Computational Methods to Describe the Magnetic Properties of SMM Systems

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Because the magnetic and electronic properties of SMMs are dictated by the ligand field, they are theoretically predictable. In order to elucidate the subtle effects of the ligand field on the magnetic properties, two mononuclear dysprosium(III) complexes have been investigated. The ligands employed are comprised of two bidentate donors (1-hydroxy-pyridine-2-one-1,2-HOPO) with a linking chain of various lengths [1]. Depending on the identity and length of the chain, a different geometry can be enforced. Preliminary calculations indicate that such geometrical changes significantly impact the magnetic properties, revealing high sensitivity of the ground and excited states.

1 Introduction

Single molecule magnets (SMMs) are a class of compounds that contain one or more magnetic centres (d- or f-block metals). The unique magnetic behaviour of such compounds, simply put, is the ability of each individual molecule to retain its own magnetic field. The challenge faced in this field is preventing magnetic relaxation and the various paths by which this relaxation can occur. Using computational methods it is possible to predict whether relaxation will occur and by which pathway. In this regard, there are three criteria that must be met. Firstly, the ion must be of Ising-type character, i.e. should be highly anisotropic ($g_x = g_y = 0$, $g_z = 20$) in order to prevent quantum tunnelling of magnetization (QTM). Secondly, there must be a large enough energy barrier between the different states to prevent thermal relaxation of magnetism. Thirdly, the magnetic axes of the states must be aligned in order to suppress Orbach relaxation.

2 Computational Methods

Complete active space self-consistent field (CASSCF) wave functions are generated using the restricted active space self-consistent field (RASSCF) module provided by the MOLCAS 8.0 package [2]. All atoms were described using the ANO-RCC-VDZP basis sets included in the MOLCAS package [3]. Because of lanthanide contraction, accurate results are achievable by restricting the active space to the nine electrons in the seven 4f orbitals. Furthermore, as no additional electron correlation is required, the CASSCF wave functions are used without further

perturbations. Spin-orbit coupling is introduced using the state interaction program RASSI (restricted active space state interaction) using 21 sextet, 50 doublet and 50 quartet states for the f^9 ion. The spin-orbit multiplets are then used by the SINGLE_ANISO program to calculate the relevant magnetic properties. The calculations were carried out using optimised structures, as published by Daumann *et al.* [1]. The ligands employed are presented in Figure 1. Depending on the length of the chain, a different geometry is enforced, and it is the effect of this change on the magnetic properties that is being investigated.
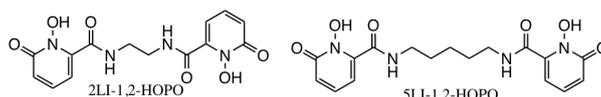

Figure 1: Ligands employed in this study.

3 Results

Both the 2LI and 5LI complexes show insufficient splitting of the M_J states to prevent thermal relaxation of magnetisation (44 and 55 cm^{-1}, respectively). While the anisotropy of the 5LI complex ($g_z = 19.12$) would be sufficient to suppress QTM, the magnetic axes of the excited states are perpendicular to each other, allowing Orbach relaxation to occur. On the other hand, the 2LI complex appears to show little Ising-type character ($g_x = 1$, $g_y = 2$, $g_z = 16$) but the local magnetic axes are parallel.

4 Conclusions

While neither complex appears to have potential as an SMM, the results illustrate notable sensitivity of the ground and excited Kramers doublet states to changes in the ligand field. Despite the small ligand field of lanthanides, it is clear that it is of central importance for molecular magnetism.

Acknowledgements

References

[1] Daumann, L. J. *et al.*, *Inorg. Chem.* **2016**, *55*(1), 114-124.

[2] B. O. Roos *et al.*, *Chem. Phys.* **1980**, *48*, 157.; F. Aquilante *et al.*, *J. Comput. Chem.* **2010**, *31*, 224.

[3] B. O. Roos *et al.*, *J. Phys. Chem. A* **2005**, *109*, 6575.