A homospin iron(II) single chain magnet†‡

Szymon W. Przybylak,[a] Floriana Tuna,*[a] Simon J. Teat[b] and Richard E. P. Winpenny*[a]

Received (in Cambridge, UK) 7th November 2007, Accepted 29th January 2008
First published as an Advance Article on the web 22nd February 2008
DOI: 10.1039/b717277j

Synthetic, structural and magnetic studies of a new Fe(II) single chain magnet are reported.

There is much current interest in slow relaxation in magnetic nanosystems such as single-molecule magnets (SMMs)[1] and single chain magnets (SCMs),[2] since they show unusual physical properties, such as quantum tunneling of the magnetization[3] and quantum phase interference[4] that are not observed in bulk magnets. Investigations have also been inspired by the idea that they could be used as high-density information storage devices.[4] Theoretical studies have also suggested that SMMs are appropriate systems to be used as quantum bits in quantum computing.[5]

The occurrence of the slow relaxation of the magnetization in a one dimensional polymer was first observed in 2001.[6] The compound—a heterospin chain: $[Co(hfac)_2\{NIT(C_6H_4OMe)\}]$ (hfac = hexafluoro-acetylacetonate; NIT(R): 2-(4′-R)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide)—illustrated for the first time a theoretical model designed by Glauber in 1963 for anisotropic Ising systems.[7] Only a few examples of single-chain magnets are currently known. The majority are heterospin systems containing at least two different spin carriers, either a d-metal ion and a radical, or two different paramagnetic d-block ions—achieved either through being heterometallic or heterovalent.[2,8a] Homospin SCMs are rare. Only three examples are known to date, and all contain Co(II): a homometallic Co(II) azide-bridged chain in which the coupling is ferromagnetic,[9] and an SCM containing canted Co(II) spins bridged by phosphonates,[10] and a carboxylate bridged system where again the interaction is ferromagnetic.[11]

The vast majority of SMMs contain Mn^{III}, due to the high anisotropy of this ion.[12] Recently SMMs containing other metal centers have been discovered, and we wished to extend work from Perlepes and co-workers[13] and Oshio *et al.*,[14] who have shown that Fe(II) can be used to produce SMMs. We reasoned that chemistry developed to make a dodecanuclear nickel SMM,[15] and an isostructural cobalt(II) wheel[16] should work with iron(II). Particularly inspirational was Perlepes observation of isostructural $\{Ni_9\}$,[17] $\{Co_9\}$[18] and $\{Fe_9\}$[13] cages with dipyridylketone.

Anaerobic reaction of $Fe(O_2CMe)_2$ with 6-chloro-2-pyridinol (Hchp) (2 : 1 molar ratio) at 130 °C, followed by ligand sublimation and recrystallization from MeCN, yielded orange single crystals. Structural analysis§ shows a complex of formula $[Fe_9(chp)_{12.4}(O_2CMe)_{5.6}]_n$ **1**, with an asymmetric unit containing nine Fe(II) centers. The structure can be described as containing two iron “butterflies” (Fe1, Fe2, Fe3, Fe4 and Fe6, Fe7, Fe8, Fe9) which are linked through an additional Fe5 atom (Fig. 1). All bond lengths are consistent with Fe^{II}. The mean planes defined by the four Fe^{II} centers of each butterfly are perpendicular to one another. The ligands attached to the first butterfly show some disorder, with partial occupancy by a mixture of chp : acetate (0.4 : 0.6) of the site occupied by O3. There are two μ_3-oxygen sites in the first butterfly; one (O6) comes from a chp ligand, while the second is associated with the disordered ligand site. In the second $\{Fe_4\}$ butterfly there is only one μ_3-oxygen (O11), again from chp, while there is also a 3.21-bridging acetate (O23 and O22, Harris notation[19]). Each Fe^{II} site is six-coordinate, but with variable coordination spheres: three (Fe1, Fe4, Fe6) are bound to three N- and three O-donors; two (Fe2, Fe8) are bound to one N- and five O-donors; three (Fe3, Fe5, Fe7) are bound only to O-donors; the final site (Fe9) is bound to two N- and four O-donors. There are three different coordination modes of the chp ligands and two different modes for acetates (Scheme 1).

The first butterfly unit is bound to five 2.21-chp ligands and two 3.31 ligands—one of which is a chp, the other disordered between chp : acetate. The second unit butterfly contains four 2.21-chp ligands, one 3.31 chp and one 3.21-acetate. The butterflies are linked through Fe5 and two 3.21-acetates (O16, O17, O18, O19) and two 3.31-chp ligands (including O7 and O13). Four 2.11-bridging acetates are also found and a 1.11 chp ligand is bound to Fe1. The disorder in the ligands raises the possibility that the magnetic behaviour observed could be due to a spin glass, however the measurements made are clearly inconsistent with such an interpretation (see below).

A one-dimensional polymer grows *via* inversion centers between the butterflies (Fig. 2); the result is that almost planar octametallic regions lie between each Fe5 site, at which point the polymer twists 90° before there is another octametallic fragment, but this time derived from the other butterfly in the asymmetric unit. The result is a helical polymer of Fe^{II} centers (Fig. 2 and Fig. S1‡). The chains are isolated with the shortest metal–metal separation between chains being around 11 Å. The helical structure is unusual, and very different from the cyclic structures that this chemistry produced with Ni^{II} and Co^{II}.[15,16]

Given the small number of Fe^{II} cages in the literature, it is difficult to predict how the magnetic behaviour relates to structure; we assumed that the angles at the bridging O-centres

---

[a] *School of Chemistry, The University of Manchester, Oxford Road, Manchester, UK M13 9PL. E-mail: richard.winpenny@manchester.ac.uk*
[b] *Advanced Light Source, Lawrence Berkeley National Lab, 1 Cyclotron Road, mail stop 2-400, Berkeley, CA 94720, USA*

‡ Electronic supplementary information (ESI) available: details of crystallographic determination and further details of the magnetic characterisation. See DOI: 10.1039/b717277j

† All reagents were used as received from Aldrich. The solvents were dried and distilled prior use. All the operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques.

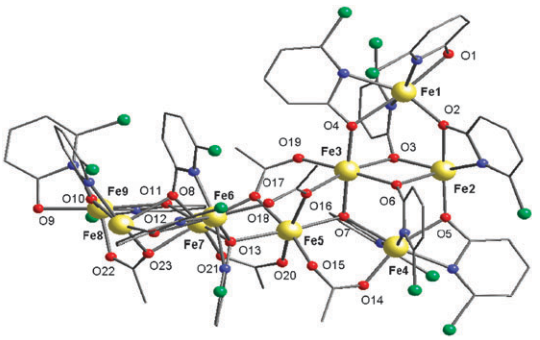
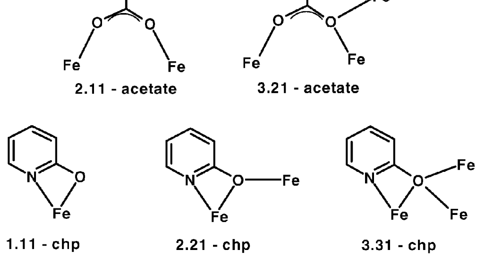


Fig. 1 The asymmetric unit in the structure of **1** in the crystal.

are relevant. The angles at O-atoms that bridge between wingtip Fe sites of the butterfly and body sites are obtuse, varying from 114 to 123° and these angles are larger than the angles at the O-atoms that link the body–body contact. Therefore for each butterfly we can assume the spins at wingtip and body sites cancel. The angles involving Fe5 are more acute to body-sites (95–98°) than to wing-tip sites (113°), so we assume Fe5 aligns parallel with the former, giving two sub-lattices, with the body Fe sites (Fe2, Fe3, Fe7 and Fe8) and Fe5 in one sub-lattice, and the wing-tip sites (Fe1, Fe4, Fe6, Fe9) in the second. The magnetic properties would then be due to ferromagnetic exchange between very anisotropic $S = 2$ $\{Fe_9\}$ repeat units.

Variable-temperature (2–300 K) DC magnetic susceptibility measurements were performed on powdered crystals of **1** under applied magnetic fields of 0.1, 0.5, 1, 5 and 10 kG (Fig. S2‡). The $\chi_M T$ value at room temperature is *ca.* 29.2 cm^3 K mol^{-1} (1 T field), which is larger than the spin-only value (27 cm^3 K mol^{-1}) expected for nine non-interacting metal ions with $S = 2$ and $g = 2.00$. This is ascribed to the orbital contribution of Fe^{II} in an octahedral ligand field.[20] With decreasing temperature, $\chi_M T$ decreases to a minimum value of 15.2 cm^3 K mol^{-1} at 18 K, after which it increases to reach a field-dependent maximum (58.6 cm^3 K mol^{-1} at 0.1 kG field; Fig. 3 and Fig. S2) before dropping again at very low temperatures due to saturation effects and/or magnetic anisotropy. The decrease of $\chi_M T$ above 18 K is mainly due to the spin–orbit coupling of the Fe(II) centers, but may also indicate predominant antiferromagnetic exchange. By contrast, the magnetic behaviour below 18 K suggests dominant ferromagnetic interactions leading to a non-zero ground state. A scaling procedure[8b] of the χ_MT data of **1** (Fig. S3) clearly indicates a linear regime characteristic of Ising 1D systems. The ln($\chi_M T$) *versus* $1/T$ plot increases linearly between 13 and 6 K, with an energy gap of 9.0 K. Below this temperature, saturation effects become important and produce a deviation from the linear regime.



Scheme 1 Coordination modes of the ligands in **1**.

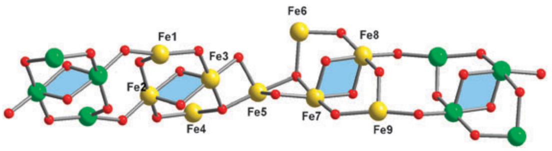


Fig. 2 The Fe^{II}–O core within the polymeric strands in **1**. The Fe sites in one asymmetric unit are yellow, and in neighbouring units green.

Variable field (0–70 kG) magnetization experiments on **1** were performed at temperatures of 1.8, 2 and 4 K. The magnetization does not saturate up to a field of 70 kG (Fig. S4‡), due to the strong anisotropy of the material. It is thus impossible to assign a 'spin-ground' state. The magnetization recorded at 1.8 K reveals the presence of a hysteresis loop (280 G coercive field, inset Fig. 3). Below 2.7 K, there is a divergence between zero-field cooled and field cooled magnetization (inset Fig. S4‡).

To probe the magnetization relaxation in **1**, zero-field ac susceptibility measurements between 1.8 and 10 K were carried out at frequencies of 1, 14, 104, 480 and 1200 Hz with a 1 G ac field (Fig. 4). Below 5.5 K, both the in-phase (χ'_M) and out-of-phase (χ''_M) components of the ac susceptibility are strongly frequency dependent. This result precludes any tri-dimensional ordering. Moreover, the relative variation of the temperature of the maximum of χ''_M with respect to the frequency is measured by a parameter $\phi = (\Delta T_{max}/T_{max})/\Delta(\lg \nu) = 0.13$, which is in the range of normal superparamagnets[11,21] and excludes the possibility of a spin glass.[22]

The magnetization relaxation times obtained from ac experiments were fitted to the Arrhenius equation $\tau = \tau_0 \exp(\Delta E/k_B T)$, where τ is the relaxation time, ΔE is the energy barrier for the relaxation of the magnetization and τ_0 is the pre-exponential factor. From the least-squares fit, ΔE was found to be 61 K (42.4 cm^{-1}) and $\tau_0 = 1.5 \times 10^{-11}$ s. The ΔE value obtained here is larger than that of the two reported iron(II) SMMs.[13,14] Previous SCMs containing Fe(II) are limited to two Fe^{II}–Fe^{III} heterospin polymers, whose energy barriers (27 K[23a] and 19 K,[23b] respectively) are also substantially smaller than that of **1**.

At fixed temperatures between 2.9 and 3.4 K and zero applied magnetic field, we obtained semicircle Cole–Cole diagrams (χ''_M *versus* χ'_M), which could be fitted by a generalized Debye model, with the α parameters in the range

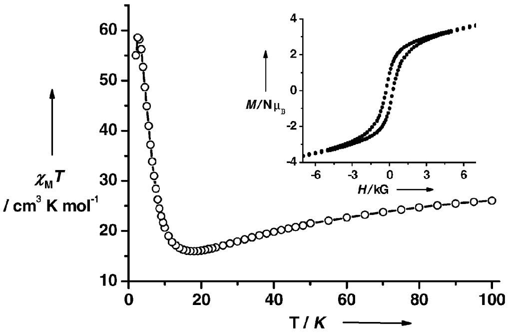


Fig. 3 Temperature dependence of $\chi_M T$ for a polycrystalline sample of **1** measured at 0.1 kG. In the inset: Hysteresis loop measured at 1.8 K.

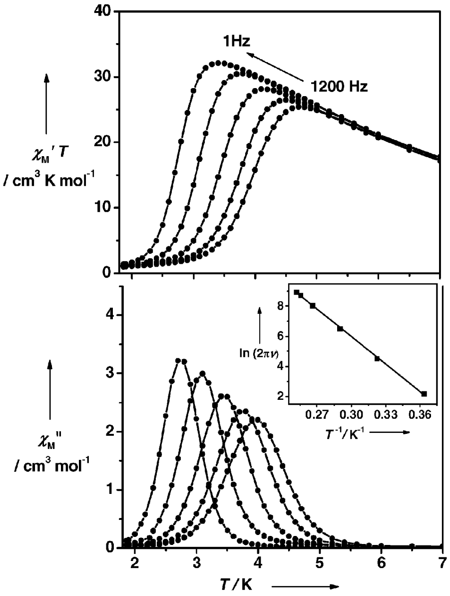


Fig. 4 Temperature dependence of the in-phase and out-of-phase susceptibilities of **1** measured with an ac field of 1 G oscillating at frequencies of 1–1200 Hz. In the inset the temperature dependence of the relaxation time extracted from ac measurements.

0.31–0.36, which indicates a moderate distribution of relaxation time (Fig. S5‡).[24] The energy barrier extracted from the *ac* susceptibility data, ΔE, is significantly larger than that obtained in the scaling procedure of the $\chi_M T$ curve, Δ_ξ, suggesting that the relaxation mechanism in this single chain magnet cannot be described by a simple Glauber model;[24] additional contributions associated with the relaxation of the individual nonanuclear units must be taken into account. Such a mechanism has been already proposed in the literature.[2b,d]

To the best of our knowledge, compound **1** is the first example of a Fe(II) homospin SCM, and has a higher energy barrier to loss of magnetization than Fe(II) SMMs[13,14] or other homospin SCMs.[9–11] Further experiments are underway to quantify the different contributions to this behaviour.

This work was supported by the EPSRC (UK). S.W.P. thanks EC for a Marie Curie Intra-European fellowship (MCIF-CT-2003-502191).

Notes and references

1. Fe(OAc)$_2$ [99%] (0.696 g; 4.00 mmol) and 6-chloro-2-pyridinol [*chpH*] (1.037 g; 8.00 mmol) were heated in a Schlenk tube with cooling finger at 130 °C for 15 minutes. The excess of ligand was eliminated by sublimation (*ca.* 1 h) under vacuum. After cooling to rt, 50 ml of MeCN was added. The resulting orange solution was filtered and allowed to crystallize at rt. X-ray quality yellow single crystals of **1** were obtained after 2 days. Yield 0.25 g (23%). Elemental analysis calcd (%) for $C_{73.2}H_{54}Cl_{12.4}Fe_9N_{12.4}O_{23.6}$: C 36.23, H 2.24, N 7.16, Cl 18.10, Fe 20.71; found: C 35.69, H 2.50, N 7.15, Cl 18.22, Fe 20.59.

Magnetic measurements

Magnetic measurements were performed in the temperature range 1.8–300 K, using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

§ Crystal data for $C_{77.6}H_{60.6}Cl_{12.4}Fe_9N_{14.6}O_{23.6}$, **1**.2.2 MeCN.: triclinic, $P\bar{1}$, a = 13.7988(12), b = 13.9589(12), c = 26.605(20) Å, α = 93.344(2), β = 90.670(2), γ =109.256(2)°, V = 4827.0(7) Å^3, M = 2517.43, D_c = 1.732 g cm^{-1}, Z = 2, $R1$ = 0.0473 for 13 167 reflections. Data collection, structure solution and refinement used SHELXL.[25]

1 (*a*) D. Gatteschi and R. Sessoli, *Angew. Chem., Int. Ed.*, 2003, **42**, 268–297; (*b*) C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.*, 2007, **129**, 2754–2755.

2 (*a*) L. Pogani, C. Sangregorio, R. Sessoli and D. Gatteschi, *Angew. Chem., Int. Ed.*, 2005, **44**, 5817–5821; (*b*) K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi and R. Sessoli, *J. Am. Chem. Soc.*, 2006, **128**, 7947–7956; (*c*) R. Lescouezec, J. Vaissermann, C. Ruiz-Perez; F. Lloret, R. Carrasco, M. Julve, M. Verdaguer, Y. Dromzee, D. Gatteschi and W. Wernsdorfer, *Angew. Chem., Int. Ed.*, 2003, **42**, 1483–1486; (*d*) M. Ferbinteanu, H. Miyasaka, W. Wernsndorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon and R. Clérac, *J. Am. Chem. Soc.*, 2005, **127**, 3090–3099; (*e*) L. M. Toma, R. Lescouezec, J. Pasan, C. Ruiz-Perez, J. Vaissermann, J. Cano, R. Carrasco, W. Wernsdorfer, F. Lloret and M. Julve, *J. Am. Chem. Soc.*, 2006, **128**, 4842–4853.

3 (*a*) L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli and B. Barbara, *Nature*, 1996, **383**, 145–147; (*b*) W. Wernsdorfer, N. Aliaga-Alcade, D. N. Hendrickson and G. Christou, *Nature*, 2002, **416**, 406–409.

4 W. Wernsdorfer and R. Sessoli, *Science*, 1999, **284**, 133–135.

5 M. N. Leuenberger and M. N. Loss, *Nature*, 2001, **410**, 789–793.

6 A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, *Angew. Chem., Int. Ed.*, 2001, **40**, 1760–1763.

7 R. J. Glauber, *J. Math. Phys.*, 1963, **4**, 294–307.

8 (*a*) C. Coulon, H. Miyasaki and R. Clérac, *Struct. Bond.*, 2006, **122**, 163–206; (*b*) C. Coulon, R. Clerac, L. Lecren. W. Wernsdorfer and H. Miyasaka, *Phys. Rev. B: Condens. Matter, Mater. Phys.*, 2004, **69**, 132408.

9 T.-F. Liu, D. Fu, S. Gao, Y.-Z. Zhang, H.-L. Sun, G. Su and Y.-J. Liu, *J. Am. Chem. Soc.*, 2003, **125**, 13976–13977.

10 Z.-M. Sun, A. V. Prosvirin, H.-H. Zhao, J.-G. Mao and K. R. Dunbar, *J. Appl. Phys.*, 2005, **97**, 10B305/1–10B305/3.

11 Y.-Z. Zheng, M.-L. Tong, W.-X. Zhang and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2006, **45**, 6310–6314.

12 G. Aromí and E. K. Brechin, *Struct. Bond.*, 2006, **122**, 1–67.

13 A. K. Boudalis, B. Donnadieu, V. Nastopoulos, J. M. Clemente-Juan, A. Mari, Y. Sanakis, J.-P. Tuchagues and S. P. Perlepes, *Angew. Chem., Int. Ed.*, 2004, **43**, 2266–2270.

14 H. Oshio, N. Hoshino, T. Ito and M. Nakano, *J. Am. Chem. Soc.*, 2004, **126**, 8805–8812.

15 H. Andres, R. Basler, A. J. Blake, E. K. Brechin, C. Cadiou, G. Chaboussant, C. M. Grant, H.-U. Güdel, S. G. Harris, M. Murrie, S. Parsons, C. Paulsen, F. Semadini, V. Villar, W. Wernsdorfer and R. E. P. Winpenny, *Chem.–Eur. J.*, 2002, **8**, 4867–4876.

16 E. K. Brechin, O. Cador, A. Caneschi, C. Cadiou, S. G. Harris, S. Parsons, M. Vonci and R. E. P. Winpenny, *Chem. Commun.*, 2002, 1860–1861.

17 G. S. Papaefstathiou, A. Escuer, R. Vicente, M. Font-Bardia, X. Solans and S. P. Perlepes, *Chem. Commun.*, 2001, 2414–2415.

18 G. S. Papaefstathiou, S. P. Perlepes, A. Escuer, R. Vicente, M. Font-Bardia and X. Solans, *Angew. Chem., Int. Ed.*, 2001, **40**, 884–886.

19 Harris notation describes the binding mode as [X.Y1Y2Y3...Y*n*], where X is the overall number of metals bound by the whole ligand, and each value of Y refers to the number of metal atoms attached to the different donor atoms. See: R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2000, 2349–2356.

20 O. Kahn, *Molecular Magnetism*, Wiley-VCH, 1993, p. 37.

21 E. Pardo, R. Ruiz-Garcia, F. Lloret, J. Faus, M. Julve, Y. Journaux, M. A. Novak, F. S. Delgado and C. Ruiz-Perez, *Chem.–Eur. J.*, 2007, **13**, 2054–2066.

22 ϕ = 0.01 is a typical value for a spin glass. For details, see J. A. Mydosh, *Spin Glasses: An Experimental Introduction*, Taylor & Francis, London, 1993.

23 (*a*) T. Kajiwara, M. Nakano, Y. Kaneko, S. Takaishi, T. Ito, M. Yamashita, A. Igashira-Kamiyama, H. Nojiri, Y. Ono and N. Kojima, *J. Am. Chem. Soc.*, 2005, **127**, 10150–10151; (*b*) H. Tanaka, T. Kajiwara, Y. Kaneko, S. Takaishi and M. Yamashita, *Polyhedron*, 2007, **26**, 2105–2109.

24 (*a*) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, **9**, 341–351; (*b*) S. M. Aubin, Z. Sun, L. Pardi, J. Krzysteck, K. Folting, L. J. Brunel, A. L. Rheingold and D. N. Hendrickson, *Inorg. Chem.*, 1999, **38**, 5329–5340.

25 *SHELX-PC Package*, Bruker Analytical X-ray Systems, Madison, WI, 1998.