Title:	Exploiting Strong {CrIII–DyIII} Ferromagnetic Exchange Coupling to Quench Quantum Tunneling of Magnetization in a Novel {CrIII2DyIII3} Single-Molecule Magnet
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Abstract:	The {3d–4f} pentanuclear complexes with the formula [CrIII2LnIII3(PhCO2)7(OH)6 (iPrO)(NO3)(H2O)3] (iPrO = isopropoxide) (where Ln = Dy (1), Gd (2)) have been synthesized and characterized using magnetic and theoretical studies. The metal core of complexes 1 and 2 has a trigonal bipyramidal arrangement with three LnIII ions in the triangular plane and two CrIII ions occupying the axial positions. These ions are held together by six μ3-OH bridges and seven carboxylate bridges. The dc magnetic susceptibility data reveal ferromagnetic interactions presiding between CrIII and LnIII ions in 1 and 2. The fitting of the susceptibility curve employing the DFT calculated J (vide infra), yield JGdIII–GdIII = +0.008 cm–1, JCrIII–GdIII = +0.27 cm–1, and JCrIII–CrIII = −0.007 cm–1 for 2. The dynamic (ac) magnetic susceptibility studies on 1 indicate slow relaxation of magnetization with a Ueff value of 30.9 K (21.4 cm–1) and τ0 = 4.09 × 10–10 s. These extracted parameters are among the highest for any reported {CrIIIDyIII} complexes. DFT and ab initio CASSCF/RASSI–SO/SINGLE_ANISO/POLY_ANISO calculations were carried out to estimate the exchange interactions and their role in quenching the quantum tunneling of magnetization (QTM) behavior. Ab initio calculations on the DyIII ions reveal three asymmetric DyIII centers with the estimated single ion barrier in the range of 78–184 cm–1, however, with a large QTM probability. Despite a triangular {Dy3} motif, the gzz axes do not align in the triangular plane as observed in the {CrIIIDyIII6} single-molecule toroids (SMT) reported earlier by us. This is essentially due to the presence/absence of the iPrO–/carboxylate group that alters the charge distribution around the DyIII ion and hence the orientation of the corresponding gzz axis. The combination of DFT and ab initio CASSCF calculations yield JDyIII–DyIII = +0.012 cm–1, JCrIII–DyIII = +1.20 cm–1, and JCrIII–CrIII = −0.95 cm–1 for 1. The mechanism of magnetization relaxation developed for the {CrIII2DyIII3} cluster reveals that the relatively strong ferromagnetic CrIII–DyIII exchange interaction reduces the ground state QTM significantly yielding a Ueff of 38.6 cm–1, which agrees with the experimental value. Thus, our study iterates the importance of CrIII ion to enhance the exchange coupling in the {3d–4f} family of clusters.
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