MOLECULAR MAGNETIC MATERIALS – Emeritus Professor Keith Murray

PROJECTS

- Single molecule magnets (SMMs)

The project will aim to synthesize novel polynuclear (i) 3d, (ii) mixed 3d/4f and (iii) pure 4f metal clusters, using various organic bridging ligands. The magnetic and structural properties of these molecular materials will then be studied, with the design of the clusters to be either (a) of the single molecule magnet (SMM) type or (b) ring shaped clusters, (c) toroidal systems, (d) clusters (of Gd) displaying a large magneto-caloric effect (MCE). A SMM is a compound that can retain its magnetization upon application and removal of a magnetic field and thus displays hysteresis at a molecular level (Fig. 1 (right)). This potentially allows for new molecular scale devices that store or manipulate information using the orientation of their molecular spin. The prerequisites for a complex to behave as an SMM are a large magnetic ground state, obtained from the interactions between metal ions in polynuclear clusters and a large anisotropy, which results in an energy barrier to magnetization reversal between the ‘up’ and ‘down’ states (Fig.1 (left)). The current research aims to increase the blocking temperature of these devices which is currently < 15 K. Another property of high-spin polynuclear compounds is the observation of a large magneto-caloric effect (MCE). This phenomenon is based upon a change of magnetic entropy upon application and removal of a magnetic field, resulting in a large decrease in temperature of the material. Hence these type of materials function as a molecular refrigerator (at temperatures below 10 K).

![Fig. 1. Barrier to reorientation of the magnetization for a S = 10 ground state, with the barrier height from the M_s = 0 to the M_s = ±10 given by U_{eff} = S^2 |D| (left). Hysteresis loop for a {Mn_{12}} SMM with a S = 10 ground state (right).](image)

New polynuclear complexes can be easily synthesized via a self assembly mechanism (See Fig. 2).
Once an initial product is isolated simple synthetic variations can be performed to isolate families of complexes to study how the magnetism changes upon these variations. Single crystals need to be grown however to unambiguously determine the structure of these complex molecules via X-ray crystallography, thus experience and knowledge of this technique will be obtained.

Upon synthesis of any new polynuclear cluster and after characterization via X-ray crystallography the magnetic properties of the sample will be measured using a superconducting quantum interference device (SQUID). This will accurately measure the magnetic moment of sample and will give us information on the magnetic interactions and will tell us if the compound displays any single molecule magnet behavior, or if it will potentially display a large magneto-caloric effect.

![Fig. 2](image_url)

**Fig. 2.** Two examples of polynuclear complexes as determined by x-ray crystallography that we have made in our group: (left) A \{Mn\textsubscript{32}\} cluster and (right) a heterometallic 3d/4f \{Cr\textsubscript{2}Dy\textsubscript{2}\} cluster (Chem. Comm. 2016, 52, 10976-10979).

- **Spin crossover complexes**

Spin crossover centres such as complexes of iron(II) d\textsuperscript{6}, iron(III) d\textsuperscript{5} and cobalt(II) d\textsuperscript{7} are a well-known form of an inorganic electronic switch, for which a variation of temperature, pressure or light irradiation leads to a change in d-electron configuration (high-spin to low-spin) often accompanied by a change in structure, colour and magnetism. The project involves synthesis, structural crystallography (including use of the Australian synchrotron) and magnetic measurements. We collaborate with Prof Rajaraman, IITB, Mumbai on theoretical calculations and with Assoc Prof Guy Jameson, Otago, NZ, on \textsuperscript{57}Fe Mössbauer spectroscopy. Future applications of such materials are in “switchtronic” materials and in display electronics.
typical recent paper is one by Post-doctoral fellow Dr Wasinee Phonsri; it involves detailed synthesis, structures and magnetism of Fe(III) complexes containing two different tridentate ligands; *Chem. Eur. J.* 2016, **22**, 1322 - 1333; see Figure 3.

![Chemical structures](image)

**Fig. 3.** (a) and (b) The two different tridentate ligands; (c) and (d) two different solvates, with two structurally different Fe(III) sites, in mixed ligand iron(III) spin crossover complexes. (W. Phonsri et al. *Chem. Eur. J.* 2016, **22**, 1322 - 1333)