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Spin-Relaxation Properties of a High-Spin Mononuclear $Mn^{III}O_6$-Containing Complex

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S *Supporting Information*

ABSTRACT: The magnetic properties of the mononuclear manganese(III) complex $[Mn\{(OPPh_2)_2N\}_3]$ are investigated by means of magnetometry and dual-mode X-band electron paramagnetic resonance spectroscopy. Slow relaxation of magnetization is induced in the presence of external magnetic fields.

After the first observation of slow relaxation of magnetization in a 4f-based mononuclear complex,[1] the number of mononuclear single-molecule magnets has been increasing, constituting a subclass of molecular magnetic materials. During the past few years, investigations have been expanded to systems containing 3d metal ions and research has focused mainly on iron and cobalt complexes.[2] Relevant studies with mononuclear manganese(III) complexes are still missing from the literature. Octahedral manganese(III) complexes are usually Jahn−Teller distorted, and the ^5E ground state ($t_{2g}^3e_g^1$) is split into B_{1g} and A_{1g}. Tetragonal elongation results in a B_{1g} ground state that typically shows negative zero-field-splitting (ZFS) parameters, leading to a ground state of uniaxial anisotropy.[3] Therefore, it is worth further exploring the magnetic relaxation properties of mononuclear high-spin manganese(III) complexes.

Very recently, Ishikawa et al. reported on the magnetic relaxation properties of a dinuclear $[Mn^{III}Co^{III}]$ complex in which the high-spin Mn^{III} center is bridged via CN^- to a diamagnetic Co^{III} center.[4] Herein, we report on the synthesis and spin-relaxation properties of the genuine mononuclear octahedral manganese(III) complex $[Mn\{(OPPh_2)_2N\}_3]$ (**1**). The presence of three $[(OPPh_2)_2N]^-$ ligands gives rise to a MnO_6 coordination sphere, similar to that found in $[Mn(acac)_3]$ (acac = acetylacetonato)[3a,5] and in other systems as well.[6] It should be noted that because $[Mn(acac)_3]$ crystallizes in multiple forms[3a,5] the investigation of its magnetic properties is complicated. Dichalcogenated imidodiphosphinato ligands, $[R_2P(E)NP(E')R_2]^-$, can be easily modified,[7] allowing for the investigation of the potential effects of the first (E, E′ = O, S, Se, Te) and second (R = aryl or alkyl group) coordination spheres on the magnetic properties of the corresponding manganese(III) complexes. The crystal structure of **1** has been previously reported; however, the crystals were deposited during unsuccessful attempts to crystallize $[Mn^I(CO)_4\{(OPPh_2)_2N\}]$ in air.[8] Herein, complex **1** was synthesized purposely in order to investigate its magnetic properties. The synthesis of **1** was carried out either by oxidation of a Mn^{II} salt in the presence of a base or, preferably, by substitution of all three acetylacetonato ligands of $[Mn^{III}(acac)_3]$ by $Ph_2P(O)NHP(O)Ph_2$, in CH_2Cl_2.

Purple-blue crystals of **1** were obtained from a CH_2Cl_2/*n*-hexane solution. Complex **1** crystallizes in space group $P\bar{1}$, revealing the same unit cell (Table S1 in the SI) with the published structure.[8] Selected bond lengths and angles are listed in Table S2 in the SI. The MnO_6 coordination sphere of **1** exhibits a tetragonal elongation along the O1−Mn−O5 axis (Figure 1). In the crystal structure presented in this work, the O1−Mn−O5 angle is 179.9° and the axial Mn−O bonds [av. 2.159 Å] are 0.226 Å longer than the equatorial Mn−O bonds [av. 1.933 Å]. The O−Mn−O angles within the equatorial plane are not equal because two of them are smaller whereas the other two are larger than 90°, indicating distortion of the equatorial plane as well. Each MnO_2P_2N metallacycle adopts a distorted boat conformation, with the Mn and N atoms occupying the apexes in order to accommodate the smaller bite of the octahedral geometry.[9] The shortest distance between neighboring Mn^{III} centers is 9.87 Å; hence, they are not expected to magnetically interact with each other. No obvious intermolecular

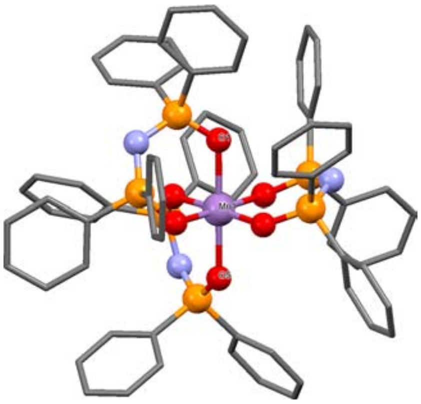

Figure 1. Crystal structure of **1** in which the O1, Mn1, and O5 atoms define the Jahn−Teller axis.

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interactions (for instance, the $\pi-\pi$ type) are observed between the aromatic rings of the ligands.

The temperature dependence of the $\chi_M T$ product of a powdered sample of **1** is shown in Figure 2. The inset displays the field dependence of magnetization at 2.0, 5.0, and 10.0 K. At room temperature, $\chi_M T$ (=3.0 cm^3 mol^{-1} K) is consistent with an isolated Mn^{III} ion with $S = 2$ and $g = 2.0$. As the temperature is lowered, $\chi_M T$ remains constant until ~30 K and then decreases abruptly at liquid-helium temperatures. This behavior is due to combined Zeeman and ZFS effects expressed by the following spin Hamiltonian:

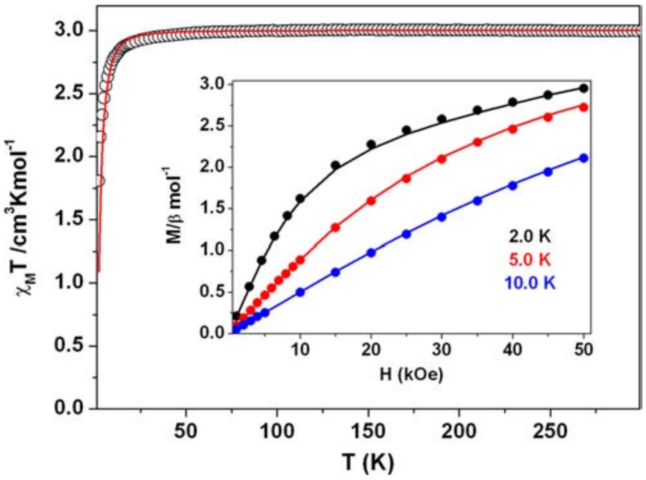

Figure 2. Temperature dependence of $\chi_M T$ of a powdered sample of **1** at 10 kOe. Inset: Field dependence of magnetization. The solid lines are simulations on the basis of eq 1, as described in the text.

$$H = D[S_z^{\,2} - 2] + E[S_x^{\,2} - S_y^{\,2}] + O(4) + g\beta S\mathbf{H} \qquad (1)$$

in which D and E are the axial and rhombic ZFS parameters, respectively, whereas $O(4)$ accounts for the fourth-order terms.[3a]

The best simulations of the $\chi_M T$ versus T and M versus H curves were obtained for $D = -3.4$ cm^{-1} and $g = 2.0$. The simulations are insensitive to variations of the term E and/or fourth order terms, the involvement of which is shown by dual-mode X-band electron paramagnetic resonance (EPR) spectroscopy. The negative sign of D is compatible[3] with the tetragonal elongation of the MnO$_6$ octahedron (Figure 1).

Dual-mode X-band EPR spectroscopy is useful in the study of mononuclear high-spin manganese(III) complexes.[3a,10] In Figure 3, the 4.2 K dual-mode X-band EPR spectra of a powdered sample of **1** are shown (see also Figure S2 in the SI). In perpendicular mode (Figure 3, top), a broad peak at $g \sim 8.2$ is observed that could arise from a high-spin Mn^{III} center.[11] Compelling evidence that the signal does arise from such a species is provided by spectra recorded in parallel mode (Figure 3, bottom). In this mode, the signal at $g \sim 8.2$ is much stronger compared with the one in perpendicular mode, proving that it arises from a non-Kramers doublet.[12] The signals are readily attributed to the $|\pm 2\rangle$ non-Kramers doublet of the $S = 2$ system. Their temperature dependence (Figures S3 and S4 in the SI) reveals that the corresponding transitions arise from a ground state, corroborating the negative sign of D. In an ideal D_{4h} symmetry, transitions within the $|\pm 2\rangle$ doublet are strictly forbidden and the system is EPR-silent. The very fact of the observation of such transitions indicates deviations from this symmetry, suggesting involvement of the rhombic E and/or fourth-order ZFS terms of eq 1.

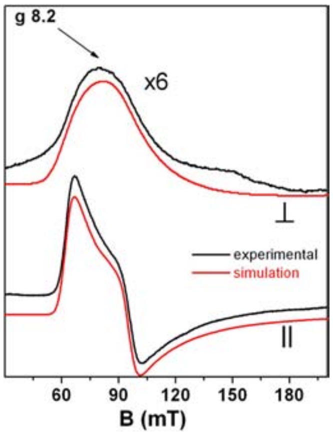

Figure 3. Experimental (black lines) and theoretical (red lines) dual-mode X-band EPR spectra of a powdered sample of **1** at 4.2 K.

Herein, we consider the effect of E to reproduce the X-band EPR spectra. The signals depend upon the parameters D, E/D, and g_z.[12] For analysis of the spectra, it is also required to take into account the term between the electronic spin and the ^{55}Mn ($I = {}^5/_2$) nucleus through the interaction $H_{hf} = I\mathbf{A}S$. No resolved hyperfine lines were observed in the 4.2 K spectra, but a partially resolved six-line hyperfine pattern was evidenced in the parallel-mode spectra at higher temperatures (Figure S5 in the SI). The hyperfine term affects the line shapes of the signals. In addition, the line shape is influenced by possible distributions of the ZFS parameters. The value of D (=−3.4 cm^{-1}) was taken by analysis of the dc magnetic susceptibility measurements, whereas g_z was set to 2.0. The spectra are reproduced by $E/D = 0.11$ (±0.01), $A_z = 155$ MHz, a Gaussian distribution of E/D with a width of $\sigma_{E/D} = 0.015$, and a residual line width of 1.0 mT. The A_z value is similar to the one found for other tetragonally elongated Mn^{III}O$_6$-containing systems.[3a,10] A full description of the EPR properties of **1** with the possible involvement of fourth-order terms awaits ongoing studies at high frequencies and fields. Nevertheless, the present simulations indicate involvement of terms that lead to mixing of the spin states.[13] This mixing is crucial for the magnetic relaxation properties reported below.

The relaxation properties of **1** were studied by means of alternating-current (ac) magnetic susceptibility measurements. In the absence of a dc magnetic field, the imaginary part of the susceptibility χ'' is negligible down to 1.9 K even at the highest available frequency (~9 kHz; Figure S6 in the SI). Analysis of the X-band EPR spectra indicates involvement of terms that favor quantum tunneling of magnetization through mixing of the states.[13] In the presence of dc magnetic fields, quantum tunneling is suppressed and χ'' exhibits nonzero values accompanied by a decrease in the real part of the susceptibility, χ'. The strongest χ'' signals were observed for $H_{dc} > 2.0$ kOe; representative plots of the dependence of χ' and χ'' on the temperature for various frequency values at 2.25 kOe are shown in Figure 4. Data collected at different dc magnetic fields are shown in Figure S7 in the SI. The temperature dependence of both χ' and χ'' indicates a thermal activation process for spin relaxation. No maxima in the χ'' versus T curves are observed down to 1.9 K, indicating lower blocking temperatures.

In order to estimate the temperature dependence of the spin relaxation, the dependence of the quantity $\ln(\chi''/\chi')$ as a function

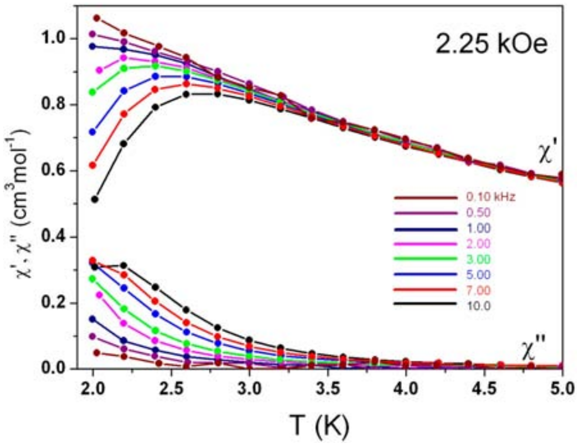

Figure 4. Temperature and frequency dependences of the real (χ') and imaginary (χ'') parts of the magnetic susceptibility of a powdered sample of **1** with a H_{dc} = 2.25 kOe. The solid lines are guides to the eye.

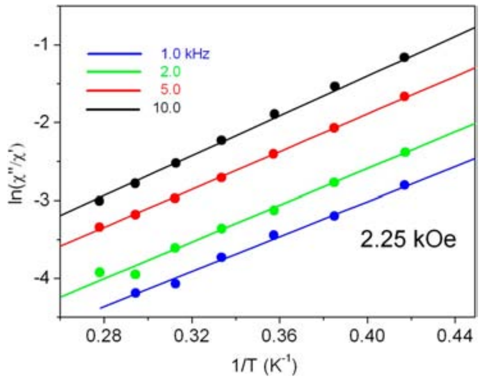

Figure 5. ln(χ''/χ') versus $1/T$ plots for H_{dc} = 2.25 kOe. The solid lines are fits obtained by eq 2.

of $1/T$ for various values of the dc magnetic field was examined. In Figure 5, representative plots are shown, with data obtained at a magnetic field of 2.25 kOe. Similar plots obtained for different dc magnetic fields are shown in Figure S8 in the SI. These studies reveal that ln(χ''/χ') depends linearly on $1/T$ in the 2.3−3.5 K temperature range. Such linear dependence will be observed if the relaxation time obeys the Arrhenius law $\tau = \tau_0 e^{\Delta/kT}$, with τ_0 being a preexponential factor and Δ representing an effective barrier for the reversal of magnetization through the relationship[14]

$$\ln(\chi''/\chi') = \ln(2\pi\nu\tau_0) + \Delta/k_bT \quad (2)$$

From analysis of the experimental data on the basis of eq 2 for various values of the dc magnetic field, the values for τ_0 and Δ were obtained (Table S3 in the SI). τ_0 of the order of 10^{-7} s, is compatible with paramagnetic relaxation involving transition-metal ions. On the basis of the ZFS values, the calculated thermal barrier is Δ_{calc} ($\sim 4|D|$) ~ 13.6 cm^{-1}. Analysis of the ac magnetic susceptibility measurements suggests a smaller value ($\Delta \sim 8$ cm^{-1}). This lowering Δ can be associated with quantum tunneling due to the effect of the rhombic and/or fourth-order terms.

In summary, the present work and the recent report by Ishikawa et al.[4] demonstrate that high-spin single manganese(III) complexes exhibit relaxation behavior akin to 3d-metal-based mononuclear single-molecule magnets previously established only for certain iron and cobalt complexes.[15]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, synthesis and crystallographic/spectroscopic characterization of **1**, physical measurements, additional EPR spectra and magnetic data, and additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions by all authors.

Notes

The authors declare no competing financial interest.

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