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# A Mixed 3d−4f 14-Metallacrown-5 Complex That Displays Slow Magnetic Relaxation through Geometric Control of Magnetoanisotropy

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We describe the synthesis and magnetic properties of a unique mixed 3d−4f 14-metallacrown-5 complex. This is the first metallacrown family to feature $\mu$-O and $\mu$-OH bridges as well as to incorporate a $\mathrm{Ln^{III}}$ ion into the ring. Alternating-current SQUID magnetometry of the Tb, Dy, and Ho derivatives reveals slow magnetic relaxation, a hallmark property of single-molecule magnets. For the Dy structure (**4**), an effective energy barrier $U_{\mathrm{eff}}$ of 16.7 K and a relaxation time of $4.9 \times 10^{-8}$ s were calculated. Because of the relatively small total spin, this behavior most likely results from a large magnetoanisotropy, which is controlled through geometric constraints.

The tremendous interest in creating large metallamacrocycles, such as the metallacrown (MC) family of clusters, has been based on the promise of multifunctional properties associated with such metal-rich complexes.[1] First described in 1989,[2] the number of reported structures and various uses of MCs have grown dramatically over the past 2 decades.[1,3] MCs can be described as inorganic analogues of crown ethers, in that both MCs and crown ethers have a central cavity available to bind cations. However, MCs distinguish themselves from crown ethers by the presence of metals and heteroatoms in the ring that can allow for the exploitation of properties not available to organic structures. One example is interesting magnetic behavior, achievable through the incorporation of metals with unpaired spins into this framework.

Since the first reported single-molecule magnet (SMM) by Christou, Hendrickson, Gatteschi, and co-workers in 1993,[4] there have been countless additional SMMs reported.[5] In recent years, many mixed 3d−4f SMMs have been identified.[6] The logic behind these molecules is that lanthanides inherently provide large amounts of anisotropy to a system[7] as well as a large number of unpaired spins. Lanthanides are well-isolated from neighboring magnetic atoms because of their contracted valence orbitals, limiting the possibility of antiferromagnetic exchange. The utility of this approach has been shown by the introduction of a lanthanide into a system with a high total spin, but that did not display SMM behavior, in order to induce SMM behavior.[6d]

Few SMMs have been designed from the outset to maximize anisotropy through structural control.[7] This lack of geometric control has led to materials with extremely large spin values ($S$)[6c] that do not behave as SMMs because there is no (or positive) Ising-type magnetoanisotropy ($D$). To circumvent this issue, we sought to utilize the MC structure, known to create planar structures,[2a,5,6f] aligning the easy-axes parallel to each other, in order to create an SMM. Herein, we report the preparation, single-crystal X-ray structure, and magnetic measurements

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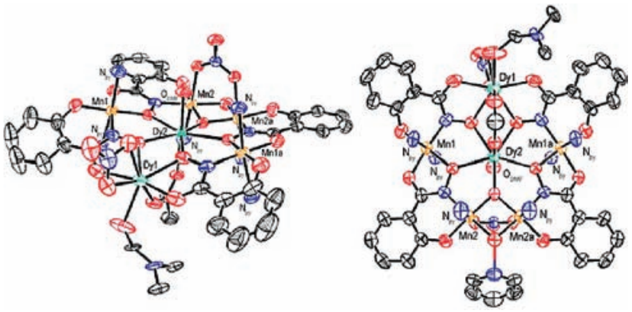

**Figure 1.** ORTEP diagram of **4** with ellipsoids at the 50% probability level. Color code: black, carbon; blue, nitrogen; red, oxygen; aqua, $Dy^{III}$; orange, $Mn^{III}$. Coordinated solvents are emitted for clarity. See Figure S1 in the Supporting Information for a full description.

of $[Ln^{III}(O_2CCH_3)(NO_3)_2$ 14-$MC_{Mn(III)Ln(III)(\mu\text{-}O)(\mu\text{-}OH)N(shi)}$-5]$\cdot 3C_3H_7NO\cdot 7C_5H_5N\cdot H_2O$ [$shi^{1,2}$ = salicylhydroximate$^{3-}$; Ln = $Y^{III}$ (**1**), $Gd^{III}$ (**2**), $Tb^{III}$ (**3**), $Dy^{III}$ (**4**), and $Ho^{III}$(**5**)]. This is a new MC class containing two lanthanides as well as four $Mn^{III}$ ions. High-spin $Mn^{III}$ is known to be highly anisotropic as well as contribute four unpaired d electrons. It was believed that these $Mn^{III}$ ions, in addition to $Ln^{III}$ ions, would lead to a complex that had both large spin and large molecular anisotropy. Of these MCs, only the $Gd^{III}$ and $Y^{III}$ examples did not display frequency dependence in an alternating magnetic field, a requirement for SMM behavior.

$Ln^{III}$ 14-MC-5 (Figure 1) is unique among the described MCs. Unlike other M−N−O MCs, 14-MC-5 lacks a pseudo-$C_n$; instead, it has a $\sigma_v$. This new MC class differs from previous structures featuring cyclic M−N−O repeats; a connectivity of [M−N−O−M−N−O−Ln−O−N−M−O−N−M] is observed. It is the only MC to incorporate a lanthanide in the MC ring. It is also the first M−N−O MC to incorporate both $\mu$-O and $\mu$-OH in the ring. While many mixed-metal[1b,8] and mixed-ligand[1b,8a] MCs are known, this also represents the first MC with the inclusion of one metal that differs from the other ring metals. Winpenny and co-workers have shown molecular wheels with monosubstituted metals that have interesting magnetic properties, so we felt that a monosubstituted MC would also merit magnetic investigation.[9]

The $Ln^{III}$ 14-MC-5 has a plane of symmetry running down the $Ln^{III}$, $Ln^{III}$, oxo, and hydroxo plane. Two $Mn^{III}$ ions on each half of the molecule are connected through this M−N−O connectivity found in other MCs, while the two identical $Mn^{III}$ ions on either side of the mirror plane are connected by a $\mu$-OH, which is hydrogen-bonded to a solvent pyridine (1.935 Å), a nitrate, and an $\mu$-O that bonds with the two $Mn^{III}$ as well as the $Ln^{III}$. All four Mn ions are $Mn^{III}$ by virtue of a Jahn−Teller elongation along the axis of a distorted octahedron, which are all parallel to each other and perpendicular to the MC plane.

The equatorial plane Mn1 is comprised of a six-membered iminophenolate ring from one $shi^{3-}$ ligand and a five-membered hydroximate ring from another $shi^{3-}$ ligand. The axial positions are occupied by pyridines. The equatorial plane of Mn2 is also comprised of a six-membered ring, but the other two axial positions are occupied by an oxo ligand and a hydroxo ligand. This can also be seen by the bond lengths because the bound hydroxo has a Mn−O bond length of 1.925 Å while the oxo has a Mn−O bond length of 1.876 Å. The axial positions are occupied by a pyridine and a nitrate bridging its symmetry-related Mn ion.

The two lanthanides fall on the mirror plane of the molecule. Ln1 is above the plane of the molecule by 1.734 Å. Ln1 is eight-coordinate, bound by two five-membered hyroximate rings, a dimethylformamide (DMF), an $\eta_2$-nitrate, and an acetate, which bridges it to Ln2. Ln2 is seven-coordinate, with four equatorial sites occupied by oxygen atoms from the hydroximate of the $shi^{3-}$ ligand and the fifth equatorial spot occupied by an $\mu_3$-oxo that bridges the symmetry-related Mn ions. The axial positions are occupied by the acetate bridge shared with Ln1 and by a coordinated DMF. Ln2 is only 0.30 Å above the plane. Thus, only at the fifth metal of the MC ring is the structure not planar. The planarity of the molecule is important because the likelihood of anisotropy vectors canceling each other decreases significantly.

From direct-current (dc) SQUID magnetometry conducted at an applied field of 2000 G, it was found that, for **3** and **4**, $\chi_M T$ remained nearly level from 300 to 10 K. Below 10 K, the curve decreased rapidly, indicative of antiferromagnetic coupling in the complex. For **5** at the same applied field, there was a continuous decrease in the $\chi_M T$ curve as the temperature decreased from 300 to 8 K, possibly indicating the presence of low-lying excited states. Below 8 K, the $\chi_M T$ curve decreased dramatically, as has been seen in the other samples (see the Supporting Information). For **1**, a Hamiltonian describing the coupling is given in Figure S22 in the Supporting Information.

In addition to variable-temperature studies, variable-field studies were conducted in an attempt to elucidate the ground spin state of the complexes. Because of the large amount of *jj* coupling normally associated with lanthanides, the ground spin states could not be determined because the samples' magnetization did not saturate. Regardless, complexes **3**−**5** showed very large magnetization values at 5.0 K and an applied field of 55 000 G: 75 913, 87 419, and 104 498 G cm$^3$ mol$^{-1}$, respectively (see the Supporting Information).

Using the imaginary component of the magnetic susceptibility, one can determine through frequency dependence if a given compound is behaving like an SMM and estimate the effective energy barrier $U_{eff}$. For **1** and **2**, there is no frequency dependence in the out-of-phase component. For **4**,[10] there is strong frequency dependence at all frequencies. Because the

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(10) Crystals of **4** have been structurally characterized with a formula of $[Dy_2Mn_4(O_2CCH_3)(NO_3)_2(shi^{3-})_4(O)(OH)]\cdot 8C_5H_5N\cdot 3C_3H_7NO\cdot H_2O$. Elem anal. Calcd for **4**: $C_{79}H_{83}N_{17}O_{26}Mn_4Dy_2$ (fw = 2231.38): C, 42.52; H, 3.75; N, 10.67. Found: C, 42.35, 42.46; H, 3.60, 3.60; N, 10.69, 10.63. Crystal data for **4**: $M_r$ = 2231.38, crystal dimensions (mm) 0.06 × 0.04 × 0.01, orthorhombic, space group *Pnnm* (No. 58), $a$ = 29.125(4) Å, $b$ = 16.760(3) Å, $c$ = 18.514(3) Å, $\alpha = \beta = \gamma$ = 90.00°, $V$ = 9037(2) Å$^3$, $Z$ = 4, $\rho_{calc}$ = 1.640 mg m$^{-3}$, $\mu$ = 2.827 mm$^{-1}$, $T$ = 150 K, synchrotron ($\lambda$ = 0.774 90 Å), $2\theta$ = 49.348°, 9569 unique of 98 380 reflections collected. A total of 9569 reflections and 729 parameters were used for the full-matrix least-squares refinement of $F^2$, $R_{int}$ = 0.1291, R1 = 0.0519 [$I > 2\sigma(I)$], R1 = 0.0904 (all data); wR2 = 0.1332 [$I > 2\sigma(I)$], wR2 = 0.1538 (all data). Further details are given in the Supporting Information. CCDC 774866 (**4**) contains the supplementary crystallographic data for this paper. The atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

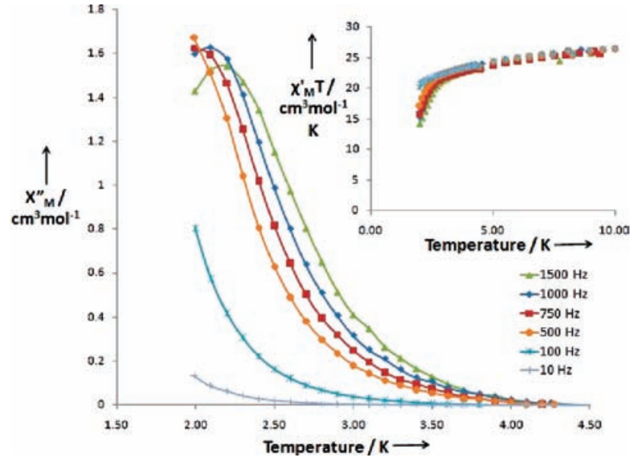

**Figure 2.** Out-of-phase magnetic susceptibility of **4**. Inset: In-phase magnetic susceptibility of **4**.

maximum of the $\chi''_{\mathrm{M}}$ vs $T$ plot corresponds to the blocking temperature, one can determine the barrier height of **4**. Using the Arrhenius equation [$\tau = \tau_0 \exp(U_{\mathrm{eff}}/k_{\mathrm{B}}T)$], one can determine the barrier of the spin double well at the corresponding temperature. For **4**, $U_{\mathrm{eff}}$ was 16.7 K with a $\tau_0$ of $4.9 \times 10^{-8}$ s (Figure 2). The calculated $U_{\mathrm{eff}}$ is one of the largest measured for Mn/Ln$^{\mathrm{III}}$ SMMs and $\tau_0$ is similar to that of other reported Mn/Ln$^{\mathrm{III}}$ complexes.[6,11] Both **3** and **5** show a weak frequency dependence. However, because the maximum of the peak was not observable within our SQUID's temperature range, we cannot determine $U_{\mathrm{eff}}$. Because of the extremely low observed blocking temperatures of **3**−**5**, we were unable to perform hysteresis experiments to definitively characterize these complexes as SMMs. Subsequently, it is extremely difficult to observe if quantum tunneling of magnetization is a major factor in the low blocking temperatures. Only one other group[6c−e,11] has systematically altered the Ln$^{\mathrm{III}}$ ion in a Mn/Ln$^{\mathrm{III}}$ SMM with the intent of determining the impact of the Ln$^{\mathrm{III}}$ choice on single-molecule magnetism.

From these experiments, one can see the importance of the choice of Ln$^{\mathrm{III}}$ on the SMM properties. Complexes **3**−**5** all displayed slow magnetic relaxation, while **1** and **2** did not. Additionally, **4** showed the highest blocking temperature. All of these complexes are isostructural, so the effect of changing the symmetry or coordination environment on the magnetism is essentially minimized. We can conclude from **1** that the MC itself is not an SMM simply because of the presence of Mn$^{\mathrm{III}}$. We can also conclude that it is not sufficient to simply "add" spin to the complex by incorporating Gd$^{\mathrm{III}}$. Rather, the slow magnetic relaxation behavior of the complex depends on both the spin and anisotropy components of Ln$^{\mathrm{III}}$. This is not unique to this system because Powell and co-workers have seen similar results with their complexes.[6d] They too reported that the Dy$^{\mathrm{III}}$ analogue showed the highest blocking temperature, suggesting that Dy$^{\mathrm{III}}$ may have the right "blend" of spin and anisotropy needed for effective SMMs.

In conclusion, we have prepared and characterized a new structure class of MCs that contain the first examples of Ln$^{\mathrm{III}}$ ion in the ring, $\mu$-OH and $\mu$-O bridges, and a monosubstituted ring metal. By systematically varying the Ln$^{\mathrm{III}}$ ions, we demonstrated that certain Ln$^{\mathrm{III}}$ 14-MC-5's exhibit slow magnetic relaxation consistent with being SMMs. The optimal behavior was obtained with Dy$^{\mathrm{III}}$, yielding the second highest energy barrier reported for an Mn/Ln$^{\mathrm{III}}$ SMM. We see by comparison that reasonable unpaired spin and single-ion anisotropy are requisite for the desired magnetic properties. The Ln$^{\mathrm{III}}$ 14-MC-5 class demonstrates that one may use fewer metals (compared with the complex having the highest Mn/Ln$^{\mathrm{III}}$ effective barrier to relaxation[6d]) and still achieve a reasonable performance through geometric considerations. This should encourage the development of new complexes that feature geometric control rather than large metal concentrations.

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**Supporting Information Available:** Experimental preparation, crystal structure data of **1**−**3** and **5**, dc magnetic susceptibility and magnetization data of **1**−**5**, ac SQUID magnetic susceptibility for **1**−**3** and **5**, predicted ground spin states, a spin-exchange Hamiltonian, and crystallographic data for **1** and **3**−**5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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