IITB-Monash Research Academy

Indian Institute of Technology Bombay | MONASH University

An Indian-Australian research partnership

Project Title: **New Generation Molecular Magnetic Materials: Experiment and Theory**

Project Number **IMURA0247**

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Research Academy Themes:

Highlight which of the Academy's Theme(s) this project will address?
(*Feel free to nominate more than one. For more information, see www.iitbmonash.org)*

1. Advanced computational engineering, simulation and manufacture
2. Infrastructure Engineering
3. Clean Energy
4. Water
5. **Nanotechnology ****
6. Biotechnology and Stem Cell Research

The research problem

Magnetic materials play an important role in current information technology. One possible way to increase the capacity of information storage is to decrease the system size of the storage devices. This suggests the use of nanoscale materials and clusters as information storage devices. The discovery that a cluster of manganese (III, IV) ions, $\{Mn_{12}\}$ retains its magnetisation in the absence of magnetic field (Single Molecule Magnets, SMM) may prove to be of immense technological importance. [1] Among several possible applications, the most promising is in the field of super-computers because of the possible high density data storage and the fascinating possibility of realising quantum computing. [2]

The number of polymetallic cages reported increases every year and to date, approximately one hundred SMMs have been reported - yet the barrier height for the reversal of magnitisation has not been significantly raised. Therefore the synthesis of a new generation of single molecule magnets with enhanced properties is still a major challenge. The energy barrier for reorientation of the magnetisation is given by DS^2 (for integer spin systems) and is related to the spin ground state (S) and the zero-field splitting (D). Control over the magnetic exchange constant, *J* (and thus a large S) and D is crucial to obtain a large barrier height and the magnitude of the *J* value needs to be very high in order to have an isolated spin ground state - a necessary condition for future technological applications. [1,2] In this proposal we are aiming to synthesise new generation magnetic materials and subject it to thorough characterisation using physical techniques (magnetic and spectroscopic) and then to employ state-of-the-art computational (DFT/ab initio) methods to gain in-depth understanding of the microscopic spin Hamiltonian parameters. The computational method can also be used to predict novel compounds with expected magnetic properties which can then be synthesised and the previsions can be verified.

The research problem is made up of a number of interrelated and cohesive parts that are chemically and theoretically based and deal with modern aspects of magnetochemistry *viz* molecule based magnetic materials at the nano-scale. The theoretical work will be carried out at IITB under Dr Rajaraman's supervision[3] while the chemical synthesis, crystallography, spectroscopy and magnetochemistry will be carried out at Monash University under Professor Murray's supervision.[4] All necessary infrastructure, equipment and lab facilities are in place, including access to the Australian synchrotron, situated next to Monash. In this kind of research, the post graduate student involved will gain a broad experience, at a high level, across experimental and theoretical inorganic chemistry.

The research problem is to synthesise new mononuclear and polynuclear d-block transition metal ion, d-block/organic radical and d-f mixed transition metal-lanthanoid compounds in order to understand the nanomagnetic properties of these three classes via structural, magnetic and theoretical techniques. For the synthesised compounds the experimental spin Hamiltonian parameters (obtained from physical characterisation) will be compared to the computed ones and finally we are planning to explore the possibility of implementing the specific magnetic properties (e.g energy barrier, tunnel properties etc) via predictions. Our particular focus here will be on the cluster compounds having nano-sized dimensions and displaying quantum properties and slow magnetisation reversal, so-called single molecule magnets (SMMs). A long term aim of such fundamental work is to develop useful nano-molecular materials to incorporate in to devices such as displays, memory and sensors.

Project aims

The aims of the project are given in dot point form below. There are two ways to approach the project, the first being to start with calculations (see below) and then see how experiment agrees with such calculations. The second is to start with syntheses of a group of target molecules, observe the physical properties and then do the theoretical calculations thereon. The supervisors will decide on the approach to be used:

- To synthesise and characterise a range of mononuclear and polynuclear complexes of iron(II) and manganese(III) so that a library of compounds can be obtained, of known geometry and structure, and for which theoretical calculations will be made, as described below.
- To synthesise mixed {d-block-organic radical species} of the nitroxide type (in part collaboration with Dr D. W. Lupton, Monash University) so that a full understanding of the magnetic and spin exchange properties of such multifunctional materials can be deduced.
- To synthesise and characterise mixed d-block/f-block clusters that display nanomagnetic single molecule magnet (SMM) features such as quantum effects and slow magnetisation reversal.
- To undertake detailed structural, magnetic and spectroscopic measurements on these compounds.
- To carry out detailed density functional/ ab initio calculations to obtain the Spin Hamiltonian parameters such as *g*-factors, the zero-field *D* and *E* parameters and the exchange coupling *J* for the mononuclear 'building block' complexes to test out the theory and, subsequently, to transfer the information gained for the building blocks on to the large cluster species, with focus on SMM systems. For isotropic f-block and mixed d-block/f-block clusters, DFT calculations will be performed using the Jaguar suite of software.
- The DFT calculations are of limited use for the anisotropic f-block and mixed d-block/f-block clusters due to the presence of degeneracy and large spin-orbit coupling exhibited by these anisotropic 4f ions. One can study these systems only through highly correlated *ab initio* methods. Given the size of the system of interest and the delicate nature of the properties to be computed, realistic level of theory one can employ is CASSCF/PT2 or SORCI methods. The CASSCF/PT2 method is very appealing as its success already been documented. The CASSCF/PT2 calculations will be performed using MOLCAS software package while SORCI calculation will be performed using ORCA package.[5]

References:

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5. Neese, F.; Univ. Bonn, Germany.

Expected outcomes

The expected outcomes are:

- A range of new d-block, d-block-organic radical and mixed d/f-block clusters will be prepared and structurally characterised.
- The magnetic and spectroscopic properties of these compounds will be explored and fully interpreted.
- New theoretical models will be developed to interpret the fundamental electronic structures and exchange coupling of both the 'building block' compounds and in the large cluster compounds made from the building blocks.
- By thorough physical and theoretical studies, control over the microscopic spin Hamiltonian parameters can be achieved.
- Publication of the results in the best, highest ranking journals.