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Molecular Magnets Incorporating Orbitally-Degenerate 4d, 5d or 4f Ions

Single molecule-magnets (SMMs) are a class of materials exhibiting slow relaxation of the magnetization. As opposed to superparamagnetic nanoparticles, where the blocking temperature is influenced by the particle size, the magnetic properties of SMMs are intrinsically molecular. Following the suggestion that the blocking temperature may be increased by incorporating transition metal ions with orbitally degenerate ground terms, attention has been given to SMMs that incorporate the either high-symmetry transition metal building blocks or lanthanide ions. We have recently synthesized and characterized the first examples of SMMs incorporating the heavier transition metals Ru^{III} and Os^{III}. The combination of a nearly cubic ligand field and strong spin-orbit coupling present for those metal ions ($4d^5$ and $5d^5$) isolates as ground state a strongly anisotropic Kramers doublet. The combination of large orbitals and anisotropic exchange interaction effectively contributes to a higher blocking temperature. Whereas 3d-based molecular nanomagnets have been largely studied and their relaxation mechanisms are well understood, little is known for their novel 4f-based counterparts. In lanthanide (4f) ions the crystal field splittings are much smaller than those found for transition metal ions and the orbital angular momentum is left unquenched. This, in combination with a large total spin present for several lanthanide ions, gives rise to a large total angular momentum. A new synthetic approach to di-, tri- and poly-nuclear chromium(III)-lanthanide clusters involving fluoride-bridges and their magnetic properties are presented.

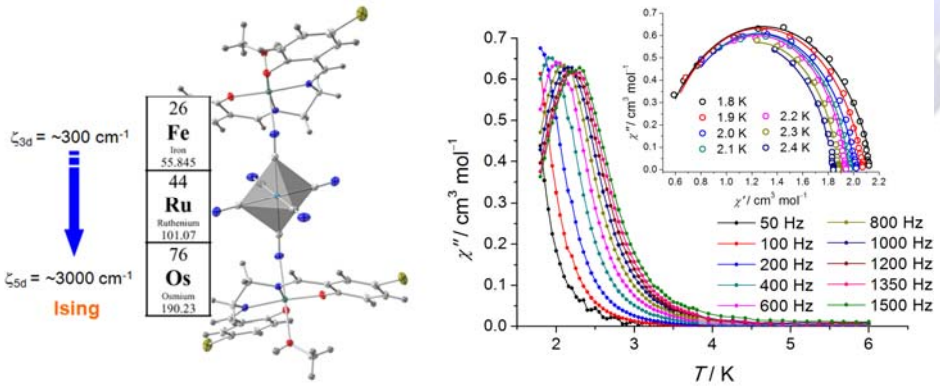

Figure 1. The structure of the studied Mn–M–Mn (left) with emphasis on the high-symmetry, octahedral moiety and out-of-phase ac susceptibility signal (right) for the ruthenium incorporating compound suggesting SMM behaviour.

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