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Magneto-Structural Properties of Boron-Containing Rare-Earth Magnets Synthesised Through Ionic Liquid

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Aims & Objectives

Aim:

The main aim of this research is to understand and control ionic liquid synthesis of molecular cluster magnets. It is expected that this will become the foundation for the development of new molecular magnet topologies.

Objectives:

- ***Synthesise novel molecular magnets with spin-cooperative behaviour***
- ***Understand the formation mechanisms of molecular cluster magnets in ionic liquids***
- ***Explore the magneto-structural property relationships in these systems***

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Molecular Magnetism

Molecular magnets are a class of materials capable of displaying ferromagnetism and other more complex magnetic phenomena in molecular sizes.

These molecules can show very high magnetic moments in proportion to their structural features. Therefore, this provides the potential to understand and control magnets at the molecular level using chemical methods.

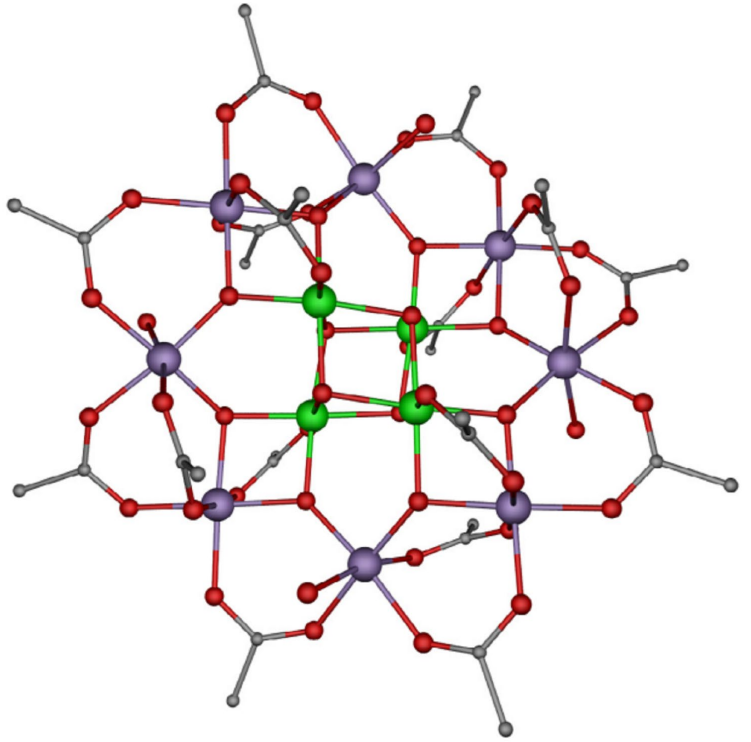

Fig.1 Structure of Mn^{12}-Ac Color code: Mn^{III}, Mn^{IV},carbon and oxygen in purple, green, grey and red, respectively. Hydrogen atoms have been omitted for the sake of clarity.

[1] R.Sessoli et al.,Nature,1993,365,141.

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Molecular Magnetism

High Spin States

High number of unpaired electrons leads to larger magnetic moment

In rare-earths, Gd, Dy, Nd are just a few of these examples of having much unpaired electrons.

Example: Mn12-Ac with S = 10

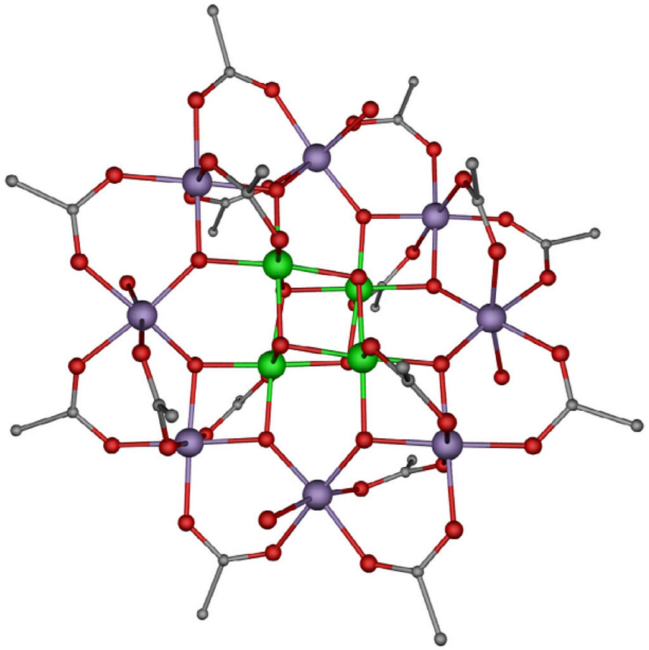

Fig.2 Structure of Mn^{12}-Ac Color code: Mn^{III}, Mn^{IV},carbon and oxygen in purple, green, grey and red, respectively. Hydrogen atoms have been omitted for the sake of clarity.

Large Magnetic Anisotropy

This makes the magnetic moment of the material more stable in a certain direction.

4f orbital of lanthanides structure can give significant orbital angular momentum for create strong magnetic anisotropy.

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Molecular Magnetism

200 GB in^{-2}

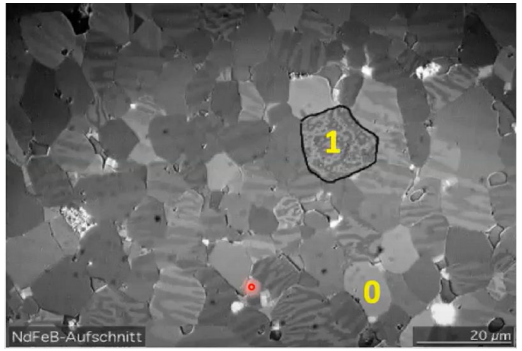

Fig.4 NdFeb HDD and its magnetic domain structure under a Kerr-microscope.

4 nm^2 bit^{-1} ≈ 20000 GB in^{-2}

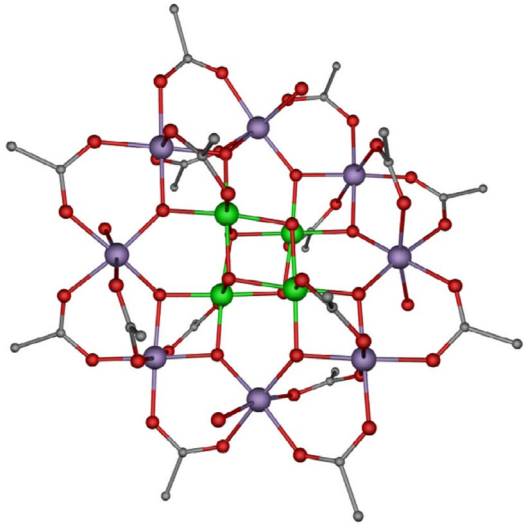

Fig.3 Structure of Mn^{12}-Ac Color code: Mn^{III}, Mn^{IV},carbon and oxygen in purple, green, grey and red, respectively. Hydrogen atoms have been omitted for the sake of clarity.

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Ionothermal Synthesis

BMIM acetate: unique ionothermal synthesis environment

Dissolves rare-earth and transition metal acetates

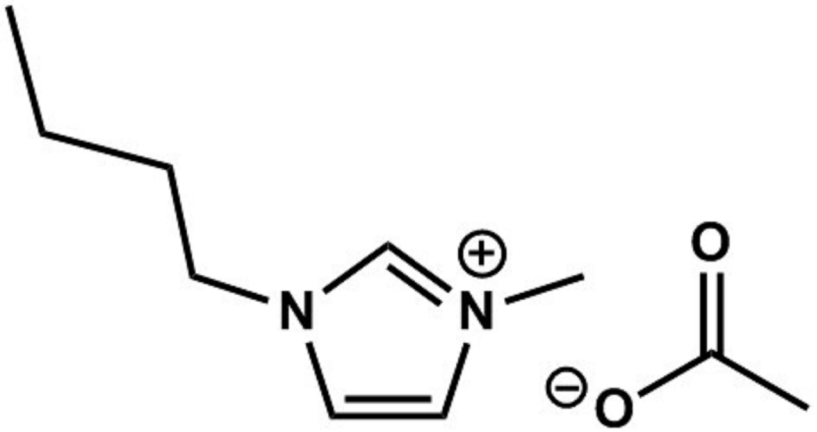

Fig.5 BMIM acetate molecular structure

Can dissolve oxide and borate anions for varied ligands

Potential to form complex molecular magnets

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Ionothermal Synthesis

Fig.6 Samarium and cobalt acetates are dissolved in BMIM acetate.

Rare earth and transition metal acetates dissolved in BMIM acetate at 120°C

Dissolve boric acid and oxalic acid, which were intended to be used as ligand donors.

Slow cooling resulted in crystal formation

Fig.7 Nd acetate crystals precipitate in BMIM acetate

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Ionothermal Synthesis

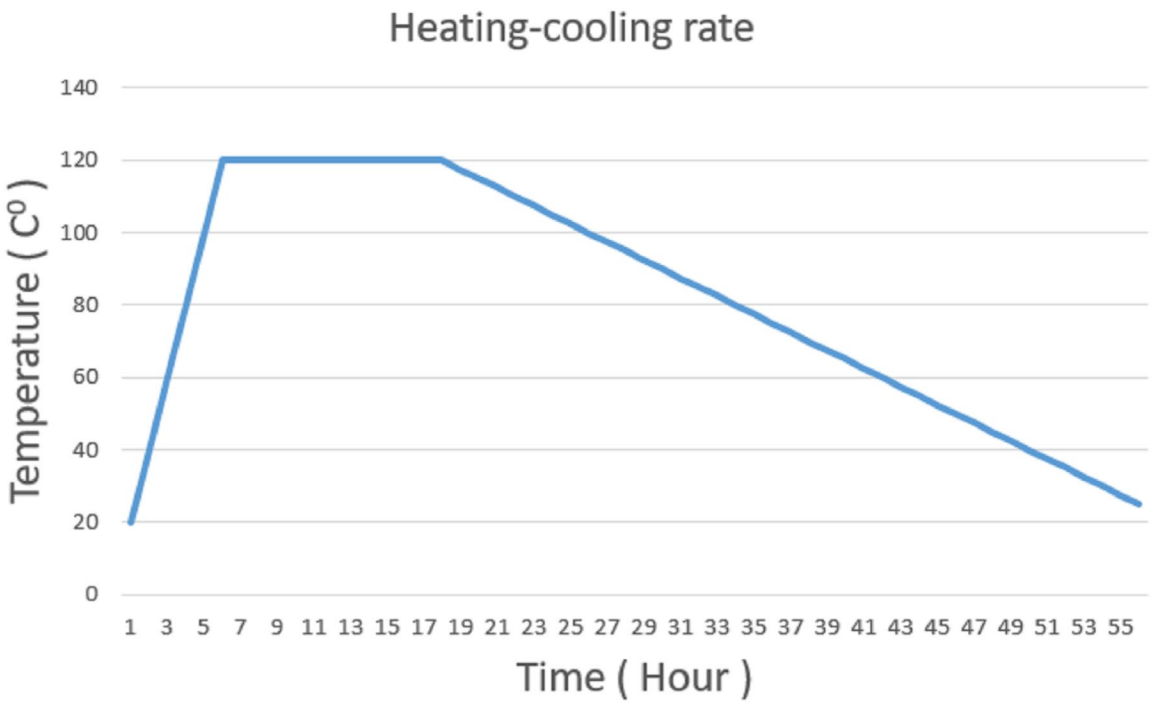

Fig.8 ionothermal synthesis temperature – timeline

The mixture was heated to 120 degrees and kept at this temperature for 12 hours. It was then cooled to room temperature at a cooling rate of 2.5 degrees per hour., BMIM acetate ionic liquid solutions were repeatedly able to form crystals in this conditions.

However, as a result of ongoing experiments, the ligands used as donors have not yet been added to the molecule structure in a controlled manner and in a way that could lead to successful repeated experiments.

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Ionothermal Synthesis

As a result of repeated experiments;

-Although BMIM chloride ionic liquid solution dissolved rare earth chloride in similar temperature ranges and times, it did not form a crystal form.

-BMIM[BOB] ionic liquid solution, although potentially an excellent [BOB] donor, was unable to dissolve nitrates, chlorates and acetates of rare earth elements.

-Na[BOB], although potentially an excellent [BOB] donor, was not dissolved in ionic liquid solutions.

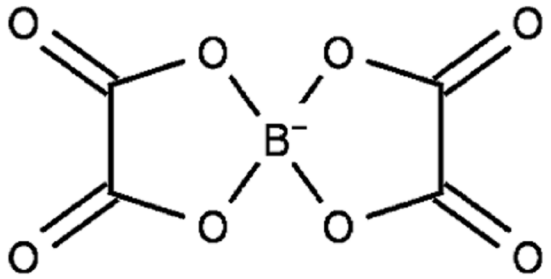

Fig.9 The bridging molecule, [BOB] (bis(oxalato)borate)

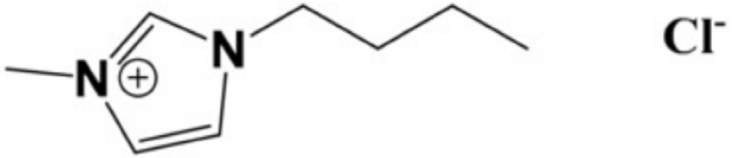

Fig.10 BMIM chloride(1-butyl-3-methylimidazolium chloride) molecular structure

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Hydrothermal Synthesis in an Ionic Liquid

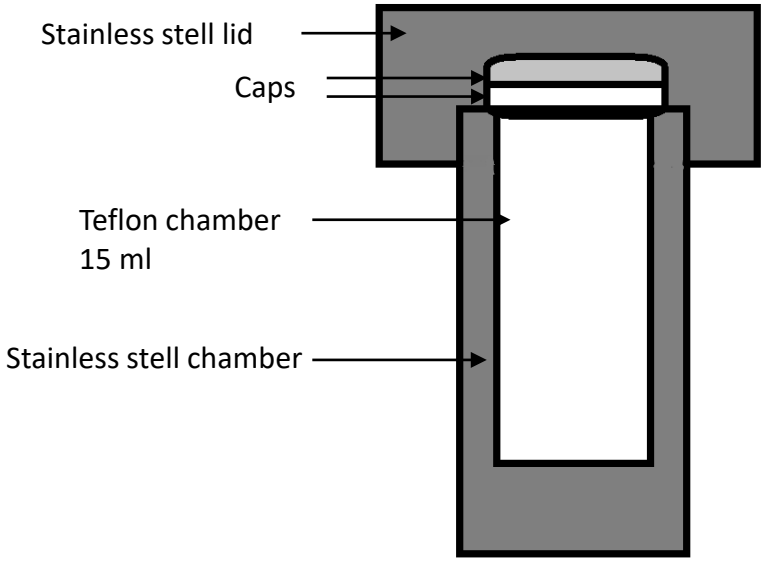

Fig.11 Structure of the autoclave used in the hydrothermal synthesis method.

This growing single crystals that relies on the ability of water, under high temperature and pressure conditions, to dissolve and recrystallize materials that are relatively insoluble under normal conditions.

In this study, the experiments were completed by heating in the oven for 3 days at 200 degrees Celsius, followed by slow cooling for 2 days.

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Results

Nd acetate monohydrate: polymeric structure

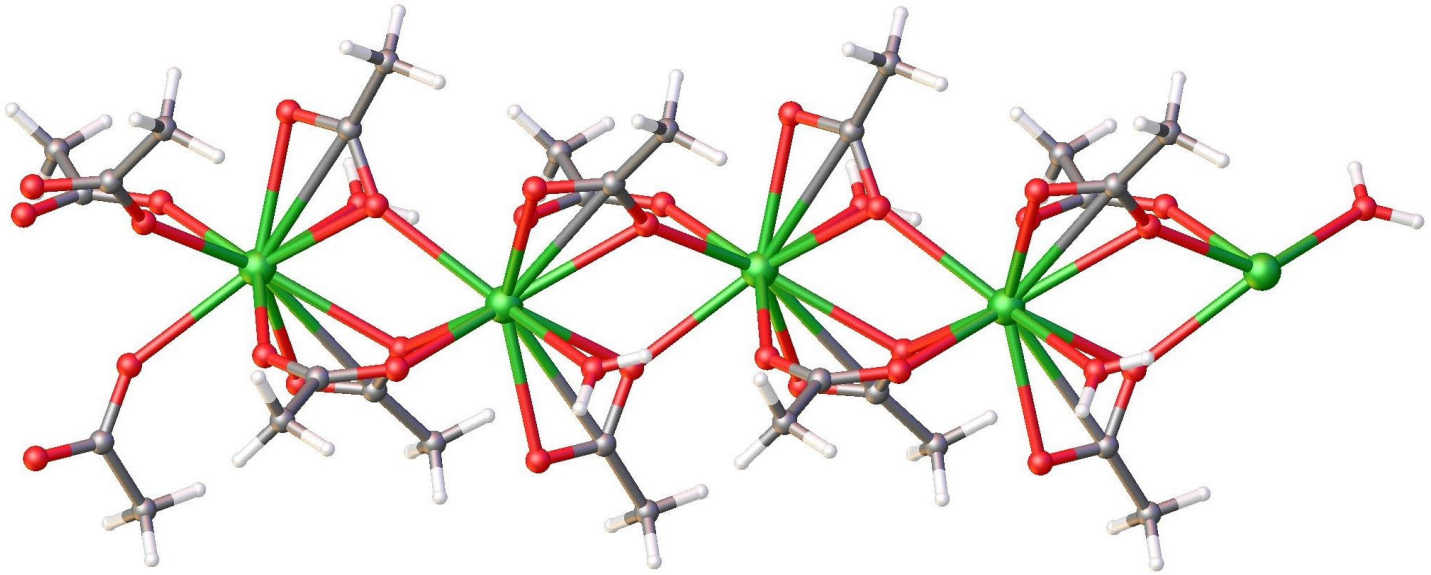

Fig.12 $Nd(CH_3COO)_3H_2O$,polymeric structure neodymium acetate monohydrate molecule. Nd=Green,O=red,C=gray,H=white

- Achieved with the mentioned experimental design
- Close proximity of rare earth atomic centres
- Acetate ligands between centres
- Potential for creating magnetic features

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Results

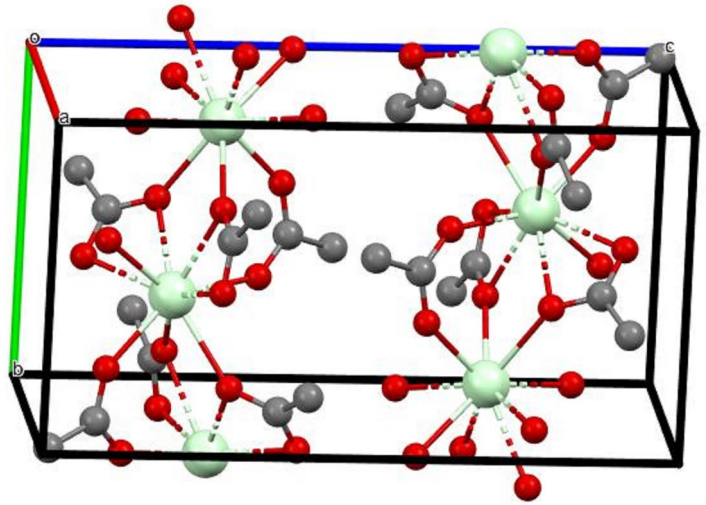

Fig.13 Molecule structure and packing of Nd acetate monohydrate. Nd=Green,O=red,C=gray (Hydrogen atoms have been ignored.)

Spin-spin cooperative behavior can be achieved by introducing ligands into the molecular structures.

Magnetic spin interactions between atomic centers.

Bridging ligands can facilitate the magnetic exchange interaction between metal ions, leading to the formation of magnetic clusters or networks.

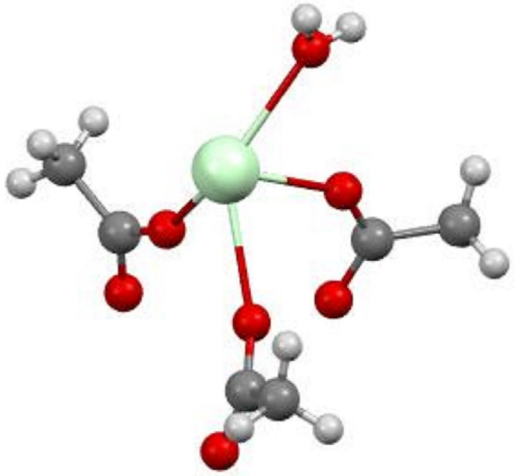

Fig.14 Nd acetate monohydrate asymmetric unit Nd=Green,O=red,C=gray,H=white

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Future works

- *Explore various ionothermal conditions for molecular magnet synthesis*
- *Investigate hydrothermal synthesis with ionic liquids*
- *Synthesise new rare-earth molecular magnets using solid-state chemistry*
- *Analyse magnetic properties using SQUID and SCXRD*
- *Determine effect of bridge ligands on magnetic properties*

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Future works

Titles	PhD Education Timetable (Each column represents a period of two months.)																		Notes
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Start month January
Literature review																			Scanning the literature related to the subject in the literature and expanding the ideas and knowledge about the subject.
Initial Review																			Within 3-4 months of first registration
Experimental design																			Analysing the experiments in the literature and designing a new experimental scheme.
Preliminary experiments																			Synthesise novel molecular cluster magnets with spin-cooperative behaviourusing ionic liquid
Differentiation																			First APR
Desing and Synthesis																			To complete the experimental steps and material selection and to obtain the desired type and property of the product.
Data analysis and interpretation																			Understanding the formation mechanism of magnets synthesised through ionic liquid pathway.
Magnetic characterisation of the molecular cluster																			Magnetic characterisation of molecular cluster magnets will be performed using SQUID magnetometry and EPR, and their spin-spin cooperative behaviour will be modelled for an in-depth understanding of magnetic interactions.
Records of meetings with supervisor																			At least 10 meetings / Year
Annual Progress Review																			May/June of year.
Postgraduate Research Day																			Early to mid-June each year.
Intention to Submit request																			Three months before your estimated date of submission.
Thesis Submission																			At the end of your third year
This timetable includes details of formal meetings and three APRs, which are a legal requirement. The training is planned for 3 years and the timetable can be updated if necessary.																			Still in progress/ Completed

Fig.15 Research project Gantt chart

Future works

Potential challenges or limitations

→ Designing experiments to control ligand incorporation

→ Identifying new borate donors for molecular structure

→ Developing crystallisation methods for rare earth and transition metal complexes with strong magnetic cooperation

→ Strategies to address each challenge:

- Systematic screening of reaction conditions and ligands
- Literature search and collaborations for borate donor discovery
- Optimisation of crystallisation techniques and exploration of novel methods

Acknowledgements

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Thanks for listening.

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QUILL Research Centre