Heptanuclear 3d–4f cluster complexes with a coaxial double-screw-propeller topology and diverse magnetic properties†

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Two novel coaxial double-screw-propeller heptanuclear 3d–4f cluster complexes are ferromagnetic: one exhibits a large magnetocaloric effect while the other a magnetic relaxation behavior, depending on the lanthanoid ions used.

Recently, the investigation of polynuclear cluster complexes with high spin ground states has witnessed flourishing progress owing to not only their intriguing structures but also their potential applications in many fields such as quantum computing, magnetic information storage devices and magnetic cooling technology. A specially attractive goal has been the synthesis of single-molecule magnets (SMMs) that exhibit the slow magnetization relaxation coming of high spin ground states and uniaxial Ising-like magnetocrystalline anisotropy. On the other hand, the magnetically isotropic nature of large spin in polynuclear cluster complexes may lead to an enhanced magnetocaloric effect (MCE) at low temperature. To date, most related studies focused on the transition-metal clusters, only a few polynuclear 3d–4f cluster complexes with high spin ground states have been reported recently. It is still a great challenge to design and synthesize ferromagnetic polynuclear 3d–4f cluster complexes with high spin ground states.

Polydentate ligands often play a critical role in the construction of polynuclear cluster complexes. We are interested in salicylaldoxime ligands (R-saoH, R = H, Me, Et, Ph etc.) because they were successfully utilized to synthesize a series of SMMs. Nevertheless, their potential to construct heteronuclear 3d–4f cluster complexes has not been explored adequately, only one such a compound [Mn11Ce3O8(Me-sao)6(NO3)4(OAc)2(H2O)2]·6MeCN was reported before. Our recent interest is also directed toward the design and architecture of polynuclear complexes with high spin ground states. Herein, we report two novel heptanuclear 3d–4f cluster complexes constructed from the Et-sao2 ligand, MnIII6,MnIVO5Ln3(OH)(piv)2(2-alkoxide)(EtO)2(EtOH)(Et-sao), (Ln = Gd, Dy; Ln = Dy, 2; piv = pivalate),† which show a unique coaxial double-screw-propeller topology. Interestingly, I displays a large MCE while 2 shows a magnetic relaxation.

Complexes 1 and 2 are isostuctural, so only the structure of 1 is described here as representative. As shown in Fig. 1, the heptanuclear cluster structure of 1 is composed of two triangles cumulated one above the other. The above triangle consists of three gadolinium atoms bridged by a central η1-OH2 group, whose oxygen atom lies 0.903 Å above the triangular plane, and the edge of this triangle is bridged by the carboxylato group of the pivalate ligand; while the bottom triangle possesses three MnIII ions at the corners and one MnIV ion in the center but its edges are fictitious. The manganese oxidation states were established by bond-valence sum (BVS) calculations and charge-balance considerations. The Gd3 triangle and the MnIII3MnIV triangle are shared with three tetrahedral η1-O2− atoms. These two triangle planes are almost parallel to each other, with a very small dihedral angle of 0.2°. Notably, both triangles are arranged in an interleaving mode to avoid forming a triangular-pyramidal-frustum-like topology. Alternatively, a unique coaxial double-screw-propeller topology, whose axis is defined by the central η1-hydroxy oxygen atom and the MnIV atom, is generated since the Mn/O/Gd core has a virtual C3 symmetry. This is quite different from the well-known disk-like topology that the heptanuclear cluster complexes generally possess.

Each central η1-O2− anion connects with two GdIII ions in the Gd3 triangle as well as a peripheral MnIII ion and the central MnIV ion in the MnIII3MnIV triangle, a cubane topology is thus formed by the three GdIII ions, the MnIV ion, the η1-hydroxy oxygen atom and the three η1-O2− anions (Fig. 1b). Furthermore, the corner MnIV ion and the adjoining GdIII ion are also bridged by a bismonodentate pivalate anion or an η1-alkoxide oxygen atom. Each Gd atom is eight-coordinated by three carboxylato oxygen atoms, two central η1-oxygen atoms, one η1-hydroxy oxygen atom, one η1-alkoxide oxygen atom and one ethanolate oxygen atom. The Gd–O bond lengths of 2.326(6)–2.496(6) Å are in the normal range. The MnIV ion adopts a distorted octahedral configuration, coordinated by three central η1-oxygen atoms and three oxime oxygen atoms, where the MnIV+Otetrahedral bond distances [1.868(5)–1.873(6) Å] are a little smaller than the MnIV+Oaxial bond lengths [1.899(6)–1.915(6) Å]. Differently, the MnIII ion exhibits a distorted square pyramid configuration, whose basal plane is defined by one oxime nitrogen atom and one phenolate oxygen atom from an Et-sao2 ligand as well as one central η1-oxygen atom and one η1-alkoxide oxygen atom, while a carboxylato oxygen atom occupies the apical site. Such a square
The large spin ground state \( S \) of 1 may bring a large MCE owing to the large magnetic entropy changes on magnetization/demagnetization. The isothermal magnetic entropy changes \( \Delta S_m \) can be derived from Maxwell relations by integrating over the magnetic field change, \( \Delta S_m(T) = \int \frac{\partial M(T,H)}{\partial H} dH \). The entropy-temperature curves are depicted in Fig. 3b for several field changes. The trend is that the \( \Delta S_m \) value increases gradually with the increasing \( \Delta H \), reaching a value of 7.4 J kg\(^{-1}\) K\(^{-1}\) at 6 K for the experimentally accessible maximum \( \Delta H \) of 50 kG.

The thermal variation \( \chi T \) for 2 under a 1 kOe applied field in the temperature range of 2–300 K is shown in Fig. 4a. The \( \chi T \) value at room temperature is 53.93 emu K mol\(^{-1}\), in good agreement with that expected (53.39 emu K mol\(^{-1}\)) for three Mn\(^{3+}\) (\( S = 2 \)), one Mn\(^{4+}\) (\( S = 3/2 \)) and three Dy\(^{3+}\) (\( S = 5/2 \), \( \lambda = 5\), \( 6\text{H}_{15/2} \)) non-interacting ions. Similar to 1, upon cooling the \( \chi T \) product of 2 increases continuously and ascends rapidly when \( T < 50 \) K, suggesting intracluster ferromagnetic interactions. However, unlike 1, a maximum value of 91.80 emu K mol\(^{-1}\) appears at 3 K for 2. After this maximum, \( \chi T \) descends probably due to zero-field splitting, Zeeman effects, and/or weak intercluster interactions. Above 10 K, the \( 1/\chi \) vs. \( T \) plot obeys the Curie–Weiss law with \( \theta = 3.74 \) K and \( C = 54.14 \) emu mol\(^{-1}\) K. The small positive \( \theta \) value makes sure the weak ferromagnetic interaction.

The magnetization variation \( \chi T \) at different applied fields was determined between 2 and 7 K (Fig. 4a, inset). The obvious nonsuperposition of the isofield lines suggests the zero-field splitting. The above magnetic anisotropy difference between 1 and 2 is mainly attributed to the stronger magnetic anisotropy of the Dy\(^{3+}\) ion with respect to the Gd\(^{3+}\) ion. The entropy-temperature curves for several field changes of 2(Fig. 4b) indicate that the \( \Delta S_m \) values of 2 are obviously smaller than the corresponding values of 1. For example, the experimentally accessible maximum value of \(-\Delta S_m\) for 2 (3.7 J kg\(^{-1}\) K\(^{-1}\) at 6 K and under an \( \Delta H \) of 50 kG) is only half of that for 1 (7.4 J kg\(^{-1}\) K\(^{-1}\)). In addition, the \( M \) vs. \( H \) plot of 2 does not show any hysteresis at 2 K.

When the dc field was zero, slow paramagnetic relaxation was not observed at low frequencies \( \leq 250 \) Hz from ac susceptibility studies of 2 under a 2.5 Oe oscillating field (Fig. 5a). However, the
onset of the out-of-phase signal was detected when the frequency was up to 997 Hz. Under a dc field of 2 kOe, the \( \chi'' \) signals clearly unveil at all frequencies, suggesting a slow relaxation of magnetization (Fig. 5b). Similar phenomena were also observed at all temperatures, the evaluation of \( U_{\text{eff}} \) for \( \text{Dy}^{3+} \) ion in \( \text{Ho}_{3} \) to show a large MCE, while the large magnetic anisotropy \( R \) was up to 997 Hz. Under a dc field of 2 kOe, the \( \chi'' \) signals clearly unveil at all frequencies, suggesting a slow relaxation of magnetization (Fig. 5b).

In summary, this work presents a family of ferromagnetic heptanuclear 3d–4f cluster complexes with a coaxial double-screw-conical structure of the \( \text{Dy}^{3+} \) ion in \( \text{Ho}_{3} \) to show a large MCE, while the large magnetic anisotropy \( R \) was up to 997 Hz. Under a dc field of 2 kOe, the \( \chi'' \) signals clearly unveil at all frequencies, suggesting a slow relaxation of magnetization (Fig. 5b).
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