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From Serendipitous Assembly to Controlled Synthesis of 3d–4f Single-Molecule Magnets

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Supporting Information

ABSTRACT: Learning from serendipitous assembly, we have prepared a new family of designed 3d–4f Mn_6Ln complexes. The dynamics of relaxation of the magnetization via alternating-current magnetic susceptibility for the new Mn_6Ln complexes **1** (Ln = La), **2** (Ln = Tb), and **4** (Ln = Dy) have been studied down to 0.2 K.

Serendipitous self-assembly[1] is a widely accepted synthetic method to obtain high-nuclearity coordination complexes. Clearly, the serendipitous self-assembly route does not allow chemists to predict the outcome of the reaction; however, the chemist can take control once the serendipitous self-assembly product has been identified. The syntheses of complexes as large as Mn_{84}[2] or Mn_{12}[3] are usually uncontrolled processes. In fact, the interest in high-nuclearity complexes of the first-row transition metals is largely due to the discovery of the single-molecule-magnet (SMM) properties of Mn_{12} in the early 1990s by Christou and co-workers[4] and Gatteschi and co-workers.[5] Mn_{12} and later Fe_8[6] were found to behave as magnets at the molecular level, being able to retain magnetization after removal of an applied field below the blocking temperature, T_B. Since then, many efforts have been devoted to raising the operating temperature of SMMs. One of the strategies proposed has been to mix first-row transition metals with Ln ions in order to attempt an improvement on the magnetic properties of the prepared complexes. Many groups have devoted much effort in preparing 3d–4f complexes and studying the magnetic properties, even though the understanding of the 3d–4f magnetic interaction is still far from satisfactory.[7] In 2004, the first mixed 3d–4f SMMs were reported.[8] Since then, many 3d–4f SMMs have been reported,[9,10] in the search for an enhancement of the SMM properties observed in transition-metal complexes. One of such examples is Powell's $Mn_{18}Dy$, in which the SMM properties are triggered when Dy^{III} is incorporated into a Mn_{19} complex by directed synthesis.[11] However, the expected breakthrough of better, usable SMMs has not been achieved yet. The synthetic methodologies are still mostly based on serendipitous assembly. In our group, we have been interested in finding new ways of preparing coordination complexes and have studied nonconventional synthetic methods like solid-state decomposition[12] or microwave-assisted synthesis applied to coordination chemistry.[13] In 2013, we reported a Mn_7 complex prepared using a substituted salicylato ligand.[14] In particular, we were interested in improving the solubility, crystallinity, and volatility of the prepared complexes, so we investigated the coordination chemistry of 3,5-di-*tert*-butylsalicylic acid ($SALOH_2$ from now on). During our studies, we isolated the complex $[Mn_7(OH)_3(C_5H_{12}NO)_2(C_5H_{13}NO)(SALO)_6(SALOH)_3]$. The compound contains three Mn^{III}_2 units around a central Mn^{II} ion, which is in a very distorted coordination environment. The central Mn^{II} ion is in a large cavity of about 50 $Å^3$ (taking the cavity as an ideal sphere with a radius equal to the shortest Mn–O distance). The Mn^{II} ion is coordinated to two O atoms with a Mn–O distance of 2.293 Å, three O atoms with $d = 2.446$ Å, and three O atoms with $d = 2.507$ Å. The structure of this complex could not be predicted by looking at the reaction reagents, and it was a new example of serendipitous self-assembly, leading us to new structural types in coordination chemistry. However, it was clear that the central Mn^{II} ion was not "comfortable" because the central cavity of the complex was much better suited for a larger ion, like a Ln.

Given the interesting magnetic properties of the Mn_7 complex, which displayed the tail of an out-of-phase peak in the alternating-current (ac) magnetic susceptibility,[14b] substitution of the central Mn(II) ion by a Ln ion seemed to be an interesting option: first, in order to see if a design element could be introduced in this complicated coordination chemistry and, second, to study the effect of a Ln ion in the magnetic properties. We studied the same reaction system mixing manganese and lanthanide (La^{III}, Tb^{III}, Gd^{III}, and Dy^{III}) salts, and as we had predicted, new mixed 3d–4f complexes were obtained in which the central Mn^{II} position is now occupied by a Ln^{III} ion (Ln = La, **1**; Tb, **2**; Gd, **3**; Dy, **4**). To substitute Mn^{II} by a Ln^{III} ion, one must take into account the different charges in the complex: in the new complexes, the amino alcohol ligands coordinated in Mn_7 have been substituted by uncoordinated dipropylammonium cations, and the bridging OH^- groups of Mn_7 are now monatomic oxo groups. This was taken into account and the experimental procedure optimized to obtain the new complexes **1**–**4**. We have been able to introduce an important component of design in a coordination chemistry reaction after learning from

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the serendipitous assembly product. We will describe here the crystal structure of complex **1**, shown in Figure 1. Complexes **1**–**4** are isostructural, with formula [*n*-$PrNH_2$]$_3$[$Mn_6LnO_3(OMe)_3(SALO)_6(SALOH)_3$] (Ln = La, **1**; Tb, **2**; Gd, **3**; Dy, **4**). For charge balance, three protonated dipropylammonium cations from the weak base used in the reactions are necessary. The complexes crystallize in the monoclinic space group $P2_1/n$, and the asymmetric unit consists of one Mn_6Ln anion, three protonated dipropylammonium cations, and disordered solvent molecules. Crystallographic data are summarized in Table S1 in the Supporting Information (SI). For complex **4**, Mn_6Dy diffraction data were poor and only the Mn–Dy core could be elucidated. Three Mn^{III}_2 units are arranged around a central La^{III} ion. The La^{III} ion displays coordination number 9 and is linked to the three Mn^{III}_2 units by three μ_3-O ions and three O atoms from fully deprotonated SALO ligands (see the SI for a scheme with the coordination modes of the SALO and SALOH ligands). The oxidation state of the Mn ions was checked by bond valence sum calculations and close examination of the structural parameters. The six Mn^{III} ions display Jahn–Teller elongations and are hexacoordinated in a distorted octahedral fashion. In each Mn^{III}_2 unit, the Mn ions are bridged by one μ_3-O and one μ-OMe, with Mn–O–Mn angles from 89° to 104°. The three protonated dipropylammonium cations are strongly hydrogen-bonded to the Mn_6Ln complex. Thus, when electrospray ionization mass spectrometry (ESI-MS) spectra of the complexes were collected, two of the cations were still attached to the Mn_6Ln anion. The ESI-MS spectra confirmed the presence of six Mn and one Ln (La in **1**, Tb in **2**, Gd in **3**, and Dy in **4**) because the isotopic pattern calculated matches the observed spectra in all cases (see the SI for the spectra).

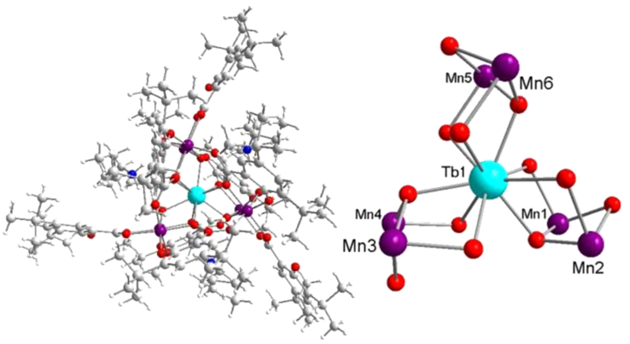

Figure 1. Crystal structure of the anion of complex **2** and the labeled core of complex **2**.

The magnetic properties of complexes **1**–**4** were studied on a Quantum Design SQUID magnetometer. Direct-current (dc) magnetic susceptibility data showed that, as the temperature decreased, the χT product increased, except for complex **4**. In the case of complex **1**, the magnetic response was only due to the six Mn^{III} centers, while for complexes **2**–**4**, the coupling of the six Mn^{III} ions to the paramagnetic Ln^{III} center was also reflected, along with the thermal depopulation of the Stark sublevels of Tb^{III} ($^7F_6$, $S = 3$, $L = 3$, $J = 6$, and $g_J = {}^3/_2$) and Dy^{III} ($^6H_{15/2}$, $S = {}^5/_2$, $L = 5$, $J = {}^{15}/_2$, and $g_J = {}^4/_3$) in complexes **2** and **4**. The exchange coupling in complex **1** is primarily ferromagnetic, as is also the case for complexes **2** and **3**, but for complex **4**, there seems to be either weaker coupling between the Dy^{III} and Mn^{III} ions or some antiferromagnetic coupling mediated by the Dy^{III} ion. Using the software *PHI*,[15] the susceptibility data for complex **1**, Mn_6La, were fitted to a model of three independent Mn^{III}_2 units. This is a very simple model that does not take into account the coupling between the Mn^{III} units, which are bridged by *syn*,*anti*-carboxylato groups and could be mediated by the diamagnetic La^{III} cation.[16]

The fitting parameter was $J = +5.0\ cm^{-1}$, and the single-ion anisotropy was reflected in a second-rank Stevens operator of $|11.8|\ cm^{-1}$, with $g = 1.99$; this is shown in Figure 2 as a solid line.

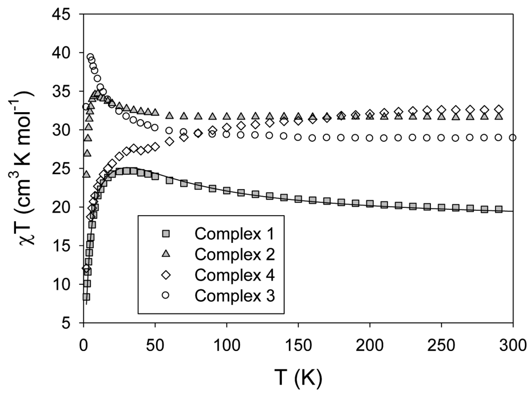

Figure 2. dc magnetic susceptibility for complexes **1**–**4** at 0.3 T applied dc field.

These values were used to simulate the magnetization data for complex **1** with a giant spin model of three isolated dimers of $S = 4$ and $g = 1.99$, with anisotropy reflected in a fitted Stevens operator of rank 2, which for the best fit had a value of $|9.5|\ cm^{-1}$ (see Figure S3 in the SI). The magnetization versus field measurements at 2 K do not show clear saturation with the field, indicating that an isolated ground state is not present in these complexes because of low-lying excited states and strong anisotropy. Ac magnetic susceptibility data down to 2.0 K showed for complexes **1**, **2**, and **4** the tail of an out-of-phase peak, indicative of possible SMM behavior, and no signal for the Gd^{III} analogue complex **3**.

ac magnetic measurements at the University of Hyogo on a SQUID magnetometer equipped with a magnetic dilution cryostat down to 0.1 K were necessary to observe the full out-of-phase peak. The fitting of the frequency dependence of the signal to the Arrhenius law, shown in Figure 3 for complexes **1**, **2**, and **4**, yielded a very low effective energy barrier of 6 K for complex **1**, 2 K for complex **2**, and 1.30 K for complex **4**. The preexponential factors have values of $\tau_0 = 6 \times 10^{-7}$ s for complex **1**, $\tau_0 = 2 \times 10^{-5}$ s for complex **2**, and $\tau_0 = 6 \times 10^{-11}$ s for complex

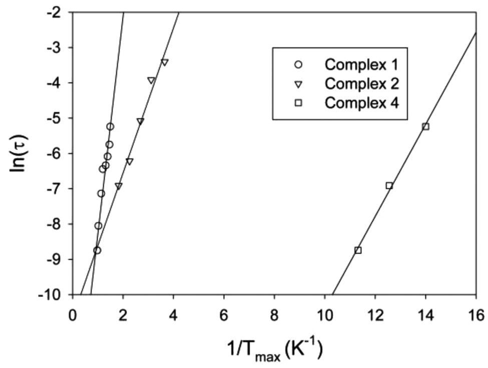

Figure 3. Arrhenius plots for complexes **1**, **2**, and **4**.

4, as expected for a magnetization relaxation process of molecular origin. Because the La^{II} complex **1** also displays an out-of-phase signal, the SMM behavior of the complexes must be due primarily to the Mn_6 part of the cluster. This would mean that adding f electrons (Gd complex **3**) or f electrons and strong spin−orbit coupling (Tb and Dy complexes **2** and **4**) should affect the SMM behavior of complex **1**: the f electrons without spin−orbit coupling, in complex **3**, result in the obliteration of the SMM behavior, while the complexes **2** and **4**, with strong spin−orbit coupling and f electrons, result in fast quantum tunneling of the magnetization and smaller effective barriers for the relaxation of magnetization.

In summary, synthetic control over the reaction product has allowed us to predict the formation of the new 3d−4f complexes **1**−**4**. The Ln ions take the predicted central position surrounded by the three Mn^{III}_2 units. A detailed study of the magnetic properties of complexes **1**−**4** show that, except the Mn_6Gd complex **3**, they are new examples of 3d−4f SMMs, displaying ac out-of-phase magnetic susceptibility peaks below 2 K. Thus, the introduction of Ln ions with strong spin−orbit coupling such as Tb^{III} and Dy^{III} result in an enhancement of the relaxation by quantum tunneling of the magnetization and in worse SMM properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org. CIF files can be obtained free of charge from the Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/) as CCDC 976879 (**3**), 976880 (**1**), and 976881 (**2**).

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Notes

The authors declare no competing financial interest.

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