The origin of the second relaxation process in the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ single-molecule magnets: 'Jahn–Teller isomerism' in the $[Mn_{12}O_{12}]$ core

Ziming Sun,[a] Daniel Ruiz,[a] Neil R. Dilley,[b] Mönica Soler,[c] Joan Ribas,[d] Kirsten Folting,[c] M. Brian Maple,[b] George Christou*[c] and David N. Hendrickson*[a]

[a] *Department of Chemistry-0358, University of California at San Diego, La Jolla, CA 92093-0358, USA. E-mail: dhendrickson@ucsd.edu*
[b] *Department of Physics, University of California at San Diego, La Jolla, CA 92093-0358, USA*
[c] *Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405-7102, USA. E-mail: christou@indiana.edu*
[d] *Department of Chemistry, University of Barcelona, 08028-Barcelona, Spain*

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The origin of the second, faster relaxation process in Mn_{12} molecules has been identified as a different relative orientation of the Jahn–Teller elongation axes of the Mn^{III} ions, which we have termed 'Jahn–Teller isomerism'.

Single-molecule magnets are of great current interest because they represent nanoscale magnetic particles of a sharply defined size that offer, amongst other things, the potential of access to the ultimate high-density information storage devices.[1–3] They also provide excellent examples of species exhibiting quantum tunnelling of magnetization.[4–6] Out-of-phase ac magnetic susceptibility signals (χ_M'') and magnetization hysteresis loops are characteristic of SMMs, whose properties result from a large spin (S) ground state and negative magnetic anisotropy. The first SMM reported was $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ **1**; ($8Mn^{III}$, $4Mn^{IV}$), with $S = 10$ and a zero-field splitting parameter (D) of $-0.5\ cm^{-1}$, and Friedman *et al.*[4] subsequently reported steps on its magnetization hysteresis plots indicative of quantum tunnelling. Since then, variation of the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ carboxylate group and/or solvent molecules of crystallization have been shown to have significant effects on the hysteresis plots and the quantum tunnelling behaviour.[2,7,8]

An interesting observation is the presence often of two different χ_M'' signals for a given complex, which we have assigned as due to two polymorphs in the sample with slightly different environments about the Mn_{12} molecules.[7,8] For $[Mn_{12}O_{12}(O_2CC_6H_4Me\text{-}4)_{16}(H_2O)_4]$ **2**, the **2**·$HO_2CC_6H_4Me$-4 (space group $C2/c$) and **2**·$3H_2O$ ($I2/a$) forms have χ_M'' peaks in the 2–4 and 4–7 K ranges, respectively.[8] The *precise* molecular origin of the differing magnetic behaviour has not been clear, however, but we herein report this as due to the existence of isomeric forms of the $[Mn_{12}O_{12}]$ core involving different relative orientations of Mn^{III} Jahn–Teller distortion axes. We have termed this new effect 'Jahn–Teller isomerism'.

The complexes $[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(H_2O)_4]$ **3** and $[Mn_{12}O_{12}(O_2CC_6H_4F\text{-}2)_{16}(H_2O)_4]$ **4** were prepared as described elsewhere.[7a] The χ_M'' *vs.* T behaviour of **4** (Fig. 1) shows that it is a mixture of the 'low-temperature' (LT) and 'high-temperature' (HT) species in an approximate 12 : 1 ratio, with peaks in the 2–3 and 4–6 K ranges, respectively. Complex **3** shows an essentially identical plot.[8b] The structure of **3**·CH_2Cl_2·CH_3NO_2† appears typical of this class of molecule but closer examination [Fig. 2(a)] reveals that one Mn^{III} Jahn–Teller (JT) elongation axis is abnormally oriented, equatorially rather than axially. As a result, the JT axis contains an oxide ion, O(18), a situation which is highly unusual; JT elongation axes usually orient as to avoid the strong Mn^{III}–O^{2-} bonds, normally the shortest bonds about the metal. The usually observed JT orientations are as in the HT molecule **2**·$3H_2O$ [Fig. 2(b)] *i.e.* all axial. In contrast, close examination of the structure of **2**·$HO_2CC_6H_4Me$-4 shows that this LT form of **2** also has an abnormally oriented JT axis, whereas **1** and other Mn_{12} species with HT χ_M'' peaks show the normal JT orientation. Thus, we conclude that the abnormal orientation of a Mn^{III} JT axis is the

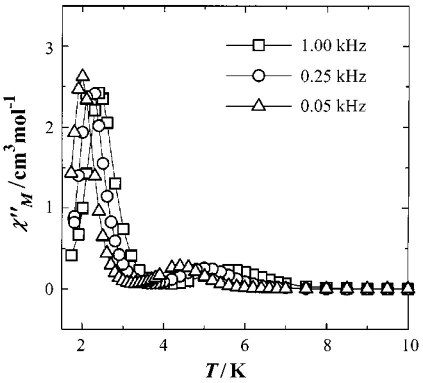

Fig. 1 Plot of the out-of-phase (χ_M'') *vs.* T behaviour of **4** at the indicated ac oscillation frequencies.

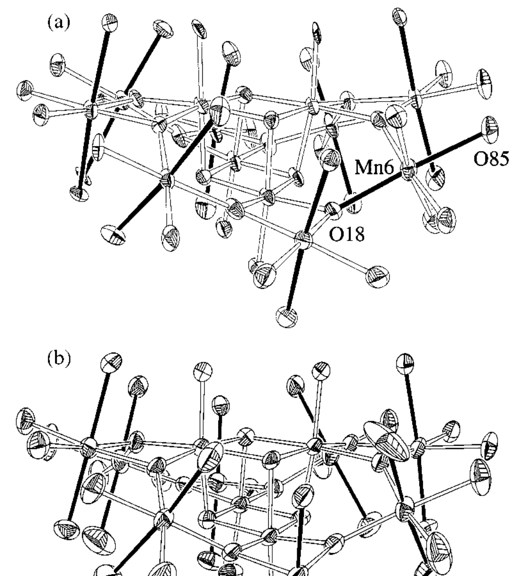

Fig. 2 The core of complex **3** emphasizing the abnormal Jahn–Teller orientation (a), and the core of **2**·$3H_2O$ showing the normal orientation (b). For **3**: Mn(6)–O(18) 2.073(7) Å, Mn(6)–O(85) 2.160(8) Å, other bonds to Mn(6) 1.873(8)–1.969(8) Å, other Mn^{III}–O^{2-} bonds 1.845(7)–1.919(7) Å.

origin of the LT χ_M'' peak.‡ This will alter the orientation of the singly occupied d_{z^2} orbital, and the influence on the relaxation rate could thus be due to a change in (i) the ground state S value, (ii) the separations to low-lying excited states, (iii) the molecular D value, or (iv) a combination of these. Further work is in progress to address this point.

The different temperatures for the LT and HT χ_M'' peaks correspond to faster and slower relaxation rates, respectively. The two separate processes were quantified for complex **4** by using the ac χ_M'' *vs.* T data to obtain Arrhenius plots; additional data on the LT process were obtained at 1.05 and 1.10 K using a Faraday magnetometer with a ^{3}He dilution refrigerator. The plots and obtained parameters are shown in Fig. 3. The HT process has an activation energy (U) of 65.2 K, similar to that of **1** (60–64 K),[1b,9] whereas the LT form has a much smaller U of 31.9 K. Similar Arrhenius data were found for complex **3**.

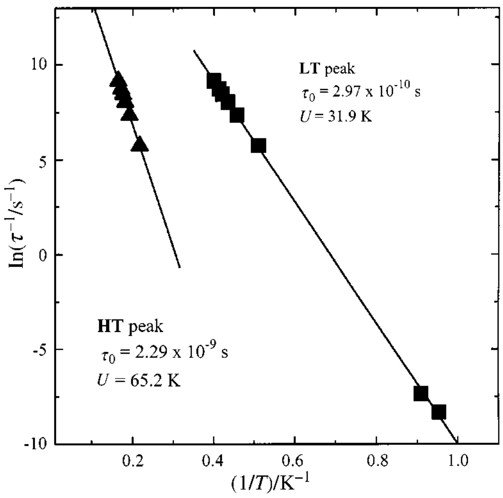

Fig. 3 Plots of the natural logarithm of the magnetization relaxation rates *vs.* 1/T for complex **4**: U is the activation energy and τ_o is the pre-exponential of the Arrhenius equation.

In summary, the LT χ_M'' *vs.* T responses of some Mn_{12} species are a result of their containing an abnormally oriented JT axis. This represents a type of isomerism not seen before and which can be defined as two or more non-equivalent forms differing in the relative orientation of one (or more) JT axes. We offer the term 'Jahn–Teller isomerism' for this new effect.

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Notes and references

† *Crystal data* for **3**$\cdot CH_2Cl_2\cdot CH_3NO_2$: $C_{98}H_{189}Cl_2Mn_{12}NO_{50}$, M = 2911.71, triclinic, $P\bar{1}$, a = 16.422(2), b = 27.434(3), c = 15.814(2) Å, α = 101.78(1), β = 101.79(1), γ = 76.90(1)°, Z = 2, U = 6699 Å^3, μ(Mo-Kα) = 11.630 mm^{-1}, D_c = 1.44 g cm^{-3}, T = −174 °C. The structure was solved by direct methods (SHELXTL) and refined (on F) using 10 081 reflections with $F > 2.33\sigma(F)$ to $R(R_w)$ values of 0.0725 (0.0563). CCDC 182/1395. See http: //www.rsc.org/suppdata/cc/1999/1973/ for crystallographic files in .cif format.

‡ Fresh samples of **3**$\cdot CH_2Cl_2\cdot CH_3NO_2$ show essentially only the LT peak. With time at room temperature, solvent molecules of crystallization are slowly lost (confirmed by elemental analysis), and the LT/HT ratio decreases. Thus, the LT form is the structurally characterised form and the relative amount of HT form increases with solvent loss. Full details will be reported in the full paper.

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