ChemComm
www.rsc.org/chemcomm

Site-specific ligation of anthracene-1,8-dicarboxylates to an Mn$_{12}$ core: a route to the controlled functionalisation of single-molecule magnets†

Mirko Pacchioni,[a,b] Andrea Cornia,*[a] Antonio C. Fabretti,[a] Laura Zobbi,[a] Daniele Bonacchi,[b] Andrea Caneschi,[b] Guillaume Chastanet,[b] Dante Gatteschi[b] and Roberta Sessoli*[b]

[a] *Dipartimento di Chimica, INSTM and Università di Modena e Reggio Emilia, via G. Campi 183, 41100 Modena, Italy. E-mail: acornia@unimore.it; Fax: +39-59-373543; Tel: +39-59-2055032*

[b] *Dipartimento di Chimica, INSTM and Università di Firenze, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy. E-mail: roberta.sessoli@unifi.it; Fax: +39-55-4573372; Tel: +39-55-4573268*

Received (in Cambridge, UK) 26th July 2004, Accepted 24th August 2004
First published as an Advance Article on the web 1st October 2004

A novel single-molecule magnet of the Mn$_{12}$ family, [Mn$_{12}$O$_{12}$(O$_2$CC$_6$H$_5$)$_8$(L)$_4$(H$_2$O)$_4$]·8CH$_2$Cl$_2$, has been synthesised by site-specific ligand exchange using a tailor-made dicarboxylate (L^{2-}), which leads to selective occupation of axial binding sites.

Single-molecule magnets (SMMs) are clusters of transition-metal ions that exhibit a magnetic hysteresis cycle under cryogenic conditions and thus offer a molecular approach to nanoscale materials for magnetic data storage.[1] The archetypal SMM is Mn$_{12}$ acetate, a mixed-valence complex with formula [Mn$_{12}$O$_{12}$(OAc)$_{16}$(H$_2$O)$_4$]·2AcOH·4H$_2$O (**1**) and idealised S_4 symmetry, comprising a central [Mn$^{IV}_4$O$_4$] cubane-like moiety held within a nonplanar ring of eight Mn^{III} ions by eight μ$_3$-O^{2-} ions (Fig. 1).[2] The attempts to enhance the potential of Mn$_{12}$ clusters for information storage have led to the synthesis of a number of derivatives, demonstrating that the Mn$_{12}$O$_{12}$ core easily undergoes both ligand-exchange and redox processes.[3] Current chemical work in the field of SMMs focusses on obtaining a clean and controllable reactivity of the clusters with two main objectives. The first one is to organise SMMs into dimers, trimers or higher aggregates of weakly-interacting clusters.[1b] The second one is to promote the binding of clusters to surfaces as a prerequisite for single-molecule addressing using scanning probe microscopies.[4] In a previous article, we reported that a Mn$_{12}$ derivative containing sixteen 16-(acetylthio)-hexadecanoate ligands forms disordered films on Au(111).[4a] To favour the formation of ordered arrays, orientational restraints to surface binding must be introduced using, for instance, site-specific ligand replacement. Carboxylate groups in axial position (A and B in Fig. 1) are in general more prone to substitution by less basic incoming ligands as compared with their equatorial counterparts (C).[3a] However, the synthesis of mixed-ligand derivatives often results in partial substitution of both axial and equatorial positions.[3b]

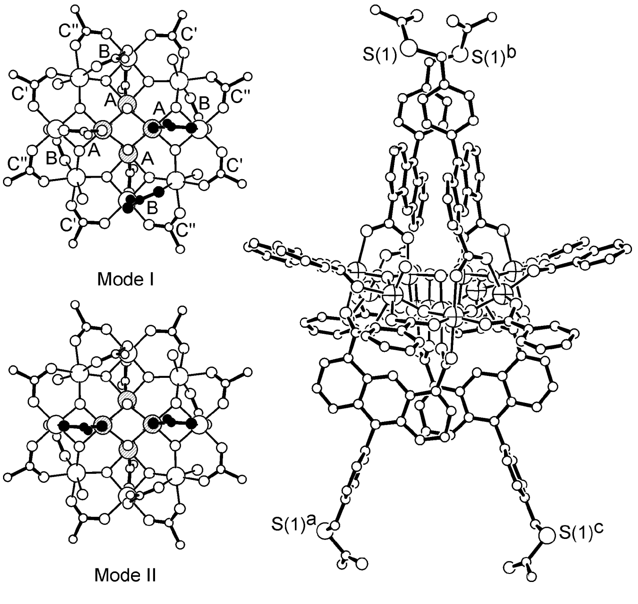
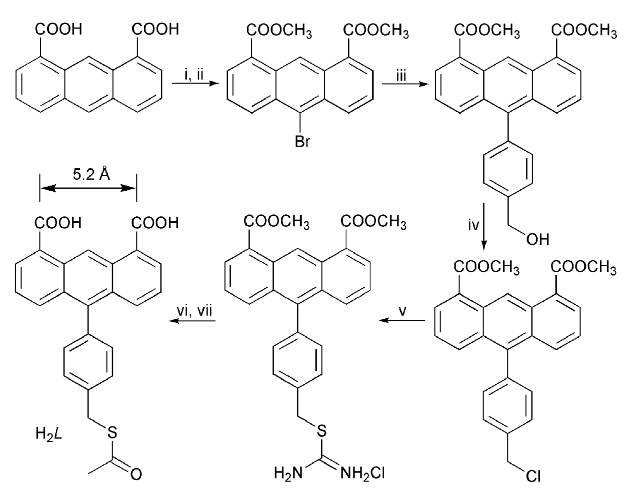


Fig. 1 (Left) Sketched structure of **1** highlighting the different types of acetate ligands and the bridging modes I and II discussed in the text (large circles = Mn, medium circles = O, small circles = C; hydrogen atoms omitted); the four central Mn^{IV} are depicted in light gray. (Right) Molecular structure of **3** (large cross-hatched circles = Mn, large circles = S, medium circles = O, small circles = C; hydrogen atoms omitted).

We have now found that dicarboxylate ligands may greatly improve the selectivity of ligand substitution, thus providing an efficient route to the controlled functionalisation of Mn$_{12}$ SMMs. Derivatives of anthracene-1,8-dicarboxylic acid, in particular, fit the geometrical requirements needed for axial ligation according to either mode I (involving Mn^{III}–Mn^{III} and Mn^{III}–Mn^{IV} pairs, d = 5.0 Å‡) or mode II (involving two Mn^{III}–Mn^{IV} pairs, d = 5.2 Å‡) in Fig. 1. In addition, the ligands can be easily functionalised by exploiting the reactivity of the 10-position of anthracene. The ligand 10-(4-acetylsulfanylmethyl-phenyl)-anthracene-1,8-dicarboxylic acid (H$_2$L), has been synthesised as outlined in Scheme 1. Reaction of [Mn$_{12}$O$_{12}$(O$_2$CC$_6$H$_5$)$_{16}$(H$_2$O)$_4$] (**2**)[3c] with 4 equivalents of H$_2$L in CH$_2$Cl$_2$ followed by careful layering of *n*-hexane affords large, black crystals of [Mn$_{12}$O$_{12}$(O$_2$CC$_6$H$_5$)$_8$(L)$_4$(H$_2$O)$_4$]·8CH$_2$Cl$_2$ (**3**·8CH$_2$Cl$_2$) showing a very weak diffracting power.§ Nevertheless, a X-ray structure investigation at 100 K¶



Scheme 1 Preparation of the H$_2$L ligand. Reagents and conditions: (i) Br$_2$, CCl$_4$, reflux 96 h; (ii) H$_2$SO$_4$, MeOH, reflux, 16 h, total yield 71%; (iii) 4-(hydroxymethyl)phenylboronic acid, PdCl$_2$(PPh$_3$)$_2$, Na$_2$CO$_3$, toluene, N$_2$, reflux, 6 h, 99%. (iv) SOCl$_2$, CH$_2$Cl$_2$, 97%; (v) thiourea, THF–EtOH, reflux, 24 h, 93%; (vi) KOH in H$_2$O, N$_2$, reflux, 3 h, 96%; (vii) acetic anhydride, pyridine, N$_2$, room temperature, overnight, 90%.

---

† Electronic supplementary information (ESI) available: Fig. A: Hystereses curves recorded at different temperature at 5 kOe min^{-1} on an oriented single crystal of **3**. Fig. B: First derivative of the hysteresis curve recorded at 2.1 K. See http://www.rsc.org/suppdata/cc/b4/b411320a/

DOI: 10.1039/b411320a

This journal is © The Royal Society of Chemistry 2004

revealed that axial benzoates have been replaced by four L^{2-} ligands (Fig. 1). The two carboxylate groups provided by each L^{2-} ligand bridge a Mn^{III}–Mn^{IV} and a Mn^{III}–Mn^{III} pair, corresponding to bridging mode I. Peripheral ligation is completed by eight benzoate ligands on equatorial sites and by four water molecules, which coordinate every second Mn^{III} ion. Clearly, because of the similar pK_a values for benzoic acid and anthracene-1,8-dicarboxylic acid,[5] site-specific replacement is likely to be driven by factors other than ligand basicity, such as entropy gain from chelate ring formation. As a result of the arrangement of the L^{2-} ligands, the four thioacetyl groups are located above and below the disk-like $[Mn_{12}O_{12}(O_2CC_6H_5)_8]$ moiety and convey to the molecule a remarkably anisotropic shape.

The field dependence of the magnetisation has been recorded at different temperatures on an oriented single crystal of **3** (the field was applied parallel to the *c*-axis), showing the appearance of magnetic hysteresis below 4 K. At this temperature, a saturation value of 19 μ_B is reached at 120 kOe which is close to the value expected for an $S = 10$ ground spin state ($\sim$20 μ_B). Below 4 K, stepped hystereses appear indicating the thermally assisted quantum tunnelling of the magnetisation which is linked to the slow relaxation of the system (see ESI†). The separation between adjacent steps is 4.7 kOe, hence slightly larger than that observed in **1** (4.5 kOe).

This relaxation has been further investigated on a polycrystalline sample with ac susceptibility measurements. Fig. 2 reports the out-of-phase susceptibility χ'' as a function of temperature in the frequency range 0.1–10 kHz. A predominant peak is observed around 6 K with a shouldering at low temperature (around 3 K) indicating the presence of two relaxation processes. The low temperature one represents about 10% of the whole behaviour. The deconvolution of the curves with two Gaussians allows to plot the relaxation rate, $2\pi\nu$ as function of the inverse blocking temperature $1/T_{max}$ (that is, the temperature at which χ'' reaches a maximum at each frequency). The Arrhenius plots thus obtained (inset of Fig. 2) lead to the dynamic parameters of the system.‖ For the high temperature dynamics, $\tau_0 = 2.6(2) \times 10^{-9}$ s and $\Delta/k_B = 65.2(4)$ K, while for the low temperature dynamics $\tau_0 = 1.6(2) \times 10^{-10}$ s and $\Delta/k_B = 41.8(5)$ K. The values of the energy barrier Δ and of the step separation in the hysteresis loops are typical of Mn_{12} clusters ($\tau_0 = 2.1 \times 10^{-7}$ s and $\Delta/k_B = 61$ K in **1**[1a]), showing that the characteristic SMM behavior is retained after the ligand-exchange reaction. In addition, a slightly enhanced magnetic anisotropy is observed in **3** as compared with **1**. However, a higher Δ is associated with a lower τ_0, revealing a more efficient spin–phonon coupling. The fast-relaxing phase may be attributed to defect molecules containing less than four L^{2-} ligands.

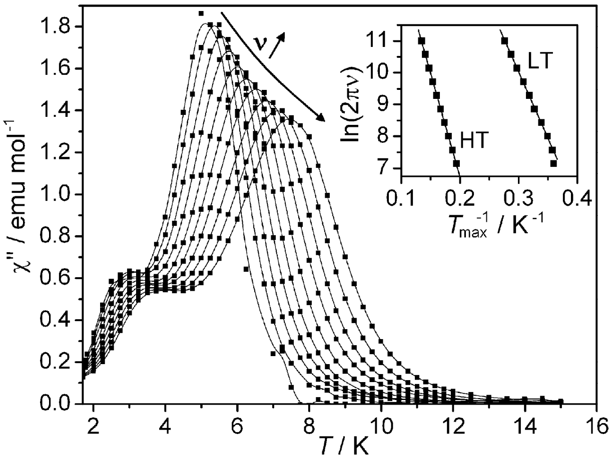


Fig. 2 Temperature dependence of the out-of-phase susceptibility for a polycrystalline sample of **3**. The inset presents the Arrhenius plots of the relaxation rate as function of inverse blocking temperature.

In conclusion, we have developed a new route for the site-specific functionalisation of Mn_{12} clusters. Our results also suggest that surfaces functionalised with anthracene-1,8-dicarboxylates may exhibit a strong affinity for Mn_{12} clusters, thus providing a simple pathway toward arrays of SMMs oriented with their easy axes perpendicular to the surface.[4d–f]

We acknowledge Prof. V. Albano and Prof. M. Monari (Dip. di Chimica "G. Ciamician", Università di Bologna) for help in X-ray experiments, and Dr G. Lusvardi (Dip. di Chimica, INSTM and Univ. di Modena e Reggio Emilia) for X-EDS data. Work supported by the Human Potential Program RTN-QUEMOLNA (FP6-504880), Italian MIUR (PRIN & FIRB projects) and German DFG (SPP-1137).

Notes and references

‡ *d* is the distance between carboxylate carbon atoms.

§ *Synthesis*: H_2L (0.0312 g, 0.0725 mmol) was added to **2**[3c] (0.0548 g, 0.0181 mmol) dissolved in CH_2Cl_2 (4.6 mL). The resulting solution was stirred for 24 h and layered with *n*-hexane. The black crystals obtained after some weeks were collected on a glass frit, washed with *n*-hexane and dried in vacuum (0.1–0.2 mmHg, 75 min). Yield 0.055 g, (85%) (Found: C, 52.0; H, 3.1; S, 3.2. Calc. for **3**: C, 52.0; H, 3.1; S, 3.6%). X-EDS (single crystal): Mn/S atomic ratio = 3.20(15).

¶ *Crystal data*: $C_{164}H_{128}Cl_{16}Mn_{12}O_{52}S_4$, $M_r = 4285.53$, tetragonal, space group $I4_1/amd$, $Z = 4$, $a = 26.2604(12)$, $c = 27.4733(13)$ Å, $U = 18946(2)$ Å^3, $T = 100(2)$ K, $D_c = 1.502$ g cm^{-3}, D_c (298 K) = 1.383 g cm^{-3} (based on $U = 20569(6)$ Å^3), D_{exp}(298 K) = 1.40(4) g cm^{-3}, $F(000) = 8656$, μ(Mo-Kα) = 1.116 mm^{-1}, 68467 reflections measured on a Bruker AXS SMART 2000 diffractometer ($2\theta \leqslant 47.34°$) and corrected for absorption, 3758 independent reflections ($R_{int} = 0.0752$) used for refinement on F_o^2; Mn_{12} clusters heavily disordered around D_{2d}-symmetry sites; L^{2-} ligand refined with half occupancy, all non-hydrogen atoms treated anisotropically, with the exception of those belonging to the $PhCH_2SC(O)CH_3$ moiety and to the CH_2Cl_2 molecule; hydrogen atoms added in idealised positions; restraints applied to the geometry and atomic displacement parameters of the L^{2-} ligand; heavily-disordered $CH_2SC(O)CH_3$ moiety constrained to have the same geometry found in ethanedithiol diacetate;[6] current R values $R1 = 0.1136$ [$I > 2\sigma(I)$] and $wR2 = 0.3464$ (all data) for 351 parameters and 72 restraints; largest peak and hole in the final ΔF map: 1.180 and -0.774 e Å^{-3}; residual electron density peaks on mirror planes suggest additional disorder due to a small fraction of L^{2-} ligand displaying bridging mode II. CCDC 246075. See http://www.rsc.org/suppdata/cc/b4/b411320a/ for crystallographic data in .cif or other electronic format.

‖ $\tau = \tau_0\exp(\Delta/k_BT)$ with $\tau = (2\pi\nu)^{-1}$.

1 (*a*) D. Gatteschi and R. Sessoli, *Angew. Chem., Int. Ed.*, 2003, **42**, 268; (*b*) W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson and G. Christou, *Nature*, 2002, **416**, 406.

2 A. Cornia, A. C. Fabretti, R. Sessoli, L. Sorace, D. Gatteschi, A. L. Barra, C. Daiguebonne and T. Roisnel, *Acta Crystallogr., Sect. C*, 2002, **58**, m371.

3 (*a*) N. E. Chakov, W. Wernsdorfer, K. A. Abboud, D. N. Hendrickson and G. Christou, *Dalton Trans.*, 2003, **11**, 2243; (*b*) J. T. Brockman, K. A. Abboud, D. N. Hendrickson and G. Christou, *Polyhedron*, 2003, **22**, 1765; (*c*) R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804.

4 (*a*) A. Cornia, A. C. Fabretti, M. Pacchioni, L. Zobbi, D. Bonacchi, A. Caneschi, D. Gatteschi, R. Biagi, U. Del Pennino, V. De Renzi, L. Gurevich and H. S. J. Van der Zant, *Angew. Chem., Int. Ed.*, 2003, **42**, 1645; (*b*) D. Ruiz-Molina, M. Mas-Torrent, J. Gómez, A. I. Balana, N. Domingo, J. Tejada, M. T. Martínez, C. Rovira and J. Veciana, *Adv. Mater.*, 2003, **15**, 42; (*c*) M. Cavallini, F. Biscarini, J. Gomez-Segura, D. Ruiz and J. Veciana, *Nano Lett.*, 2003, **3**, 1527; (*d*) J. S. Steckel, N. S. Persky, C. R. Martinez, C. L. Barnes, E. A. Fry, J. Kulkarni, J. D. Burgess, R. B. Pacheco and S. L. Stoll, *Nano Lett.*, 2004, **4**, 399; (*e*) A. Nait Abdi, J. P. Bucher, P. Rabu, O. Toulemonde, M. Drillon and Ph. Gerbier, *J. Appl. Phys.*, 2004, **95**, 7345; (*f*) G. G. Condorelli, A. Motta, I. L. Fragalà, F. Giannazzo, V. Raineri, A. Caneschi and D. Gatteschi, *Angew. Chem., Int. Ed.*, 2004, **43**, 4081.

5 R. Golden and L. M. Stock, *J. Am. Chem. Soc.*, 1972, **94**, 3080.

6 H. Fleischer and D. Schollmeyer, *Acta Crystallogr., Sect. E*, 2001, **57**, o330.