

# Single-molecule magnets: control by a single solvent molecule of Jahn–Teller isomerism in $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{H}_2\text{O})_4]$

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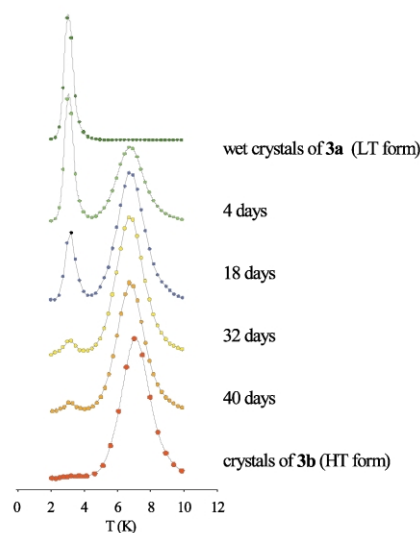
**Faster- and slower-relaxing versions of the title  $\text{Mn}_{12}$  compound have been obtained in pure forms that crystallize in the same space group and differ only in the identity of one lattice solvent molecule; solvent loss causes isomerization from the faster- to the slower-relaxing form.**

The mesoscale between classical and quantum science is a very important area of research, especially with the current miniaturization of devices to sizes where quantum effects are important. In nanomagnetism, single-molecule magnets (SMMs) represent a molecular approach to single-domain nanoscale magnetic particles,<sup>1</sup> with many advantages over classical magnetic particles, including monodispersity, crystallinity, true solubility, and a shell of organic ligands that can be varied by standard chemistry methods. SMMs straddle the classical/quantum interface in displaying magnetization hysteresis, a classical property of the macroscale, as well as quantum tunnelling of magnetization (QTM)<sup>2</sup> and quantum phase interference,<sup>3</sup> the properties of the microscale. The first and most studied SMMs are the family of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  ( $\text{Mn}_{12}$ ) complexes.

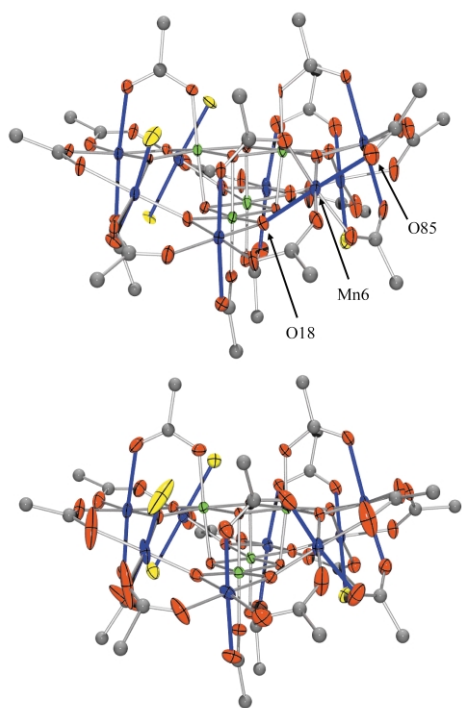
The present work concerns a recognized property of  $\text{Mn}_{12}$  SMMs, their existence in two forms: (i) the normal, “slower-relaxing” or higher-temperature (HT) form, characterized by frequency-dependent out-of-phase ac magnetic susceptibility ( $\chi_M''$ ) signals in the 6–8 K range (at a 1000 Hz ac frequency) and an effective barrier to relaxation ( $U_{\text{eff}}$ ) of 60–75 K; and (ii) a “faster-relaxing” or lower-temperature (LT) form with  $\chi_M''$  signals in the 2–4 K range and  $U_{\text{eff}}$  values approximately half those of the HT forms.<sup>4</sup> A study of crystal structures and magnetic properties of  $\text{Mn}_{12}$  complexes had previously identified the LT form to result from an abnormally oriented Jahn–Teller (JT) elongation axis at one high-spin Mn(III) centre, which we termed Jahn–Teller isomerism.<sup>4</sup> We previously reported JT isomers of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-Me})_{16}(\text{H}_2\text{O})_4]\cdot\text{C}_6\text{H}_4\text{-}p\text{-Me-CO}_2\text{H}$  (**2a**) and  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-Me})_{16}(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$  (**2b**) in ~90% isomeric purity.<sup>5</sup> The two forms crystallized in different space groups with different solvent content, and we broadly concluded that JT isomers were stabilized by the very different environments around the  $\text{Mn}_{12}$  molecules. Our understanding of JT isomerization has now been improved by (i) isolation of JT isomers of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{H}_2\text{O})_4]$  (**3**) in pure form and in the same space group; (ii) the discovery that a JT isomerization can occur; and (iii) the first attainment of hysteresis loops for single crystals of the LT form.

$[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{H}_2\text{O})_4]\cdot\text{CH}_2\text{Cl}_2\cdot\text{MeNO}_2$  (**3a**; LT form) is obtained on recrystallization of **3** from  $\text{CH}_2\text{Cl}_2\text{-MeNO}_2$ , and its structure has been previously reported and shows one abnormally oriented Mn(III) JT axis.<sup>4</sup> **3a** loses lattice solvent rapidly on removal from the mother liquor, and we explored any concomitant change in magnetic properties by ac susceptibility measurements. The results are summarized in

Fig. 1. Crystals of **3a** wet with mother liquor give a single  $\chi_M''$  signal in the 2–4 K range, confirming a 100% pure LT sample. A number of crystals were then removed from the mother liquor to initiate solvent loss, and the  $\chi_M''$  of single crystals was monitored at regular time intervals corresponding to increasing extent of solvent loss. There is a progressive decrease in the LT signal and a concomitant increase in a signal in the 6–8 K region characteristic of a HT species. After 40 days, the conversion is essentially complete. Samples that had lost solvent for >40 days analyzed as solvent-free. Loss of solvent  $\text{CH}_2\text{Cl}_2$  and  $\text{MeNO}_2$  molecules thus causes conversion of the LT form to a HT form, almost certainly by re-orientation of the abnormally oriented JT axis to a normal position. Unfortunately, crystals of **3a** that have lost solvent no longer diffract, so the JT orientations could not be confirmed directly. However, recrystallization of crude **3**, or of **3a** that had completely lost solvent, from  $\text{CH}_2\text{Cl}_2\text{-MeCN}$  gives  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{H}_2\text{O})_4]\cdot\text{CH}_2\text{Cl}_2\cdot\text{MeCN}$  (**3b**), which is a HT form with a  $\chi_M''$  signal at essentially the same position as that of dried **3a** (Fig. 1). The structure of **3b**<sup>†</sup> is crystallographically isomorphous with that of **3a**<sup>‡</sup>, except that (i) all Mn(III) JT axes are in normal orientations (Fig. 2); and (ii) there is an MeCN in **3b** at the position of the  $\text{MeNO}_2$  in **3a**; the  $\text{CH}_2\text{Cl}_2$  molecule is in the same position in both structures. We thus conclude that the conversion of the LT complex **3a** to a HT form on loss of solvent molecules is due to a JT isomerization involving re-orientation of the abnormal JT axis to a normal position. As can be seen in Fig. 2, the JT axis at Mn(III) atom Mn6 of **3a**,



**Fig. 1** Time dependent out-of-phase ( $\chi_M''$ ) ac magnetic susceptibility signal at 1000 Hz for **3a** showing conversion from the fast-relaxing (LT) form to a slow-relaxing (HT) form as solvent is lost. For comparison, the signal for fast-relaxing **3b** is also shown.



**Fig. 2** ORTEP representations as PovRay plots of complexes **3a** (top) and **3b** (bottom); for clarity, the Bu<sup>t</sup> groups have been omitted. Colour scheme: green Mn(IV); blue Mn(III); red O; yellow H<sub>2</sub>O; grey C. The elongated bonds defining the JT axes are coloured blue.

abnormally oriented towards oxide ion O18, is oriented normally in **3b**.

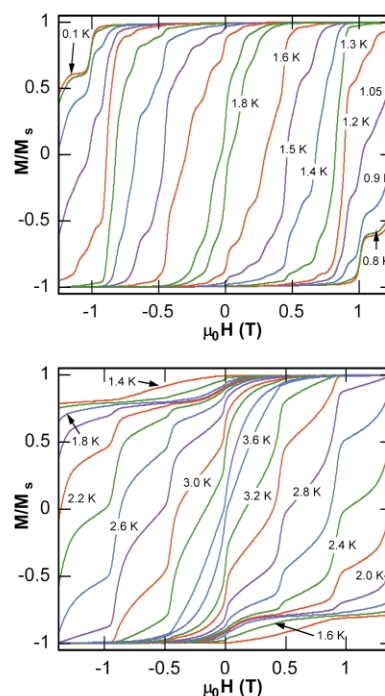
The barriers ( $U_{\text{eff}}$ ) to magnetization relaxation for **3a** and **3b** were determined down to 1.8 K from the temperatures of their  $\chi_M''$  peak maxima at different frequencies; data were collected in the 4.0 to 1488 Hz range. Relaxation data at < 1.8 K were obtained from dc magnetization decay vs. time measurements on single crystals using a micro-SQUID apparatus. The AC and DC data for **3a** and **3b** were combined, and the resulting  $\ln(1/\tau)$  vs.  $1/T$  data were fit to the Arrhenius equation, where  $\tau$  is the relaxation time. The fits gave  $U_{\text{eff}} = 62$  K and  $1/\tau_0 = 4.2 \times 10^7$  s<sup>-1</sup> for the HT form:

$$\ln(1/\tau) = \ln(1/\tau_0) - U_{\text{eff}}/kT$$

**(3b)**, and  $U_{\text{eff}} = 42$  K and  $1/\tau_0 = 4.5 \times 10^9$  s<sup>-1</sup> for the LT form **(3a)**. These values are typical of HT and LT JT isomers.<sup>4,5</sup>

Magnetization vs. DC field scans were performed on aligned single crystals of **3a** and **3b** using a micro-SQUID apparatus, and the resulting hysteresis loops are shown in Fig. 3. Both **3a** and **3b** display hysteresis with coercivities that vary with temperature, as expected for SMMs. The hysteresis loops are not smooth but instead show the steps that are the signature of quantum tunneling of magnetization (QTM). The loops for **3b** are typical of those of HT forms. The field separation between steps ( $\Delta H$ ) is proportional to the axial anisotropy (zero-field splitting) parameter,  $D$ . Measurement of the step positions for **3b** yielded an average  $\Delta H$  of  $\sim 0.45$  T (4.5 kG), giving  $|D|/g \approx 0.21$  cm<sup>-1</sup>, or  $D \approx -0.42$  cm<sup>-1</sup> for  $g = 2$ . This is typical of a HT form of Mn<sub>12</sub>. The single-crystal hysteresis loop of complex **3a** is the first for a LT form and exhibits an unusual richness of steps. This is not as expected for a well isolated ground state spin, for which the step separation is simply related to  $D$ . Our preliminary conclusion is that there is a very low-lying first excited state, and that some steps are due to tunnelling transitions between  $M_s$  levels of the ground and excited state spin manifolds, which overlap. This model is being used to simulate the hysteresis loops, and is also consistent with other dc and ac data on LT Mn<sub>12</sub> species.<sup>5,6</sup>

In summary, pure JT isomers have been prepared that crystallize in the same space group and differ only in the identity



**Fig. 3** Magnetization hysteresis loops (top) for complex **3a** in the 1.8–0.04 K range, and (bottom) for complex **3b** in the 4.4–1.4 K range, both at a 0.004 T s<sup>-1</sup> sweep rate.

of one solvent molecule of crystallization at one position. Stabilization of the LT form by such a tiny difference in the Mn<sub>12</sub> environment demonstrates a very small energy difference between JT isomers. Loss of solvent from crystals of **3a** causes isomerization from the LT to the HT form, supporting the latter to be the thermodynamically more stable form.

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## Notes and references

† Crystal data for complex **3b**: C<sub>99</sub>H<sub>189</sub>Cl<sub>2</sub>Mn<sub>12</sub>NO<sub>48</sub>; Mr = 2891.73, triclinic,  $P1$ ,  $a = 15.7567(4)$ ,  $b = 16.7633(5)$ ,  $c = 27.1828(9)$  Å,  $\alpha = 77.444(1)$ ,  $\beta = 77.490(1)$ ,  $\gamma = 78.315(1)^\circ$ ,  $Z = 2$ ,  $U = 6750.17$  Å<sup>3</sup>,  $T = 134$  K,  $R = 5.52\%$ ,  $R_w = 5.73\%$ . The CH<sub>2</sub>Cl<sub>2</sub> and MeCN were slightly disordered. Some Bu<sup>t</sup> groups were also disordered, but their disorder was well resolved. All H atoms were included, as fixed atom contributors riding on their parent atom, in calculated positions, except for the H<sub>2</sub>O ligands, which were located. CCDC 212145. See <http://www.rsc.org/suppdata/cc/b3/b306246e/> for crystallographic data in .cif or other electronic format.

‡ Crystal data of previously published complex **3a** for comparison:<sup>4</sup> C<sub>98</sub>H<sub>189</sub>Cl<sub>2</sub>Mn<sub>12</sub>NO<sub>50</sub>; Mr = 2911.71, triclinic,  $P\bar{1}$ ,  $a = 15.814(2)$ ,  $b = 16.42(2)$ ,  $c = 27.434(3)$  Å,  $\alpha = 76.900(1)$ ,  $\beta = 78.220(1)$ ,  $\gamma = 78.210(1)^\circ$ ,  $Z = 2$ ,  $U = 6699.08$  Å<sup>3</sup>,  $T = 99$  K,  $R = 7.25\%$ ,  $R_w = 5.63\%$ .

- G. Christou, D. Gatteschi, D. N. Hendrickson and R. Sessoli, *MRS Bulletin*, 2000, **25**, 66 and references therein.
- J. R. Friedman, M. P. Sarachik, J. Tejada and R. F. Ziolo, *Phys. Rev. Lett.*, 1996, **76**(20), 3830; L. Thomas, L. Lioni, R. Ballou, D. Gatteschi, R. Sessoli and B. Barbara, *Nature*, 1996, **383**, 145; J. Tejada, R. F. Ziolo and X. X. Zhang, *Chem. Mater.*, 1996, **8**, 1784; S. M. J. Aubin, N. R. Gilley, L. Pardi, J. Krzystek, M. W. Wemple, L. C. Brunel, M. B. Marple, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1998, **120**, 4991; D. N. Hendrickson, G. Christou, H. Ishimoto, J. Yoo, E. K. Brechin, A. Yamaguchi, E. M. Rumberger, S. M. J. Aubin, Z. Sun and G. Aromí, *Polyhedron*, 2001, **20**, 1479.
- W. Wernsdorfer and R. Sessoli, *Science*, 1999, **284**, 133.
- Z. Sun, D. Ruiz, N. R. Dilley, M. Soler, J. Ribas, K. Folting, M. B. Maple, G. Christou and D. N. Hendrickson, *Chem. Commun.*, 1999, 1973.
- S. M. J. Aubin, Z. Sun, H. J. Eppley, E. M. Rumberger, I. A. Guzei, K. Folting, P. K. Gantzel, A. L. Rheingold, G. Christou and D. N. Hendrickson, *Inorg. Chem.*, 2001, **40**, 2127; S. M. J. Aubin, Z. Sun, H. J. Eppley, E. M. Rumberger, I. A. Guzei, K. Folting, P. K. Gantzel, A. L. Rheingold, G. Christou and D. N. Hendrickson, *Polyhedron*, 2001, **20**, 1139.
- Details for **3a** will be provided in the full paper.