



## Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

### Single-Molecule Magnets: Characterization of Complexes Exhibiting Out-of-Phase AC Susceptibility Signals

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Version of record first published: 04 Oct 2006

To cite this article: Hilary J. Eppley, Sheila M. J. Aubin, Michael W. Wemple, David M. Adams, Hui-Lien Tsai, Vincent A. Grillo, Stephanie L. Castro, Ziming Sun, Kirsten Folting, John C. Huffman, David N. Hendrickson & George Christou (1997): Single-Molecule Magnets: Characterization of Complexes Exhibiting Out-of-Phase AC Susceptibility Signals, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 305:1, 167-179

To link to this article: <http://dx.doi.org/10.1080/10587259708045054>

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## SINGLE-MOLECULE MAGNETS: CHARACTERIZATION OF COMPLEXES EXHIBITING OUT-OF-PHASE AC SUSCEPTIBILITY SIGNALS.

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**Abstract** The structures and characterization are described of complexes that exhibit an out-of-phase AC magnetic susceptibility  $\chi_m''$ . The dodecanuclear complexes  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]^{2-}$  contain  $8\text{Mn}^{\text{III}}, 4\text{Mn}^{\text{IV}}$  or  $\text{Mn}^{\text{II}}, 7\text{Mn}^{\text{III}}, 4\text{Mn}^{\text{IV}}$  and possess ground state spins of  $S = 9$  or  $10$  ( $z = 0$ ) or  $S = 19/2$  ( $z = -1$ ). The distorted-cubane complexes  $[\text{Mn}_4\text{O}_3\text{X}(\text{O}_2\text{CR})_3(\text{dbm})_3]$  contain  $3\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}}$  and have been prepared with a variety of X groups; in every case, the ground state is  $S = 9/2$ . The anion  $[\text{Mn}_{11}\text{O}_{10}\text{X}_6(\text{O}_2\text{CPh})_{11}(\text{H}_2\text{O})_4]^{2-}$  ( $9\text{Mn}^{\text{III}}, 2\text{Mn}^{\text{IV}}$ ;  $\text{X} = \text{NCO}^-, \text{N}_3^-$ ) contains two  $[\text{Mn}_4\text{O}_3\text{X}]$  distorted-cubanes linked by a  $[\text{Mn}_3\text{O}_4]^+$  unit; the ground state is  $S = 5$ . The cation  $[\text{V}_4\text{O}_2(\text{O}_2\text{CEt})_7(\text{bpy})_2]^+$  ( $4\text{V}^{\text{III}}$ ) has a  $[\text{V}_4\text{O}_2]^{8+}$  butterfly core and a  $S = 3$  ground state. All these complexes exhibit out-of-phase AC magnetic susceptibility signals at low temperatures ( $< 8$  K). These signals are indicative of slow relaxation of the magnetization, unable to keep in phase with the oscillating AC magnetic field, and are taken as evidence for single-molecule magnetism. The origin of the barrier to relaxation is discussed.

## INTRODUCTION

The field of nanoscale magnetic particles is attracting considerable attention because of the interesting properties that such species should exhibit.<sup>1,2</sup> The synthesis of nanoscale magnets can be accomplished by fragmentation of bulk ferromagnets or ferromagnets to single-domain dimensions, but this approach unfortunately gives a distribution of particle sizes, which complicates detailed study of these systems, making diffi-

cult, for example, an accurate assessment of the variation of properties as a function of particle size. An alternative strategy is to approach nanoscale dimensions from the molecular direction, *viz* synthesize molecules that are large enough and/or have the appropriate properties to function as “single-molecule magnets”. While it might be intuitively believed that such molecules would have to comprise very large numbers of paramagnetic metal ions, it has recently become apparent that this is not necessarily the case.<sup>3,4,5</sup> Single-molecule magnets would have the advantages over fragmented ferro- and ferromagnets that a single “particle” size could be ensured, that organic ligands on the periphery could be chosen or systematically altered to ensure crystallinity and solubility in a variety of solvents, and that X-ray crystallographic and various spectroscopic and physical studies could be readily performed, in solution and/or the solid state.

Certain families of molecular complexes have now been identified that can function as single-molecule magnets for reasons arising from a combination of a high ground-state spin value and sufficiently large magnetic anisotropy. Thus, at low enough temperatures, these complexes exhibit out-of-phase AC magnetic susceptibility signals characteristic of slow relaxation of magnetization. In addition, hysteresis magnetization loops have been observed. In this paper are summarized the structures and magnetic characterization of these four distinct families of complexes:  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]^z$  ( $\text{R}$  = various;  $z$  = 0, -1),  $[\text{Mn}_4\text{O}_3\text{X}(\text{O}_2\text{CR})_3(\text{dbm})_3]$ ,  $(\text{NBu}^n)_4[\text{Mn}_{11}\text{O}_{10}\text{X}_6(\text{O}_2\text{CPh})_{11}(\text{H}_2\text{O})_4]$  and  $[\text{V}_4\text{O}_2(\text{O}_2\text{CMe})_7(\text{bpy})_2](\text{ClO}_4)$  ( $\text{bpy}$  = 2,2'-bipyridine,  $\text{dbm}$  = dibenzoylmethane anion).

### DODECANUCLEAR COMPLEXES

The first class of molecules reported to be single-molecule magnets were the complexes  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_3 \text{ or } 4]$   $\{\text{R} = \text{Me}(\mathbf{1})$ ,  $\text{Et}(\mathbf{2})$ ,  $\text{Ph}(\mathbf{3})\}$  (Figure 1),<sup>3-5</sup> which were shown to exhibit out-of-phase AC susceptibility signals,  $\chi_m''$ . In the AC susceptibility experiment, the sample is exposed to a small magnetic field (typically 1 G or less) oscillating at a fixed frequency in the 25-1000 Hz range. The magnetic moment of simple paramagnets can keep in-phase with the oscillating field, but the  $[\text{Mn}_{12}]$

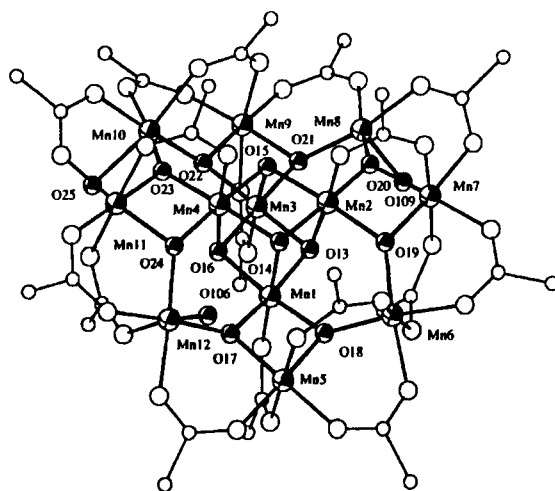


FIGURE 1 The structure of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_3]$  (2) with Me groups omitted. The metal atoms in the central cubane are  $\text{Mn}^{\text{IV}}$  and the other metal atoms are  $\text{Mn}^{\text{III}}$ .

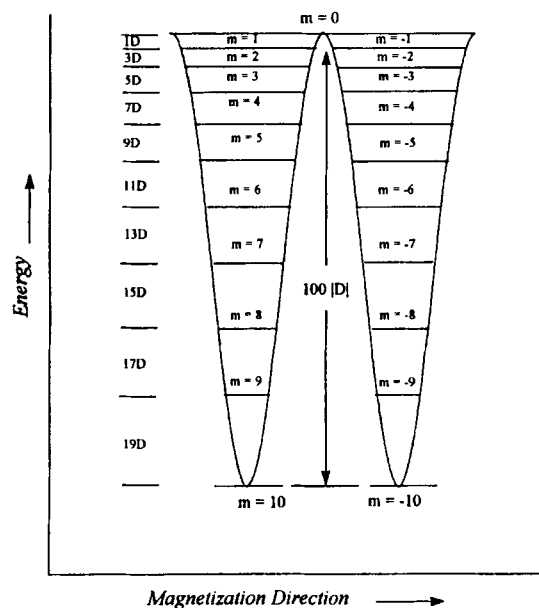


FIGURE 2 Potential energy vs magnetization direction for a complex with  $S = 10$  undergoing axial zero-field splitting (ZFS) with a negative ZFS parameter,  $D$ . The energy separation between the  $M_s = \pm 10$  and  $M_s = 0$  levels is  $|100D|$ . For  $S = 19/2$  or  $S = 9$  species, related diagrams and energy separations of  $|90D|$  and  $|81D|$ , respectively, are obtained.

complexes showed an out-of-phase signal,  $\chi_m''$ , at low temperatures ( $\leq 8$  K) characteristic of slow relaxation on the timescale of the oscillating field and indicative of a barrier to relaxation that is larger than normal for a molecular species. The barrier arises from axial zero-field splitting ( $D\hat{S}_z^2$ ) of the  $S = 9$  or  $10$  ground states of **1-3**, where the ZFS parameter is  $-0.5$  to  $-0.6$   $\text{cm}^{-1}$ . Complex **1** has  $S = 10$  and  $D = -0.5$   $\text{cm}^{-1}$ , giving an energy difference between the  $M_s = \pm 10$  and  $M_s = 0$  levels of  $S^2D = |100D| = 50$   $\text{cm}^{-1}$ . Since thermally activated relaxation of the magnetization involves the change of its orientation from  $M_s = +10$  to  $M_s = -10$  via the intermediate levels, the relaxation barrier is  $S^2D = 50$   $\text{cm}^{-1}$  (Figure 2), a relatively large value that rationalizes the appearance of an out-of-phase signal at low temperature. For **2**•H<sub>2</sub>O,  $S = 9$  and  $D = -0.6$   $\text{cm}^{-1}$ , giving a similar barrier ( $S^2D = 49$   $\text{cm}^{-1}$ ).<sup>4</sup> In Figures 3 and 4 are shown the frequency-dependent, AC susceptibility responses for **2**•H<sub>2</sub>O and (PPh<sub>4</sub>)[Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] (**4**); the latter was prepared by one-electron reduction of **2** with PPh<sub>4</sub>I, and has  $S = 19/2$  and  $D = 0.4$   $\text{cm}^{-1}$  (barrier =  $(S^2 - 1/4)D = 36$   $\text{cm}^{-1}$ ).<sup>4</sup> Complex **2**•H<sub>2</sub>O exhibits two distinct  $\chi_m''$  features whereas **4** exhibits only one in the accessible temperature range; the origin of the two features is currently thought to be two populations of [Mn<sub>12</sub>] molecules with different ground state spins, caused by differing lattice environments modulated by lattice solvent molecules.<sup>6</sup>

Both the neutral [Mn<sub>12</sub>] and charged [Mn<sub>12</sub>]<sup>+</sup> complexes display hysteresis effects, consistent with single-molecule magnetism, and those for **2**•H<sub>2</sub>O and **4** are shown in Figure 5.<sup>4</sup> Essentially identical results are also obtained for complexes solid-diluted on polystyrene (3.6 wt %) or in frozen solution, supporting the single-molecule origin of the effect. It should be emphasized that the origin of the hysteresis behavior here is different from that for ferromagnets where it is associated with the kinetics of domain wall motion.

#### TETRANUCLEAR COMPLEXES

The [Mn<sub>4</sub>O<sub>3</sub>X(O<sub>2</sub>CMe)<sub>3</sub>(dbm)<sub>3</sub>] complexes contain a [Mn<sub>4</sub>O<sub>3</sub>X]<sup>6+</sup> distorted-cubane core and have been prepared with X = Cl<sup>-</sup>, Br<sup>-</sup>, F<sup>-</sup>, N<sub>3</sub><sup>-</sup>, NCO<sup>-</sup>, MeCO<sub>2</sub><sup>-</sup>, RO<sup>-</sup>, and others.<sup>7</sup> All have  $S = 9/2$  ground states and  $D$  values in the  $-0.27$  to  $-0.38$   $\text{cm}^{-1}$  range;

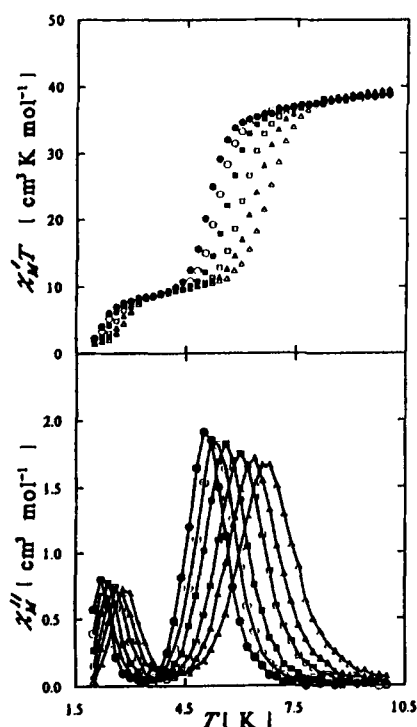


FIGURE 3 AC magnetic susceptibility for complex  $2 \cdot \text{H}_2\text{O}$ . At the top and bottom, respectively, are plotted  $\chi'_m T$  vs  $T$  and  $\chi''_m$  vs  $T$ , where  $\chi'_m$  and  $\chi''_m$  are the in-phase and out-of-phase signals, respectively. Data are at 997 ( $\Delta$ ), 499 ( $\blacktriangle$ ), 250 ( $\square$ ), 100 ( $\blacksquare$ ), 500 ( $\circ$ ) and 25 ( $\bullet$ ) Hz frequencies.

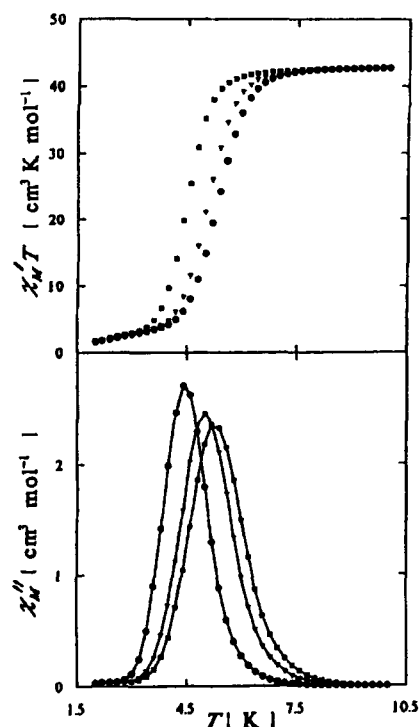


FIGURE 4 AC magnetic susceptibility for complex 4. At the top and bottom, respectively, are plotted  $\chi'_m T$  vs  $T$  and  $\chi''_m$  vs  $T$ , where  $\chi'_m$  and  $\chi''_m$  are the in-phase and out-of-phase signals, respectively. Data are at 499 ( $\blacksquare$ ), 100 ( $\blacktriangledown$ ) and 50 ( $\bullet$ ) Hz frequencies.

the  $\text{X} = \text{NCO}^-$  complex (5) is shown in Figure 6. These complexes all show frequency-dependent out-of-phase AC susceptibility signals ( $\chi''_m$ ) at  $\leq 3 \text{ K}$ .<sup>7,8,9</sup> In Figure 7 are shown those for  $\text{X} = \text{NCO}^-$  and  $\text{N}_3^-$  (6) for which  $D$  values of  $-0.27$  and  $-0.38 \text{ cm}^{-1}$ , respectively, have been calculated from reduced magnetization vs field fittings. The calculated barriers ( $20D$ ) of  $5.4$  and  $7.6 \text{ cm}^{-1}$ , respectively, are consistent with the lower temperatures required to observe the out-of-phase signals *vis-à-vis* the  $[\text{Mn}_{12}]$  complexes. Out-of-phase signals are also seen for frozen  $\text{CD}_2\text{Cl}_2/\text{C}_6\text{D}_5\text{CD}_3$  glasses, supporting their

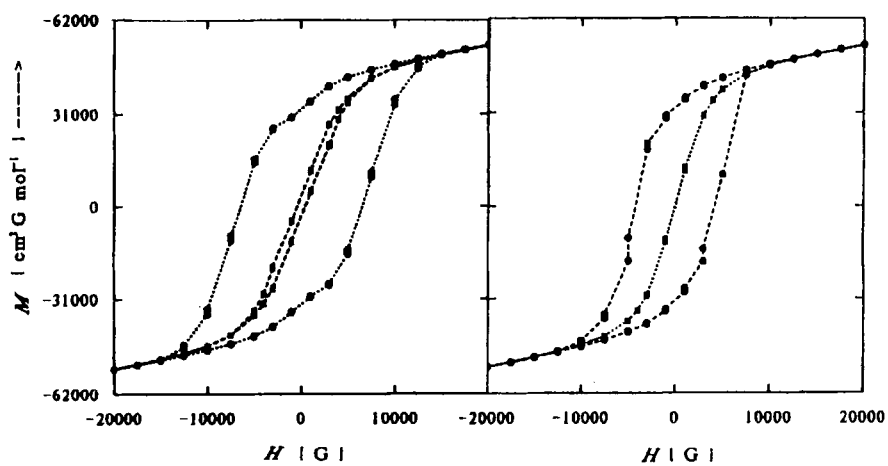


FIGURE 5 Hysteresis loops for  $2 \cdot \text{H}_2\text{O}$  (left) and **4** (right) at 2.2 (●) and 2.8 (■) K.

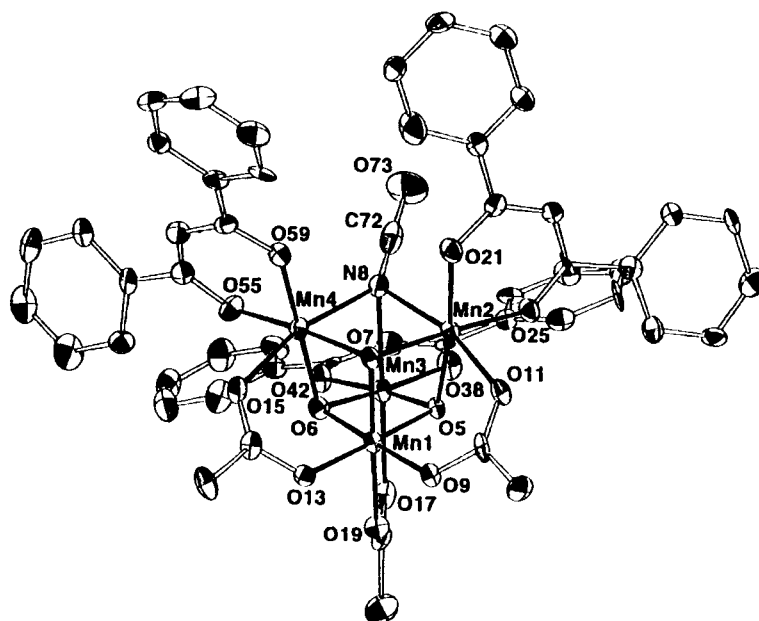


FIGURE 6 The structure of  $[\text{Mn}_4\text{O}_3(\text{NCO})(\text{O}_2\text{CMe})_3(\text{dbm})_3]$  (**5**).

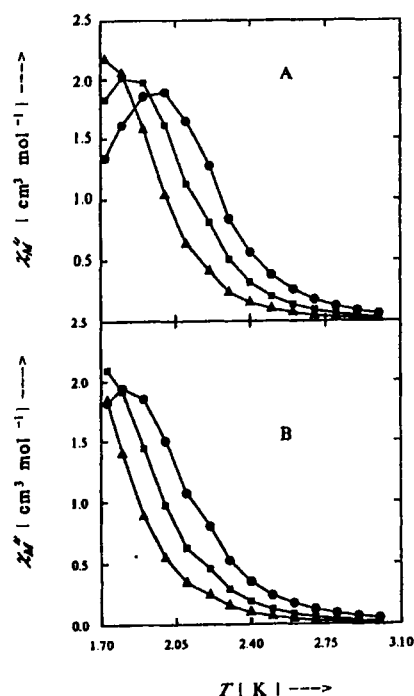


FIGURE 7 Out-of-phase AC magnetic susceptibility for two  $[\text{Mn}_4\text{O}_3\text{X}]^{6+}$  complexes with  $\text{X} = \text{N}_3^-$  (A) and  $\text{NCO}^-$  (B). Data are at 997 (●), 499 (■) and 250 (▲) Hz frequencies.

single-molecule origin, although some small differences are apparent in the temperature dependence plots.<sup>9</sup> In Figure 8 are shown the DC susceptibility data (10 kG applied field) for the  $\text{X} = \text{Cl}^-$  complex (7) as a microcrystalline solid and a frozen  $\text{CD}_2\text{Cl}_2/\text{C}_6\text{D}_5\text{CD}_3$  glass; these and related magnetization vs field studies confirm the complex retains a  $S = 9/2$  ground state in solution. Figure 9 shows the out-of-phase AC signal,  $\chi''$ , for the same two samples of 7, and it can be seen that there is a broadening and a shift to higher temperatures of the  $\chi''$  signals of the frozen solution. The broader signals might simply reflect a greater distribution in environment experienced by complex 7 in a frozen solution compared with a crystalline sample. The slight shift to higher temperatures might reflect a small change in barrier height,  $(S^2 - 1/4)D$ , arising from a small increase in  $D$  for the individual molecules of 7 in going from a crystalline to a glass environment.

There are now a number of  $[\text{Mn}_{12}]$ ,  $[\text{Mn}_{12}]^+$  and  $[\text{Mn}_4]$  complexes available that exhibit out-of-phase AC signals and for which reliable  $S$  and  $D$  values have been ob-



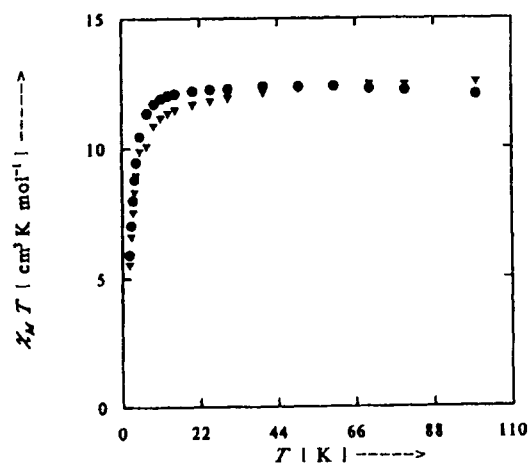


FIGURE 8 DC magnetic susceptibility data in a 10 kG applied field for  $[\text{Mn}_4\text{O}_3\text{Cl}(\text{O}_2\text{CMe})_3(\text{dbm})_3]$  (7), plotted as  $\chi_M T$  vs  $T$ . Data are for a parafilm-restrained microcrystalline solid (●) and a frozen  $\text{CD}_2\text{Cl}_2/\text{C}_6\text{D}_5\text{CD}_3$  glass (▼).

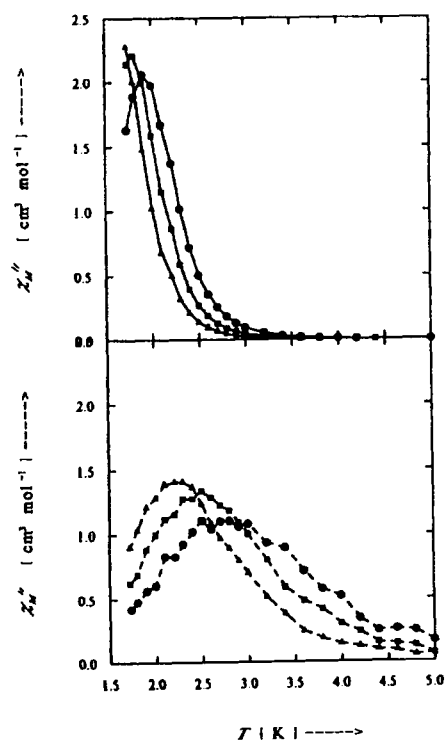


FIGURE 9 Out-of-phase AC magnetic susceptibility for complex 7 as a microcrystalline solid (top) and as a frozen  $\text{CD}_2\text{Cl}_2/\text{C}_6\text{D}_5\text{CD}_3$  glass (bottom).

tained. In Figure 10 are plotted the calculated energy barriers vs the temperature of the  $\chi_m''$  peak maximum at 997 Hz, and a correlation is seen suggesting that the appearance and position (temperature) of out-of-phase signals do scale with the calculated energy barrier.<sup>9</sup>

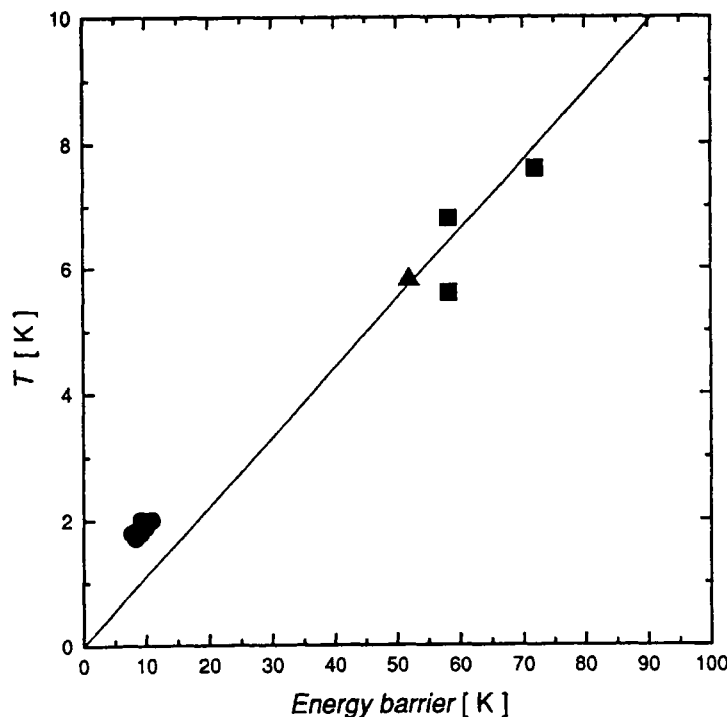


FIGURE 10 Plot of the temperature at which there is a maximum in  $\chi_m''$  at 997 Hz vs the calculated energy barrier for relaxation of magnetization. Data are presented for  $[\text{Mn}_{12}]$  (■),  $[\text{Mn}_{12}]^+$  (▲) and  $[\text{Mn}_4]$  (●) complexes.

#### UNDECANUCLEAR COMPLEXES

The  $[\text{Mn}_{11}\text{O}_{10}\text{X}_6(\text{O}_2\text{CPh})_{11}(\text{H}_2\text{O})_4]^{2-}$  ( $\text{X} = \text{N}_3^-$  (8),  $\text{NCO}^-$  (9)) complexes contain two  $[\text{Mn}_4\text{O}_3\text{X}]$  distorted-cubane cores (as in the tetranuclear complexes above) “bridged” by a linear  $[\text{Mn}_3\text{O}_4]^+$  unit (Figure 11). Preliminary studies indicate a  $S \approx 5$  ground state. The  $\text{X} = \text{N}_3^-$  complex 8 exhibits an out-of-phase signal at  $\leq 4$  K (Figure 12) but no peak maximum is observable above 1.7 K.<sup>10</sup>

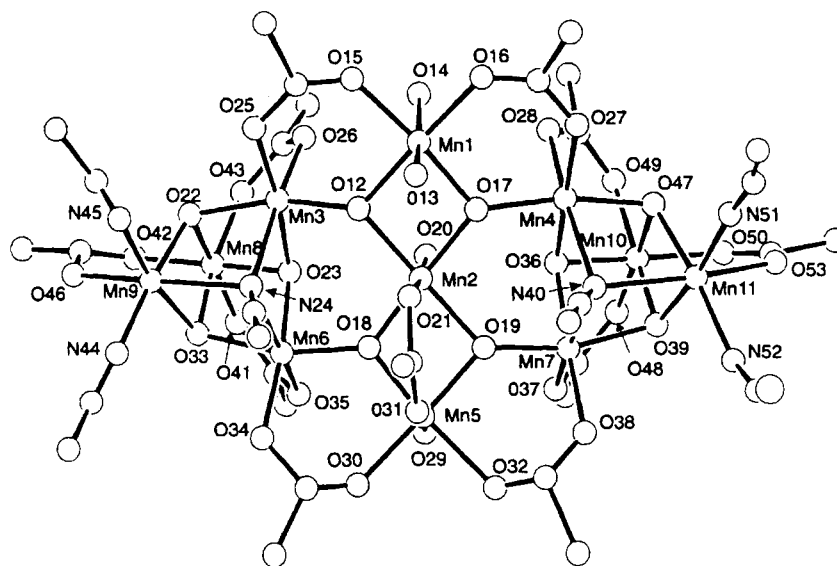


FIGURE 11 The structure of  $[\text{Mn}_{11}\text{O}_{10}(\text{NCO})_6(\text{O}_2\text{CPh})_{11}(\text{H}_2\text{O})_4]^{2-}$  (**9**); only the *ipso* C atom of each Ph ring is shown.

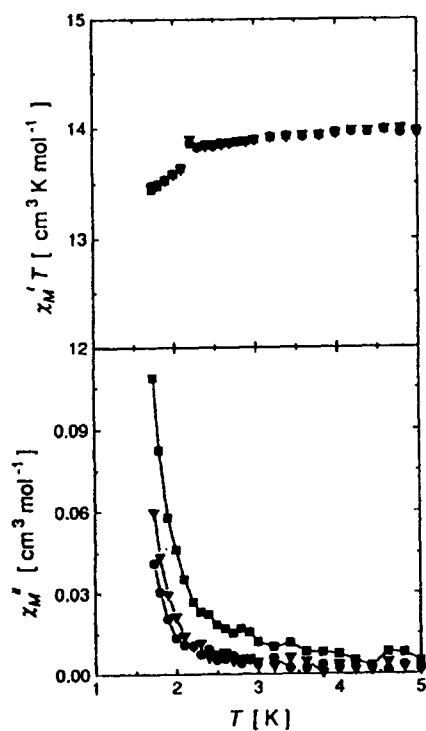


FIGURE 12 Out-of-phase AC susceptibility signals for complex **9** at 250 (●), 500 (▼) and 1000 (■) Hz.

### TETRANUCLEAR VANADIUM(III) COMPLEX

The recently prepared complex  $[\text{V}_4\text{O}_2(\text{O}_2\text{Cet})_7(\text{bpy})_2]^+$  (**10**) has a butterfly-like  $[\text{V}_4\text{O}_2]^{8+}$  core comprising octahedral  $\text{V}^{\text{III}}$  centers (Figure 13).<sup>11</sup> The ground state is  $S = 3$  with a low-lying  $S = 4$  first excited state. The complex exhibits an out-of-phase AC susceptibility signal very similar to that for complex **8**, becoming apparent at  $T \leq 4$  K but not yet reaching a maximum at 1.7 K (Figure 14).

### CONCLUSIONS

We have now extended to four the number of families of complexes that exhibit the frequency-dependent, out-of-phase AC susceptibility signals that are characteristic of single-molecule magnets. These comprise the  $[\text{Mn}_{12}]^{0+}$ ,  $[\text{Mn}_4]$ ,  $[\text{Mn}_{11}]$  and  $[\text{V}_4]$  species, with studies of the latter two types being in their infancy. The essential requirements for a species to exhibit single-molecule magnetism are (i) a large  $S$ , (ii) a large  $D$ , and (iii) a negative  $D$ : the ability to synthetically control all three of these is absolutely necessary if the directed synthesis is to be achieved of complexes that display single-molecule magnetism at higher temperatures approaching or exceeding liquid nitrogen. This represents a challenge for the future of considerable magnitude and importance.

### ACKNOWLEDGEMENTS

This work was supported by NSF grants CHE-9311904 (G.C.) and CHE-9420322 (D.N.H.), and Department of Energy grant ER 13702 (G.C.). The AC magnetic susceptibility measurements were performed with an AC SQUID susceptometer provided by the Center for Interface and Material Science, funded by the W. A. Keck Foundation. H.J.E. was supported by an NSF Predoctoral Fellowship.

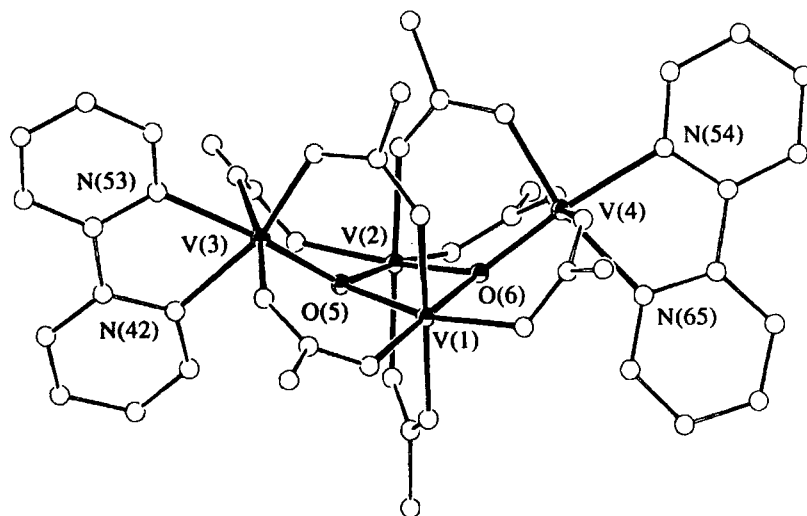


FIGURE 13 The structure of  $[\text{V}_4\text{O}_2(\text{O}_2\text{Cet})_7(\text{bpy})_2]^+$  (10) with Me groups omitted.

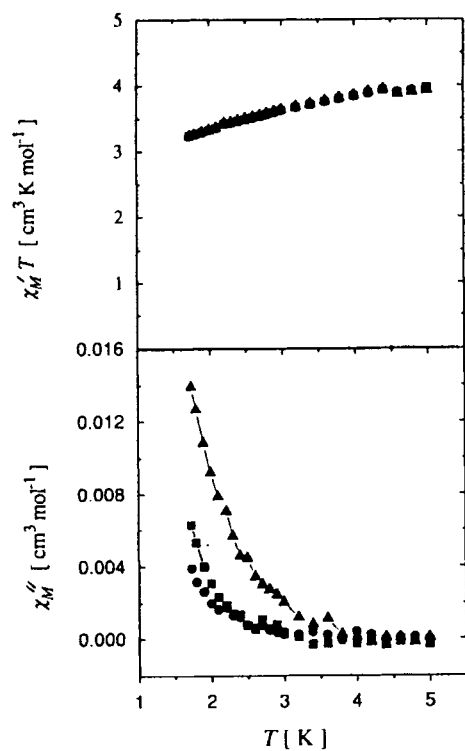


FIGURE 14 Out-of-phase AC susceptibility signals for complex 10 at 250 (●), 500 (■) and 1000 (▲) Hz.

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