Molecular Nanomagnets based on Rhenium(IV) and Manganese(III)

Final Report Summary - MONARHEMAN (Molecular Nanomagnets based on Rhenium(IV) and Manganese(III))

During this project, MONARHEMAN, we have explored the interactions and magnetic exchange between the highly anisotropic Re(IV) (5d) and Mn(III) (3d) metal ions in new octanuclear [Re2Mn6] nanomagnets or single-molecule magnets (SMMs) as well as in [Mn6][ReCl6] compounds. The over-arching aim of our research program has been the introduction of the highly anisotropic rhenium(IV) metal ion into Mn6 systems in order to enhance the anisotropic energy barrier. The energy barrier of SMMs is a very relevant parameter given the potential technological implications of these molecules in high-density information storage, quantum computing, magnetic refrigeration, molecular spintronics and even biomedical applications. Moreover, SMMs are attracting extensive and multidisciplinary attention because they represent nanoscale magnetic particles of a well-defined size. They display sluggish magnetization relaxation phenomena such as magnetization hysteresis loops and frequency-dependent out-of-phase
signals in alternating current (ac) magnetic susceptibility measurements. They are obtained synthetically by chemists and are studied in depth by physicists, since SMMs can act as an exceptional nanolaboratory for studying (predicted) fundamental quantum magnetic phenomena, including quantum tunneling of the magnetization, quantum phase interference, spin parity effects and quantum coherence. Our synthetic strategy to prepare such systems has been the use of stable and paramagnetic rhenium(IV) mononuclear species (see Figure 1 in attached file) that can act as ligands (complex as ligand strategy) towards partially blocked Mn6 complexes.

Major accomplishments and achievements:

i) Preparation, characterisation and magnetostructural study of the first cationic [Mn6]2+ compounds based on phenolic oximes.

The fact that the well-known Mn6 cages now can also be isolated as cations constitutes a step towards making more advanced materials, since this allows the scientist to tune solubility, reactivity, purification, stability and substrate specificity. In addition, the cluster cation can be charged balanced through the incorporation of anions that bring another physical property or functionality to the material, be that conductivity, luminescence or magnetism. In our case, we have used the anionic [ReCl6]2- complex for obtaining and studying new [Mn6][ReCl6] salts.

ii) Preparation, characterisation and magnetostructural study of a family of new compounds based on the highly anisotropic Re(IV) and Mn(III) metal ions.

This family is formed by the following salts and polynuclear complexes:

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\begin{align*}
\{[\text{Mn6}(\mu-3-O)2(\text{H2N-sao})6(\text{py})6(\text{H2O})2][\text{ReCl6}]\cdot2\text{py}\cdot2\text{MeCN}\cdot2\text{H2O}\} & \quad (1) \\
\{[\text{Mn6}(\mu-3-O)2(\text{H2N-sao})6(\text{py})6(\text{S})2][\text{ReCl6}]\cdot2\text{MeCN}\cdot6\text{H2O}\} & \quad (2) \text{ S being H2O or EtOH} \\
\{[\text{Mn6}(\mu-3-O)2(\text{H2N-sao})6(\text{CH3COCH3})6][\text{ReCl4(μ-ox)}]2\text{Mn6(O)2(H2N-sao)}6(\text{CH3COCH3})2\cdot6\text{CH3COCH3}\} & \quad (3) \\
\{[\text{ReCl5(μ-pyz)}]2\text{Mn6(O)2(H2N-sao)}6(\text{CH3COCH3})4(\text{H2O})2\cdot4\text{CH3COCH3} & \quad (4) \\
\{[\text{ReBr5(μ-pyz)}]2\text{Mn6(O)2(H2N-sao)}6(\text{CH3COCH3})4(\text{H2O})2\cdot4\text{CH3COCH3} & \quad (5)
\end{align*}
\]

By obtaining the [Mn6][ReCl6] compounds (1 and 2) and comparing their magnetic properties with those of the [Mn6][ClO4]2 systems (obtained with a diamagnetic anion) we have observed as the energy barrier in the cationic [Mn6]2+ complexes has been increased ca. 29 % by effect of adding the highly anisotropic rhenium(IV) metal ion as [ReCl6]2- complex (see Figure 2 in the attached file).

Compound 3 constitutes the first salt ever reported in which both cation and anion are nanomagnets. In addition, its anion shows a new coordination mode (μ3) for the [ReCl4(ox)]2- precursor in polynuclear complexes, which has also allowed to develop the coordination chemistry of the Re(IV) precursors. The octanuclear complexes 4 and 5, and also the anion in 3, are the first complexes based on the highly anisotropic Re(IV) (5d) and Mn(III) (3d) metal ions exhibiting single-molecule magnet (SMM) behaviour. This evidence is supported by micro-SQUID measurements performed on single crystals. Moreover, they are the polynuclear Re(IV) complexes of highest nuclearity obtained so far.

Finally, it is worth to point out that, from a synthetic point of view, the preparation of the compounds 1-5 is
really a challenge, given that they have to be obtained in the presence of O2- groups associated to the two trinuclear [Mn3] units that form the manganese core of the Mn6 complexes. It is well-known that in such synthetic conditions the Re(IV) ion undergoes either oxidation or hydrolysis forming Re(V) or Re(VII) species, respectively. Thus, our systems are also the first Re(IV) compounds including O2- groups associated to their molecular structure.

Conclusions and perspectives:

The MONARHEMAN project has basically been focused on the development of new nanomagnets by using two metal ions that exhibit large anisotropy, Re(IV) and Mn(III). Overall, it has established an effective and innovative approach for the development of novel 3d-5d based nanomagnets.

We think that the ensemble of results presented both herein and in future publications will be of high interest for chemists of various disciplines. Within the timescale of this work, our results are likely to be primarily of academic importance. Nevertheless, we anticipate the resulting nanomagnets will provide an important new set of model systems for more detailed studies which will be performed by collaborators in the Physics community. Additional DFT calculations, which are already being carried out, will allow us thoroughly understand the physical properties of our compounds, enabling us to establish more accurate magnetostructural correlations in the near future.

Finally, given our aesthetic molecules, these results will be easily addressable and communicated, and ideal for capturing the imagination of young students. Hence, MONARHEMAN will contribute to the efforts to increase the number of science students at Europe’s universities and will provide a very stimulating training environment for the participating young researchers and postdocs with many opportunities for cross-disciplinary training, which will enhance both their scientific capabilities and career prospects. Success in publishing these results in high-quality scientific journals will attract increased interest in Europe and will be an instrument to increase European competitiveness.

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