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Slow Relaxation of the Magnetization of an Mn^{III} Single Ion

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Supporting Information

ABSTRACT: A Mn^{III}-salen-type complex with a diamagnetic $[Co^{III}(CN)_6]^{3-}$ moiety, $[Mn^{III}(5\text{-TMAM}(R)\text{-salmen})(H_2O)Co^{III}(CN)_6]\cdot 7H_2O\cdot MeCN$ [**1**; 5-TMAM(*R*)-salmen = (*R*)-*N*,*N*′-(1-methylethylene)bis(5-trimethylammoniomethylsalicylideneiminate], was prepared. From direct-current magnetic susceptibilities, magnetization, and high-field and multifrequency electronic spin resonance measurements on powdered samples, **1** has a significant uniaxial anisotropy. Frequency-dependent alternating-current susceptibility signals were clearly observed, indicating slow magnetic relaxation. Thus, complex **1** behaves as a single-ion magnet.

New molecular magnetic materials on the nanosize level are needed for future innovation in information technology. One particular interesting class of magnetically bistable molecules are single-molecule magnets (SMMs), which have been shown to exhibit slow magnetic relaxation at low temperatures.[1] The slow magnetic relaxation originates from uniaxial magnetic anisotropy (D) and a high-spin (HS) ground state (S_T), causing an energy barrier for spin reversal [$\Delta = |D|S_T^2$ or $|D|(S_T^2 - {}^1/_4)$ for integer and half-integer spin systems]. Such molecular nanomagnets show typical quantum tunneling of the magnetization with a long coherence time and can be applied to quantum computing and high-density information storage.[2] Since the mixed-valence Mn_{12} cluster was reported as the first SMM, much effort has been devoted to searching for other examples of clusters with 3d and/or 3d−4f metal ions exhibiting SMM behavior.[1,3] In subsequent studies, the strong spin−orbit coupling involved in the magnetic single ions leading to SMM-like behavior with remarkably high activation energy barriers, which are known as single-ion magnets (SIMs), have been investigated. The first reported SIMs contained 4f ions,[4] and more recently, SIM behavior has been reported for 5f and 3d ions.[5,6] The ligand field of 3d metal ions (i.e., magnetic anisotropy of the metal ion) can be controlled via ligand design. Herein we report a new SIM composed of a HS Mn^{III}-salen-type complex, which displays slow relaxation of the magnetization.

Single crystals of $[Mn^{III}(5\text{-TMAM}(R)\text{-salmen})(H_2O)Co^{III}(CN)_6]\cdot 7H_2O\cdot MeCN$ [**1**; 5-TMAM(*R*)-salmen = (*R*)-*N*,*N*′-(1-methylethylene)bis(5-trimethylammoniomethylsalicylideneiminate] were obtained at the interface between an MeCN solution of $[Mn^{III}(5\text{-TMAM}(R)\text{-salmen})(H_2O)_2](ClO_4)_3\cdot H_2O$ and an aqueous solution of $K_3[Co^{III}(CN)_6]$ allowed to diffuse together. From single-crystal X-ray analysis, **1** consists of a neutral $Mn^{III}-Co^{III}$ unit and seven H_2O and one MeCN molecules. The Mn^{III} center has elongated tetragonal geometry with equatorial positions occupied by an N_2O_2 donor set from 5-TMAM(*R*)-salmen, one apical position occupied by a cyanide N atom of diamagnetic $[Co^{III}(CN)_6]^{3-}$, and the other occupied by an O atom of H_2O. Only one of the six CN groups of the diamagnetic $[Co^{III}(CN)_6]^{3-}$ unit coordinates to the Mn^{III} center (Figure 1).[7] The 5-TMAM(*R*)-salmen ligand adopts an envelope conformation with a torsion angle of 36.6(8)° involving the $N_{imine}-C-C-N_{imine}$ backbone and an average dihedral angle of 17.64° between phenyl rings in the crystal packing. The axial bond distances are much longer than the equatorial ones because of Jahn−Teller distortion. The neutral $Mn^{III}-Co^{III}$ units self-assemble via a one-dimensional hydrogen-bonding network with O−H···N contacts between the H_2O molecule coordinating on the Mn^{III} ion and the one of uncoordinated CN groups of neighboring $Mn^{III}-Co^{III}$ units. Furthermore, the solvents of

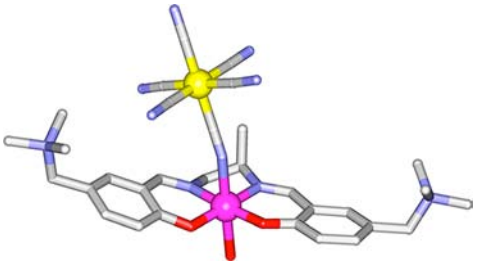

Figure 1. Molecular structure of the $[Mn^{III}(5\text{-TMAM}(R)\text{-salmen})(H_2O)Co^{III}(CN)_6]$ unit in **1**. Purple, yellow, blue, red, and gray balls and sticks represent Mn, Co, N, O, and C atoms, respectively. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg) around the Mn^{III} ion: $Mn-O_{phenolate}$ 1.895(av), $Mn-N_{imine}$ 1.993(av), $Mn-N_{CN}$ 2.228(7), $Mn-O_{water}$ 2.317(6), Mn−Co 5.218(6); $O_{water}-Mn-N_{cyanide}$ 175.16(19), $Mn-N_{cyanide}-C_{cyanide}$ 160.5(5).

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crystallization form intermolecular hydrogen-bonding networks with the free CN groups on the Mn^{III}−Co^{III} units.

From measurements of the temperature dependence of the direct-current (dc) magnetic susceptibility data on polycrystalline samples of **1**, the value of $\chi_M T$ was determined to be 3.0 cm^3 K mol^{-1} at 300 K, which corresponds to a single pure HS Mn^{III} ion ($3d^4$, S = 2) with g = 2.0, and there was no magnetic contribution from the $[Co^{III}(CN)_6]^{3-}$ moiety because of the diamagnetic low-spin (LS) Co^{III} ion. The $\chi_M T$ value remained constant at ∼70 K and then abruptly decreased at lower temperatures (Figure 2). This behavior suggests that there is

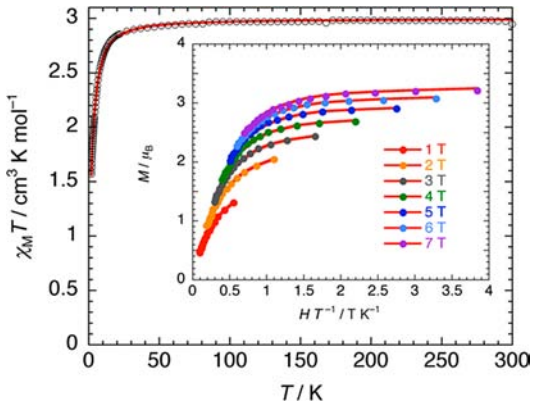

Figure 2. Temperature dependence of $\chi_M T$ for **1** at 1000 Oe. Inset: Field dependence of magnetization curves for **1**, collected from 1.8 to 10 K. The red solid lines represent best-fit curves. The fitting model is described in the text.[8]

appreciable zero-field splitting (ZFS), causing an S_{Mn} = 2 ground state for the Mn^{III} ion, which is typical for other mononuclear HS Mn^{III} derivatives.[8] Indeed, variable-field magnetization data for **1** at lower temperatures could not be superimposed, showing that there is strong magnetic anisotropy of ZFS of the HS Mn^{III} single ion (inset of Figure 2). The magnetic behavior was fit with an isolated S_{Mn} = 2 ground state with an axial ZFS term D_{Mn} of −3.3 cm^{-1}, a mean-field approximation (MFA) zJ' of −0.07 cm^{-1}, and g_{Mn} of 2.0.[8]

High-field and multifrequency (HF/MF) electronic spin resonance (ESR) measurements on polycrystalline samples of **1** at different temperatures were used to confirm directly the presence of a magnetic anisotropic energy gap between each M_S level (Figure S1 in the Supporting Information, SI). In low-frequency fields, the signal intensity increased with a decrease in the temperature, which clearly indicates that $D_{Mn} < 0$,[9] as required for SIMs. Plots of the frequency (ν) versus resonance field (H) from the HF/MF-ESR spectra are shown in Figure S1 in the SI. Extrapolation of the frequency dependence of the signals of the lowest field to H = 0 can be used to estimate the magnetic anisotropy gap because these transitions correspond to the allowed transition $M_S = -2 \leftrightarrow -1$ ($\Delta M_S = 1$). The gap was estimated to be 300 GHz (=10 cm^{-1}; Figure S2 in the SI), and if E = 0, it is equivalent to $-3D_{Mn}$.[10] Thus, D_{Mn} was estimated to be −3.3 cm^{-1} (Figure S3 in the SI), which is consistent with SQUID magnetic studies (vide supra).

From the low-temperature alternating-current (ac) susceptibility data, **1** exhibits slow magnetic relaxation phenomena in the frequency range of 1−1500 Hz in a zero dc field, where in-phase (χ_M') and out-of-phase (χ_M'') components of the ac susceptibility of **1** show strong frequency dependence below 3.0 K (right side of Figure 3). This phenomenon is clearly related to the magnetic anisotropy of the HS Mn^{III} ion of **1**. Various dc fields below 4500 Oe were applied to determine if the magnetic relaxation is suppressed in dc fields as expected in the presence of fast zero-field quantum-tunneling relaxation of the magnetization. Although there was a slight effect, the χ_M'' signals for **1**, which increased with a decrease in the temperature, barely showed any tailing, and the expected maximum value due to blocking could not be observed down to 1.8 K even in an applied dc field of 4500 Oe, as indicated by the divergence of the χ_M'' signals (left side of Figure 3).

Nevertheless, the values of Δ ($=|D_{Mn}|S_{Mn}^2$) from a negative D_{Mn} acting on S_{Mn} for **1** can be estimated from χ_M''/χ_M' versus $1/T$ plots with a semilogarithmic scale at the given frequencies of the ac susceptibility data by using the following equation derived from the Kramers−Kronig equation:[11]

$$\log\left(\frac{\chi_M''}{\chi_M'}\right) = \log(\omega\tau_0) + \frac{\Delta}{k_B T}$$

where ω ($=2\pi\nu$) is the oscillating frequency of the ac field, τ_0 is a preexponential factor of the Arrhenius law $\tau = \tau_0 \exp(\Delta/k_B T)$, k_B is Boltzmann's constant, and T is the temperature.

By fitting the data, the effective Δ (Δ_{eff}) was determined to be ≈9.3 and ≈11.5 cm^{-1} with $\tau_0 = \approx 8.0 \times 10^{-8}$ and $\approx 2.9 \times 10^{-7}$ s in a zero dc field and an applied dc field of 4500 Oe, respectively. The τ_0 values fall within the range typically observed for SIMs

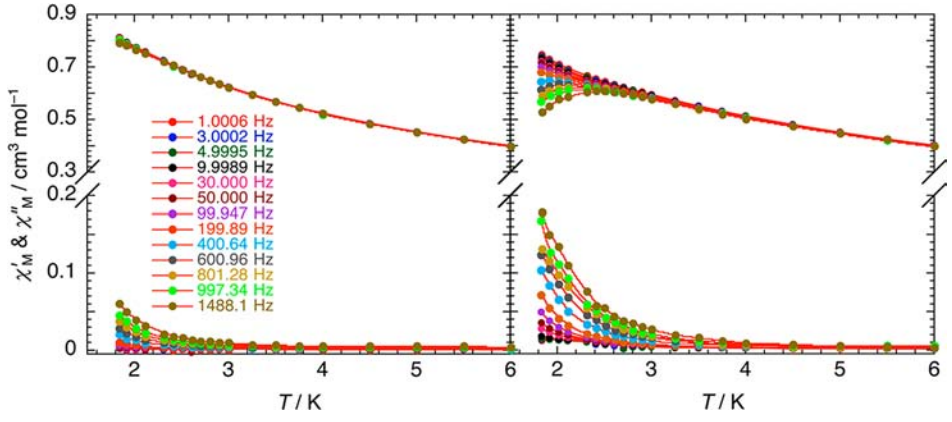

Figure 3. Temperature dependence of the ac susceptibilities (χ_M' and χ_M'') of **1** in the frequency range of 1−1500 Hz in an oscillating ac magnetic field of 5 Oe in a zero dc field (left) and an applied 4500 Oe dc field (right). The red solid lines serve as guides to the eye.

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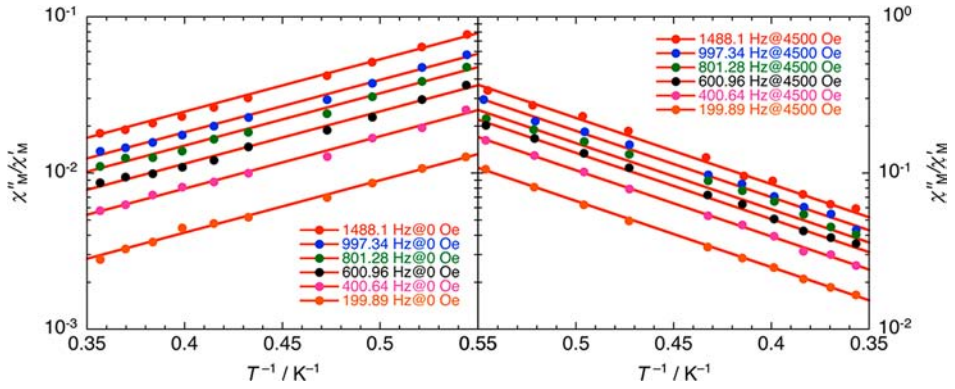

Figure 4. χ_M''/χ_M' versus $1/T$ plot for **1** at different frequencies with a semilogarithmic scale. The red solid lines were fitted as described in the text.

and SMMs (Figures 4 and S4 in the SI). Therefore, **1** is an SIM rather than a three-dimensionally ordered magnet.

In summary, SIM features of a new tricationic Mn^{III}-salen-type complex with diamagnetic $[Co^{III}(CN)_6]^{3-}$ moieties were determined. On the basis of dc magnetic susceptibility and magnetization studies, **1** has significant uniaxial anisotropy for an isolated $S_{Mn} = 2$ with $D_{Mn} = -3.3\ cm^{-1}$ and $g_{Mn} = 2.0$, which was supported by HF/MF-ESR studies on powdered samples. Consequently, the observed uniaxial magnetic anisotropy leads to slow magnetic relaxation, as evidenced by frequency-dependent ac magnetic susceptibilities.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, experimental section, physical measurements, crystallographic data, and data of HF/MF-ESR spectral details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

All authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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$$\mathcal{H} = \mathcal{H}_{ZFS} + \mathcal{H}_{MFA} + \mathcal{H}_{Zeeman}$$

where $\mathcal{H}_{ZFS} = D_{Mn}[S_z^2 - ([S(S+1)]/3)]$, $\mathcal{H}_{MFA} = -J'S_{Mn}\langle S_{Mn}\rangle$, and $\mathcal{H}_{Zeeman} = g_{Mn}\mu_B S_{Mn}H$. (a) Kennedy, B. J.; Murray, K. S. *Inorg. Chem.* **1985**, *24*, 1552. (b) Baba, H.; Nakano, M. *Polyhedron* **2009**, *28*, 2087.

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