn–N distances are in the range 2.260(2)–2.287(2) Å. The dihedral angles between pyridines are 9.1(1) and $12.7(1)^{\circ}$ and the dihedral angles between the bridging phenyl ring and bipyridine units are 27.7(1) and $29.0(1)^{\circ}$. In this structure, the labile sites of each metal are occupied by one water molecule and one perchlorate. But in the structure of P-2 (Fig. 1S^{\dagger}), the vacant sites are occupied either by two methanol molecules or two perchlorate anions. The C_2 axis of P-2 lies along the metal axis and the Mn-Mn distance is



Fig. 3 The ORTEP plots of cation of *M*-2 showing partial atom labeling. The thermal ellipsoids are drawn at the 30% probability level.

7.857(2) Å. The dihedral angles between pyridines are 6.0(1) and $10.1(1)^{\circ}$ and the dihedral angles between the bridging phenyl ring and bipyridine units are 29.2(1) and 29.6(1)°. In general, twisting of L2 in 2 is less when compared with L1 in 1.

With labile coordination sites, both 1 and 2 were explored as catalysts for the epoxidation of olefin.^{31–33} As depicted in Table 1, both metallo-macrocycles can catalyse epoxidation of olefin with peracetic acid (PAA) as oxidant. 1 and 2 are very different catalysts in terms of reactivity. With 1 mol% 1 as catalyst and 4 eq of PAA, epoxidation of styrene gave 100% conversion in 15 s (entry 1). The selectivity of reaction can be improved by adding Na₂HPO₄ as an additive which minimises a background epoxide ring opening reaction. 1 also gives excellent performance with electron deficient substrates like 4-chlorostyrene and 4-fluorostyrene giving 100% conversion and more than 90% selectivity (Entries 4 and 5). It is less selective towards an aliphatic substrate like cyclooctene (Entry 9). Comparing with our previously reported manganese double stranded helicates which also have cis-labile coordination sites, 1 is a more active catalyst.³⁴ We believe a Lewis acid activated peracid species is responsible for the oxygen atom transfer.³⁵ With its labile sites cached, 2 needs a much longer reaction time (6 h) to give full conversion of substrate (Entry 10). Unlike a related mononuclear complex which gives up to 46% ee in epoxidation of styrene,36 no enantioselectivity has been observed with pseudoracemic 2. At this point we do not know if the difference in reactivity between 1 and 2 is the result of steric effect or the different configuration of the manganese. But the relatively rigid and well defined coordination of these supramolecular systems will allow us to study the effect of structure and metal configuration on the reactivity in manganese catalysed epoxidations in the future.

In summary, we have developed the synthesis of two new coordinatively unsaturated manganese macrocycles 1 and 2 using a self assembly approach. Although the ligand backbone structures are very similar, 1 and 2 are structurally quite different, one with *mer*-configurations and the other having *fac*-configurations. Their potential application in epoxidation of olefins has been explored and both are found to be active catalysts but with different reactivities. Further experiments are underway to understand the effect of structure and metal configuration on reactivity and to explore the potential of these macrocycles as bimetallic catalysts for other organic transformations.

Table 1 Catalytic epoxidation by manganese complexes^a

	all	kene Catalyst, I	$\xrightarrow{\text{PAA, Na_2HPO_4, r.t.}}_{\text{CH_3CN}}$	epoxide	
Entry	Catalyst	Substrate	Conversion ^b (%)	$\operatorname{Yield}^{b,c}(\%)$	Time (s)
1 ^d 2	1		100 100	67 94	15 15
3		Me	100	67	15
4		F	98	90	15
5		CI	100	96	15
6		Br	100	86	15
7			100	87	15
8		$\bigcirc \bigcirc \bigcirc$	100	>99	15
9			100	52	15
10	2		95	90	6 h
11		CI CI	54	91	6 h
12		\bigcirc	97	97	6 h
13		\bigcirc	100	68	6 h

^{*a*} Reaction conditions: alkene (0.05 mmol), **1** or **2** (5×10^{-4} mmol), PAA (0.2 mmol), Na₂HPO₄ (0.84 mmol), CH₃CN (0.10 ml) was used as solvent. ^{*b*} Determined by GC-FID. ^{*c*} GC yield based on conversion. ^{*d*} Reactions were carried out without addition of Na₂HPO₄.

Acknowledgements

The work described in this paper was supported by a grant from the University Grants Committee of the Hong Kong Special Administrative Region, China (Project No. [AoE/P-03/08]) and the City University of Hong Kong SRG grant (CityU 7002607).

Notes and references

 $[Mn_2(L1)_2(H_2O)_4](ClO_4)_4$: ESI-MS: m/z 986 $[Mn(C_{26}H_{18}N_4)_2](ClO_4)^+$, 1181, $[Mn_2(C_{26}H_{18}N_4)_2](ClO_4)_3^+$; CHN elemental analysis: calc. for $Mn_2(C_{26}H_{18}N_4)_2(H_2O)_4(ClO_4)_4$ ·3H₂O: C, 43.84; H, 3.72; N, 7.86; Found: C, 43.89, H, 3.63, N, 7.88%. $[Mn_2(L2)_2](H_2O)(MeOH)(ClO_4)_4$: ESI-MS: 1558.4 $[Mn_2(C_{40}H_{38}N_4)_2](ClO_4)_3^+$; CHN elemental analysis: calc. for $Mn_2(C_{46}H_{42}N_4)_2(H_2O)(MeOH)(ClO_4)_4$ ·2H₂O-0.5CH₂Cl₂: C, 54.82; H, 4.91; N, 6.27. Found: C, 54.77, H, 4.91, N, 6.35%. § *Crystal data* for 1: C₅₉H_{55.5}Cl₄Mn₂N_{11.5}O_{20.5}, *M* = 1505.33, monoclinic, space group *P2/c*, *a* = 31.0270(7), *b* = 14.2965(2), *c* = 34.680(1) Å, *V* = 13864.4(6) Å³, *Z* = 8, *D_c* = 1.442 mg m⁻³, λ (Cu-Kα) = 1.54184 Å, *F*₀₀₀ = 6176, *T* = 113 K, 45889 reflections measured, 12297 unique, *R_{int}* = 0.0410, *R* = 0.0797 (*I* > 2 σ (*I*)) and 0.0966 (for all data), wR₂ = 0.2443 (*I* > 2 σ (*I*)) and 0.2661 (for all data), CCDC 829527. **2**: C_{165.8}H_{168.6}C₁₂₁Mn_NI₁₆O₃₆, *M* = 3925.58, orthorhombic, space group *P222*1, *a* = 24.4376(3), *b* = 29.2923(3), *c* = 25.2535(3) Å, *V* = 18077.3(4) Å³, *Z* = 4, *D_c* = 1.442 mg m⁻³, λ (Cu-Kα) = 1.54184 Å, *F*₀₀₀ = 8082, *T* = 173 K, 61660 reflections measured, 12940 unique, *R_{int}* = 0.0472, *R* = 0.0944 (*I* > 2 σ (*I*)) and 0.1141 (for all data), wR₂ = 0.2577 (*I* > 2 σ (*I*)) and 0.2717 (for all data), Flack parameter: 0.005(9), CCDC 829526.

- 1 P. J. Stang and B. Olenyuk, Acc. Chem. Res., 1997, 30, 502.
- 2 M. Fujita, Chem. Soc. Rev., 1998, 27, 417.
- 3 S. Leininger, B. Olenyuk and P. J. Stang, Chem. Rev., 2000, 100, 853.
- 4 S. R. Seidel and P. J. Stang, Acc. Chem. Res., 2002, 35, 972.
- 5 G. F. Swieger and T. J. Malefetse, *Coord. Chem. Rev.*, 2002, **225**, 91.
- 6 F. Würthner, C.-C. You and C. R. Saha-Möller, *Chem. Soc. Rev.*, 2004, 33, 133.
- 7 H. J. Yoon and C. A. Mirkin, J. Am. Chem. Soc., 2008, 130, 11590.
- 8 S. J. Lee and W. Lin, Acc. Chem. Res., 2008, 41, 521.
- 9 G. Li, M. Yu, J. Ni, T. Liu, E. Sheng and Y. Cui, Angew. Chem., Int. Ed., 2008, 47, 1245.
- 10 S.-S. Sun, C. L. Stern, S. T. Nguyen and J. T. Hupp, J. Am. Chem. Soc., 2004, 126, 6314.
- 11 R. Lin, J. H. K. Yip, K. Zhang, L. L. Koh, K.-Y. Wong and K. P. Ho, J. Am. Chem. Soc., 2004, 126, 15852.
- 12 S. J. Lee, A. Hu and W. Lin, J. Am. Chem. Soc., 2002, 124, 12948.
- 13 R. V. Stone, K. D. Benkstein, S. Bélanger, J. T. Hupp, I. A. Guzei and A. L. Rheingold, *Coord. Chem. Rev.*, 1998, 171, 221.
- 14 M. Fujita, J. Yazaki and K. Ogura, J. Am. Chem. Soc., 1990, 112, 5645.
- 15 S. Akine, S. Sunaga, T. Taniguchi, H. Miyazaki and T. Nabeshima, *Inorg. Chem.*, 2007, 46, 2959.
- 16 L. Salmon, P. Thuéry, E. Rivière, S. Miyamoto, T. Yamato and M. Ephritikhine, New J. Chem., 2006, 30, 1220.
- 17 C. S. Campos-Fernández, B. L. Schottel, H. T. Chifotides, J. K. Bera, J. Bacsa, J. M. Koomen, D. H. Russell and K. R. Dunbar, J. Am. Chem. Soc., 2005, 127, 12909.
- 18 P. H. Dinolfo, M. E. Williams, C. L. Stern and J. T. Hupp, J. Am. Chem. Soc., 2004, 126, 12989.
- 19 L. J. Childs, N. W. Alcock and M. J. Hannon, Angew. Chem., Int. Ed., 2002, 41, 4244.
- 20 R. M. Haak, M. M. Belmonte, E. C. Escudero-Adán, J. Benet-Buchholz and A. W. Kleij, *Dalton Trans.*, 2010, **39**, 593.
- 21 R. N. Loy and E. N. Jacobsen, J. Am. Chem. Soc., 2009, 131, 2786.
- 22 C. G. Oliveri, N. C. Gianneschi, S. T. Nguyen, C. A. Mirkin, C. L. Stern, Z. Wawrzak and M. Pink, J. Am. Chem. Soc., 2006, 128, 16286.
- 23 N. C. Gianneschi, S. T. Nguyen and C. A. Mirkin, J. Am. Chem. Soc., 2005, 127, 1644.
- 24 M. Marty, Z. Clyde-Watson, L. J. Twyman, M. Nakash and J. K. M. Sanders, *Chem. Commun.*, 1998, 2265.
- 25 C. Kaes, A. Katz and M. W. Hosseini, Chem. Rev., 2000, 100, 3553.
- 26 O. Mamula, A. von Zelewsky and G. Bernardinelli, Angew. Chem. Int. Ed., 1998, 3, 290.
- 27 B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. V. Dorsselaer, B. Kneisel and D. Fenske, J. Am. Chem. Soc., 1997, 119, 10956.
- 28 L.-E. Perret-Aebi, A. von Zelewsky, C. Dietrich-Buchecker and J.-P. Sauvage, Angew. Chem., Int. Ed., 2004, 43, 4482.
- 29 E. C. Constable, M. J Hannon and D. A. Tocher, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 230.
- 30 L.-E. Perret-Aebi and A. von Zelewsky, Synlett, 2002, 773.
- 31 G. D. Faveri, G. Ilyashenko and M. Watkinson, *Chem. Soc. Rev.*, 2011, 40, 1722.
- 32 A. Murphy and T. D. P. Stack, J. Mol. Catal. A: Chem., 2006, 251, 78.
- 33 A. Murphy, G. Dubois and T. D. P. Stack, J. Am. Chem. Soc., 2003, 125, 5250.
- 34 K.-C. Sham, H.-L. Yeung, S.-M. Yiu, T.-C. Lau and H.-L. Kwong, *Dalton Trans.*, 2010, **39**, 9469.
- 35 I. Garcia-Bosch, A. Company, X. Fontrodona, X. Ribas and M. Costas, Org. Lett., 2008, 10, 2095.
- 36 L. Gómez, I. Garcia-Bosch, A. Company, X. Sala, X. Fontrodona, X. Ribas and M. Costas, *Dalton Trans.*, 2007, 5539.