Single-Molecule Magnets: Ligand-Induced Core Distortion and Multiple Jahn–Teller Isomerism in [Mn₁₂O₁₂(O₂CMe)₈(O₂PPh₂)₈(H₂O)₄]

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Received June 4, 2001

Single-molecule magnets (SMMs) are a relatively recent discovery that promises access to the ultimate high-density memory storage device in which each bit of digital information is stored on a single molecule. Each independent molecule of a SMM possesses the ability to function as a magnetizable magnet below a critical temperature.¹ This is due to intrinsic intramolecular properties, that is, a large spin ground state and a large and negative (easy-axis-type) magnetoisotropy, rather than to intermolecular interactions and long-range ordering. The most well studied SMMs are the [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄] (n = 0–2; 8Mnᴵᴵᴵ–4Mn⁴⁺) complexes.⁴ Evidence for the SMM behavior comes from frequency-dependent out-of-phase AC susceptibility signals (χ″(ω)) and magnetization hysteresis loops. In addition, oriented crystals display steps in the hysteresis loops indicative of field-tuned quantum tunneling of the magnetization (QTM).⁵ A substantial amount of effort has been dedicated to systematic variation of the carboxylate R group and solvate molecules of crystallization, which has recently led to the discovery of Jahn–Teller (JT) isomerism,⁶ involving differing relative orientations of the JT elongation axes of the eight Mn III centers and resulting in significantly different magnetic behavior for the different JT isomers. This includes differing positions of the χ″(ω) peaks and differing magnetization hysteresis plots, both reflecting different rates of magnetization relaxation.

Here we report on a major expansion of the Mn₁₂ SMM family by demonstrating for the first time that carboxylate ligands can be replaced by other organic ligands, in this case diphenylphosphinate groups to give [Mn₁₂O₁₂(O₂CMe)(O₂PPh₂)(H₂O)₄] (1). In addition, this species is unique in displaying three distinct JT phinate groups to give [Mn₁₂O₁₂(O₂CMe)₈(O₂PPh₂)₈(H₂O)₄] (Mn₃ phinate) (2) in 60% yield, which was crystallographically characterized as 2-¹⁴N₃MeCN⁻·¹⁰H₂O.⁷ Recrystallization from CH₂Cl₂/hexanes gives 2-¹₂CH₂Cl₂,⁸ 2-¹⁴MeCN⁻·¹₂H₂O crystallizes in space group P4/n, with the asymmetric unit containing 0.25 Mn₁₂ clusters and solvent. All three crystallographically unique molecules possess a structure similar to that of 1, with a central Mn₃ phinate cubane held within a nonplanar ring of eight Mn III ions by eight μ₃-O²⁻ ions. However, in 2 the acetate groups at the four axial Mn III–Mn III and four of the eight equatorial Mn III–Mn III carboxylate sites have been replaced by diphenylphosphinate groups, while the remaining equatorial sites and the four axial Mn III–Mn III sites remain occupied by acetates (Figure 1), resulting in a significant distortion of the [MnᵥO₄]⁴⁺ core (Figure 2). This is reflected in the bond angles and an increase of ~0.1 Å in all of the Mn----Mn distances in 2, and is most apparent as a “bowing” in each of the linear Mn₃ units, with the angles of the type Mn(3)–Mn(1)–Mn(1)’ in 2-¹₂CH₂Cl₂ decreasing from ~178° in 1 to 171° in 2. All three of the molecules possess one H₂O ligand bound to every other Mn III center (Mn(2) for 2-¹₂CH₂Cl₂), oriented alternately in opposite directions, as is observed in 1. The main difference between the three different molecules of 2 lies in the location of the JT elongation axes of the eight Mn III centers (Figure 2). The single cluster in 2-¹₂CH₂Cl₂ possesses S₄ symmetry with all eight JT axes oriented approximately parallel in the axial direction, and thus they are not pointing toward the oxide ligands. This is the same as in 1 and is the normal situation in Mn₁₂ carboxylate species. However, the two independent molecules in 2-¹⁴N₃MeCN⁻·¹⁰H₂O possess C₁ and approximate S₁ (crystallographic C₂) symmetry, with two

² Crystal data for [¹⁴N₃]⁷MCN⁻·²H₂O: C₁₈H₁₉N·Mn₂O₄P₄·5203.11 g mol⁻¹, monoclinic, C2/c, a = 55.071(4) Å, b = 33.491(3) Å, c = 27.331(2) Å, β = 114.966(2)°, Z = 8, V = 45699.0 Å³, dₐ₁ = 1.460 g cm⁻³, T = -185 °C. The structure was solved by direct methods (SHELXTL) and refined (on F) using 52 187 reflections with F > 3σ(F) and R(F) values of 0.0777 (0.0654).

Figure 1. ORTEP representation of complex 2-¹₂CH₂Cl₂ at the 50% probability level.

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1.92 and D magnetization (M/Ní dependent decrease at Trelaxation. This was confirmed by the concomitant appearance cm-1 [Mn12O12(O2CR)16(H2O)4] previously reported examples of JT isomerism. 6

In both cases, these “abnormally” oriented JT axes are located at the MnII centers with H2O ligands, as has been observed for the MnIII centers with H2O ligands, as has been observed for the

The cores of complexes: (a) I, (b) 2-12CH2Cl2, (c) the C1 molecule of 2-14/3MeCN-4/3H2O, and (d) the C3 molecule of 2-14/3MeCN-4/3H2O, emphasizing the Jahn–Teller axes as solid black bonds.

(Mn(9) and Mn(11)) and four (Mn(185), Mn(185′), Mn(186), and Mn(186′)) equatorially oriented JT axes, respectively. That is, for these species, some of the JT axes point toward oxide ligands. In both cases, these “abnormally” oriented JT axes are located at the MnII centers with H2O ligands, as has been observed for the previously reported examples of JT isomerism.6

The ground state of 2-12CH2Cl2 was determined from reduced magnetization (M/NµB) versus H/T measurements in the 1.8–25 K and 20–70 kG range.5 Fitting of the data10 gave S = 10, g = 1.92 and D = −0.41 cm−1 (−0.59 K), values typical for [Mn12O12(O2CR)16(H2O)4] clusters (S = 10, D = −0.4 to −0.5 cm−1).

AC magnetization measurements were performed on 2-12CH2Cl2 in the 1.8–10 K range in a 3.5 G AC field oscillating at 1–1500 Hz. The in-phase χ′′ M/T signal shows a frequency-dependent decrease at T < 8 K, indicative of the onset of slow relaxation. This was confirmed by the concomitant appearance

of an out-of-phase (χ′′ M) signal due to the inability of 2-12CH2Cl2 to relax sufficiently rapidly at these temperatures to keep up with the oscillating field. For the AC frequency range 1–1500 Hz, the χ′′ M peaks of 2-12CH2Cl2 occur in the range 3–7 K, again consistent with the behavior generally observed for [Mn12O12–(O2CR)16(H2O)4]. The χ′′ M data obtained by varying the oscillation frequency of the AC field can be fit to an Arrhenius equation to give the effective energy barrier for the magnetization relaxation (Ueff).9 and such an analysis indicates that Ueff for complex 2-12CH2Cl2 is ~42 cm−1 (60 K), which again is within the normal range for [Mn12O12(O2CR)16(H2O)4] of 42–50 cm−1 (60–72 K). AC measurements on 2-14/3MeCN-4/3H2O are in progress, but are hindered by crystal degradation following rapid solvent loss.

Magnetization hysteresis loops were observed for oriented crystals of 2-12CH2Cl2 at 1.8, 1.9, and 2.0 K (Figure 3). A few crystals were suspended in eicosane at 40 °C, subjected to a 70 kG field to align their principal axis of magnetization parallel to the applied field, and then cooled to low temperature. A number of steps due to quantum tunneling of the magnetization are evident in the hysteresis loop. The separation between steps was found to be 3.95 kG, indicating a value of D/λg ≈0.0.18 cm−1, which is consistent with the value of −0.21 cm−1 obtained from the fitting of the reduced magnetization data.

In conclusion, the first significantly altered derivative of [Mn12O12(O2CR)16(H2O)4] has been prepared by incorporation of non-carboxylate organic ligands, and ligand-induced core distortions result. In addition, multiple JT isomerism has been observed, emphasizing the small energy differences involved. Complex 2 is magnetochromically similar to its 16-carboxylate parent, possessing an S = 10 ground state and displaying frequency-dependent peaks in the out-of-phase AC susceptibility plots, in addition to magnetization hysteresis. Furthermore, quantum tunneling of the magnetization is evident as steps in the hysteresis loops. Therefore, the SMM properties are still retained in the diphenylphosphinate-substituted species 2, which thus represents the prototype of a major new thrust in the SMM field.

Acknowledgment. This work was supported by National Science Foundation grants to G.C. and D.N.H.

Supporting Information Available: Crystallographic details (CIF) for 2-12CH2Cl2 and 2-14/3MeCN-4/3H2O; reduced magnetization versus field plots and fit; Arrhenius plot. This material is available free of charge via the Internet at http://pubs.acs.org.

JA016341+

Figure 3. Magnetization hysteresis loops for oriented crystals measured in an eicosane matrix for complex 2-12CH2Cl2 at 1.8 (●), 1.9 (■), and 2.0 K (▲).