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Field-Induced Slow Relaxation in a Monometallic Manganese(III) Single-Molecule Magnet

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Ⓢ *Supporting Information*

ABSTRACT: High-field electron paramagnetic resonance spectroscopy shows that the structurally distorted Mn^{III} ion in $Na_5[Mn(\text{L-tart})_2]\cdot 12H_2O$ (**1**; L-tart = L-tartrate) has a significant negative axial zero-field splitting and a small rhombic anisotropy (~1% of D). Alternating-current magnetic susceptibility measurements demonstrate that **1**, which contains isolated Mn^{III} centers, displays slow relaxation of its magnetization under an applied direct-current magnetic field.

The discovery that the mixed-valence complex $[Mn_{12}O_{12}(CH_3CO_2)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2CH_3CO_2H$ (Mn_{12}ac) retains its magnetization in the absence of a magnetic field[1] established a new class of materials called single-molecule magnets (SMMs).[2] The barrier to the eventual loss of magnetization, U_{eff}, is approximately determined by the size of a molecule's spin, S, and the magnitude of the axial zero-field splitting (ZFS) present, as given by the parameter D. Thus, a great deal of effort has been invested in the synthesis of large, polymetallic assemblies, employing anisotropic metal ions as a method of maximizing both of these parameters.[3] An alternative approach increasingly developed in recent years focuses on the properties of monometallic complexes and has been particularly fruitful in the study of highly anisotropic lanthanide-based systems.[4] Indeed, the highest barrier measured so far for either type of nanomagnet is 652 cm^{-1}, as found in $[Tb[[O(C_6H_4)\text{-}p\text{-}t\mathrm{Bu}]_8\mathrm{Pc}](\mathrm{Pc}')]$ (Pc and Pc′ are phthalocyanine derivatives).[5] In 2010, this approach was extended to include the 3d transition metals, with the observation of slow magnetic relaxation in the high-spin iron(II) complex $K[(tpa^{Mes})Fe]$ {H_3tpa^{Mes} = tris[(5-mesityl-1*H*-pyrrol-2-yl)methyl]amine}.[6] Since then, further monometallic 3d systems with significant magnetic anisotropy have been described, containing Fe^{I},[7] Fe^{II},[8] Co^{II},[9] Ni^{I},[10] and Ni^{II},[11] often possessing geometrically exotic coordination environments.

Of the 3d monometallic complexes, manganese(III) is perhaps underexplored, given its paramount contribution to the magnetic properties of Mn_{12}ac. To the best of our knowledge, only three examples exist to date of monometallic manganese(III) complexes that display slow relaxation of magnetization.[12] In all of them, the central metal ion is six-coordinate with a significant tetragonal elongation arising from the Jahn−Teller effect. In this environment, D is almost always negative: the $^5B_1$ ground state is split by spin−orbit interactions, and the $m_s = \pm 2$ states lie at lowest energy. In this Communication, we describe the static and dynamic magnetic properties of $Na_5[Mn(\text{L-tart})_2]\cdot 12H_2O$ (**1**; L-tart = L-tartrate),[13] finding it to be one of the few known examples of monometallic manganese(III) compounds that display field-induced slow magnetic relaxation.

The X-ray crystal structure of compound **1** was redetermined at 100 K and found to coincide with the room temperature structure reported previously (see Table S1 in the Supporting Information, SI). Enantiopure crystals of **1** form in the space group *C*2 and consist of $[Mn(\text{L-tart})_2]^{5-}$ anionic complexes that are bridged through Na^+ ions (five per anionic unit) and H_2O molecules (Figure 1). This extended arrangement (see Figures S1−S3 in the SI) leads to nearest and next-nearest Mn···Mn distances of 6.798(2) and 9.611(2) Å, respectively. There are nine bonds connecting the closest Mn^{III} ions, and they can be considered as essentially isolated, an interpretation supported by the subsequent magnetic studies (see below). The Mn^{III} ions are

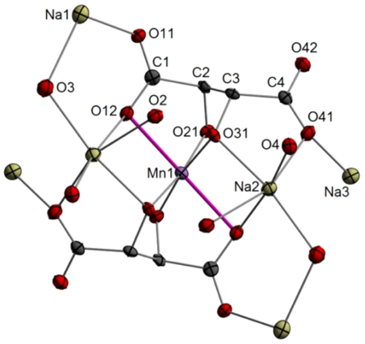

Figure 1. View of the central $[Mn(\text{L-tart})_2]^{5-}$ anionic unit and surrounding Na^+ ions. Only crystallographically independent atoms are labeled (Na3 lies on a special position with half-occupancy), H atoms are omitted for clarity, and ellipsoids are shown at the 70% probability level. The Jahn−Teller axis is thickened with respect to other bonds.

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surrounded by two fully deprotonated, symmetry-equivalent L-tart ligands, each coordinating to the central metal through three O atoms (O12, O21, and O31), leading to an $\{MnO_6\}$ first-coordination sphere. The alkoxo atoms O21 and O31 bind in the equatorial positions [av. 1.907(3) Å], while O12 is provided by the carboxylate [Mn1−O12 = 2.303(2) Å]. Therefore, the Mn^{III} ion displays a significant Jahn−Teller effect. There is also a distortion observed within the equatorial plane, with O12−Mn1−O21 bond angles that deviate considerably from the ideal 90° [77.3(1)°]. The remaining carboxylate atoms O11 and O41 link to two Na^+, helping to form the extended structure, while O42 is left free.

The variable-temperature magnetic properties of a phase-pure (Figure S4 in the SI) polycrystalline sample of compound **1** were measured in the range 300−1.8 K under an applied direct-current (dc) field of 1000 Oe (Figure 2). The room temperature value found for $\chi_M T$ of 2.97 $cm^3\ mol^{-1}$ K is in line with that expected for a high-spin Mn^{III} ion ($\chi_M T = 3.0$ $cm^3\ mol^{-1}$ K for $S = 2$ and $g = 2.0$). This value remains approximately constant upon lowering of the temperature to 30 K, where $\chi_M T$ begins to decrease because of ZFS. Variable-field magnetization measurements were not found to reach saturation at 2.0 or 5.0 K, consistent with the presence of magnetic anisotropy (Figure 2, inset). Simultaneous fits of both the susceptibility and magnetization data, performed with the program *Phi*,[14] yielded a value for D of −3.20(8) cm^{-1} (considering only D). These values are consistent with the three examples of monometallic manganese(III) SMMs found in the literature, which display values of D ranging from −3.27 to −3.4 cm^{-1}.[12]

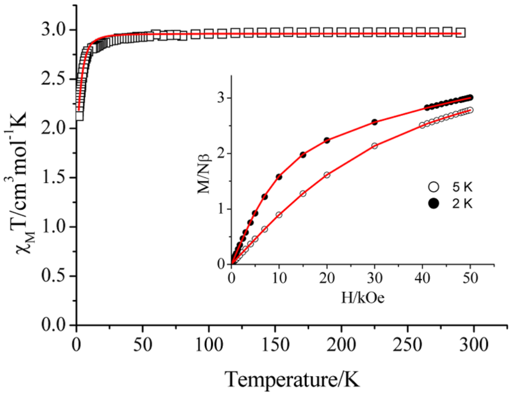

Figure 2. Temperature dependence of $\chi_M T$ for compound **1** under a dc field of 1000 Oe and (inset) M versus H. The red lines correspond to the fit (see the text for details).

In order to confirm the presence of magnetic anisotropy in **1** and its predominately axial nature, variable-temperature, high-field electron paramagnetic resonance (EPR) measurements were performed. The measurements were carried out in the frequency range from 49 to 426 GHz on a finely ground powder of compound **1** pressed into a KBr pellet to prevent torqueing/reorientation in the applied field. Representative spectra at two high frequencies are displayed in Figure 3. Exceptionally sharp EPR peaks are observed. The strong resonance close to zero field at 304.8 GHz indicates considerable ZFS, and the temperature dependence of this peak can only be explained by a negative D parameter (see the SI). The doubling of some of the peaks at higher field indicates a small rhombic E term.

Spectral fits were performed using the program *EasySpin*[15] and are included below the experimental spectra in Figure 3. These fits gave $D = -3.23$ cm^{-1} and $E = 0.032$ cm^{-1}, and an isotropic $g = 2.00$ was assumed; this parametrization gives good agreement with measurements performed at all frequencies in the 49−429 GHz range (see the SI). The E parameter is an order of magnitude smaller than that obtained for the compound in ref 12a. The D parameter agrees remarkably well with the magnetic measurements, while the small E (∼1% of D) term suggests relatively weak zero-field magnetic quantum tunneling (QTM) that ought to be suppressed via application of a moderate magnetic field (vide infra).

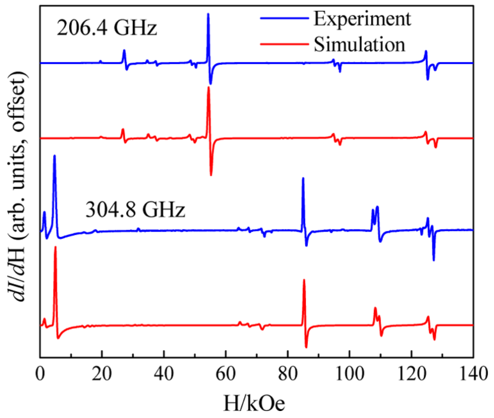

Figure 3. High-field EPR spectra (in blue) recorded in derivative mode at $T = 4$ K. The frequencies are indicated in the figure. Simulations (in red) are displayed below the experimental spectra.

Given the structural distortion observed in **1** and the ZFS evidenced by the static magnetic properties and EPR studies, alternating-current (ac) susceptibility measurements were performed. In the absence of an applied dc field, no frequency dependence was observed for the real component of the susceptibility, χ_M', nor were any signals observed for the out-of-phase component, χ_M'' (Figure S8 in the SI), perhaps because of the small rhombic component allowing QTM, as indicated by the EPR measurements. To investigate whether this QTM could be inhibited by an external magnetic field, we studied the effect of various field strengths on the dynamic magnetic properties of **1** (see the SI). Applied fields of as low as 200 Oe were sufficient to give rise to maxima in the out-of-phase susceptibility. These maxima are seen at much lower frequencies than previously observed for monometallic manganese(III) complexes that display slow relaxation of magnetization,[12] suggesting weaker QTM in **1**. The field dependence of the relaxation rate τ showed no clear local maximum and appeared to be broadly insensitive to fields above 3000 Oe (Figure S9 in the SI). Therefore, the ac susceptibility of **1** was measured as a function of the frequency over the temperature range 1.9−10 K, under applied dc fields of 500, 1500, 2000, 2500, and 5000 Oe (data measured under 2000 Oe are shown in Figure 4). The Arrhenius plots derived from the data at 500, 2000, and 5000 Oe are shown in Figure 5 (see the SI for an Arrhenius plot for all of the data collected). Clearly, U_{eff} and τ_0 are field-dependent. Fits of the data yielded values of U_{eff} (τ_0) = 9.9 (6.4×10^{-6} s), 9.0 (3.4×10^{-6} s), and 5.4 cm^{-1} (2.3×10^{-6} s) under fields of 5000, 2000, and 500 Oe, respectively.

In conclusion, we have demonstrated that the combination of an easy-axis magnetic anisotropy ($D = -3.23$ cm^{-1}) with only a very small rhombic anisotropy (∼1% of D) leads to field-induced slow magnetic relaxation arising from the isolated Mn^{III} centers in $[Mn(\text{L-tart})_2]^{5-}$. Future studies will assess how the structure

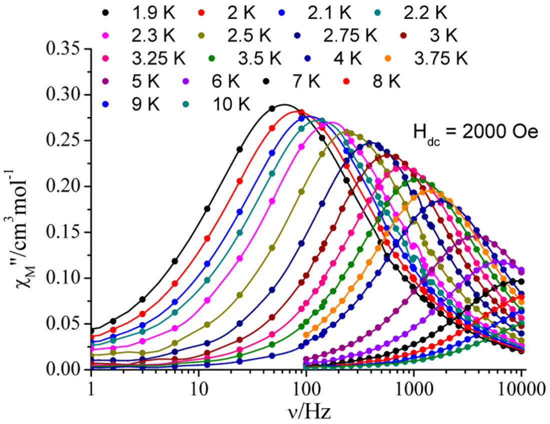

Figure 4. Frequency dependence of χ_M'' for **1** in the temperature range 1.9−10 K under an applied dc field of 2000 Oe.

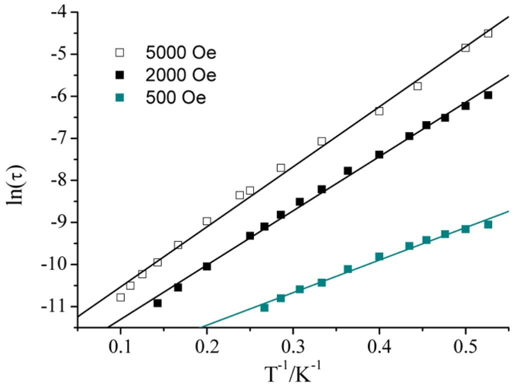

Figure 5. Arrhenius plots derived from ac susceptibility data for **1** under different fields (see the key). The solid lines correspond to fits of the data.

and magnetic properties (barrier height, ZFS, and QTM) of **1** may be tuned by applying high pressure.[16]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data, additional packing diagrams, further magnetic and EPR data, and details of physical techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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