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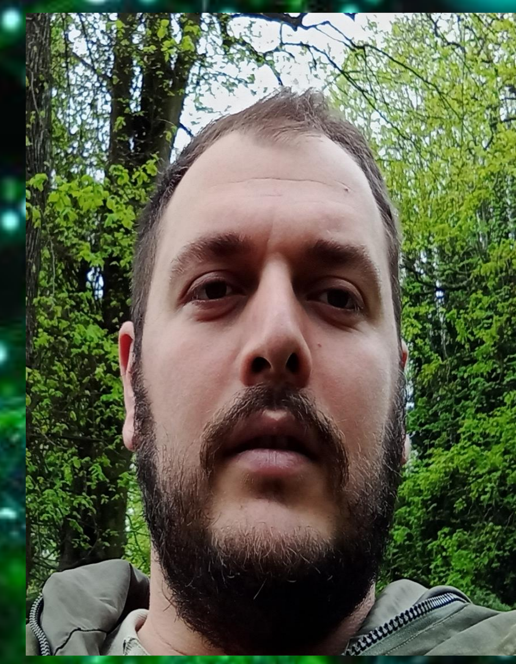
QUILL



Boron-Containing Rare-Earth Magnets Synthesized Through Ionic Liquid

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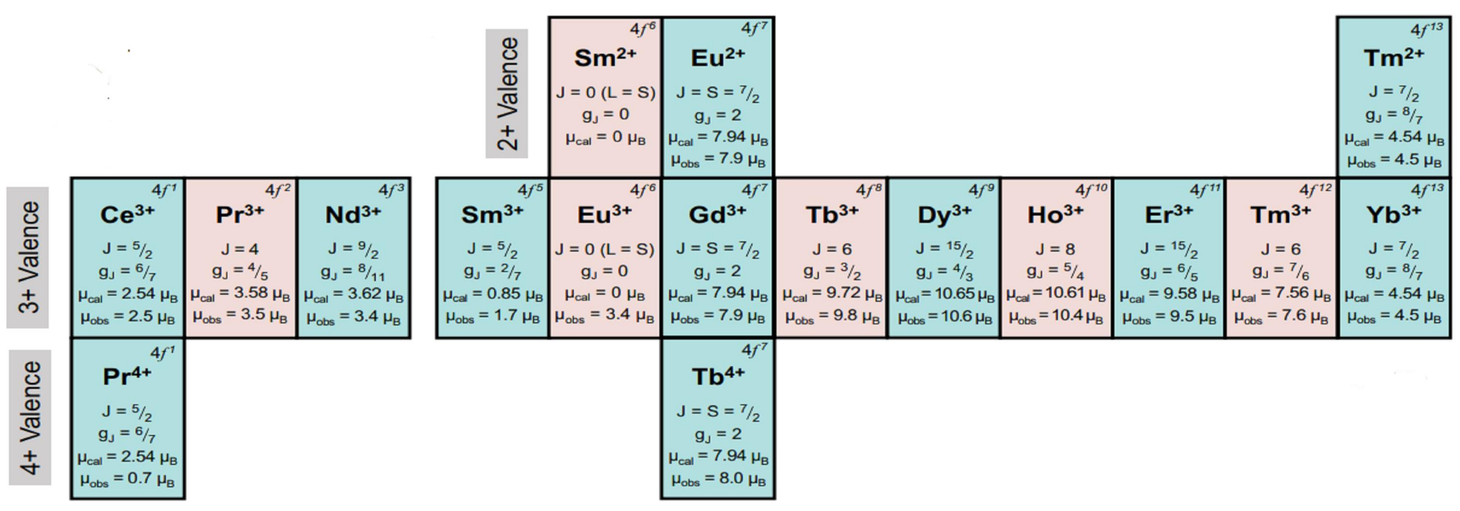
Molecular magnetism

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

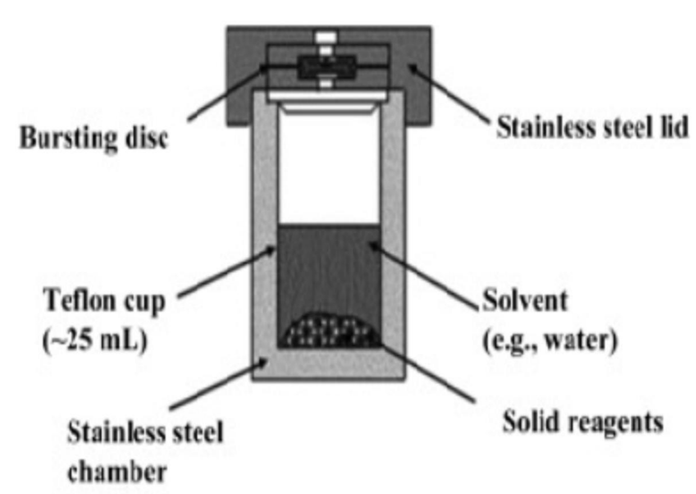


Magnetic properties of rare earth ions in their divalent (top row), trivalent (middle row) and tetravalent (bottom row) states arranged according to their number of f electrons.

Unpaired electrons give rise to a magnetic moment, and when these moments interact, they can produce complex magnetic behavior, such as paramagnetism, diamagnetism, or ferromagnetism, depending on the specific arrangement and properties of the molecules. By measuring the response of a substance to an applied magnetic field, magnetic susceptibility, it can be estimated the number of unpaired electrons present.

Another important factor in the molecular magnet structure is magnetic anisotropy. It is the required energy to deflect the magnetic moment in a single crystal from the easy to the hard direction of magnetization. The structural feature of the 4f orbital gives lanthanides high magnetic anisotropy.

Hydrothermal synthesis of rare-earth magnets

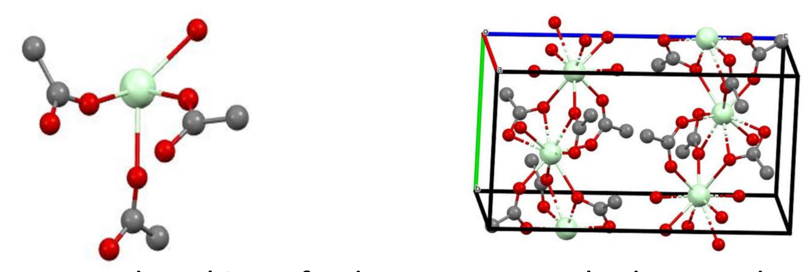


Structure of the autoclave used in the hydrothermal synthesis method.

Hydrothermal synthesis is a method of 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.

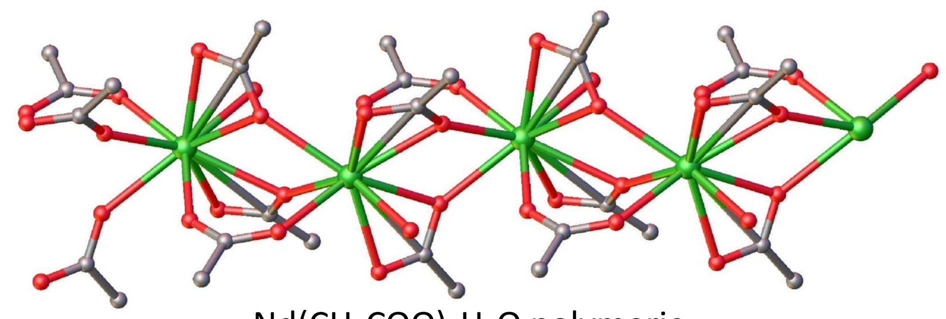
In this study, the experiments were completed by heating in the oven for 3 days at 200 degrees Celsius, followed by slow cooling for 2 days.

rare-earth containing molecular magnets



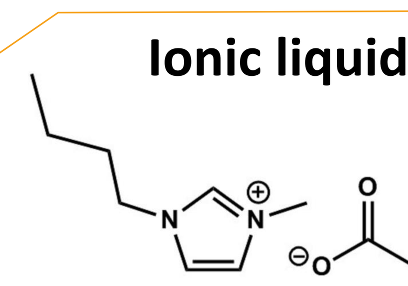
Molecule structure and packing of Nd acetate monohydrate. Nd=Green,O=red,C=gray.

In the presented neodymium acetate monohydrate molecule, the acetate groups act as ligands, bridging the neodymium centers and facilitating magnetic exchange. This polymeric neodymium acetate monohydrate complex was synthesized using an ionothermal approach, where the reaction was carried out in an ionic liquid medium as described. IL atmosphere was created with BMIM acetate and crystals were obtained by slowly cooling the solution from the reaction temperature (120^{0}C) to room temperature. Crystal structure analysis was done with the SCXRD device.

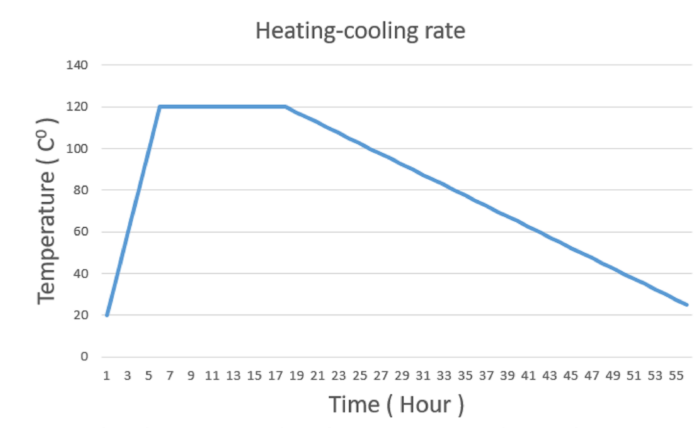


$Nd(CH_3COO)_3H_2O$,polymeric structure neodymium acetate monohydrate molecule. Nd=Green,O=red,C=gray.

Ionic liquid



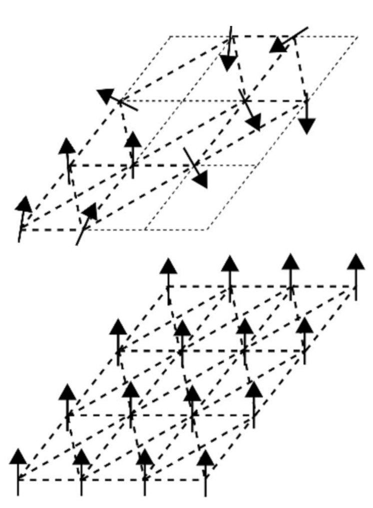
Ionic liquids, such as 1-butyl-3-methylimidazolium acetate (BMIM acetate), provide a unique ionothermal synthesis environment. In this medium, rare-earth acetates can be dissolved and subsequently crystallised, enabling the formation of novel molecular structures with potentially interesting magnetic properties.



Graph showing the heating and cooling rates applied in the ionic liquid synthesis method.

Spin-spin co-operative behaviour

The coordinated or cooperative interaction of the spins of individual magnetic centers within a molecule or complex with each other is spin-spin cooperation.

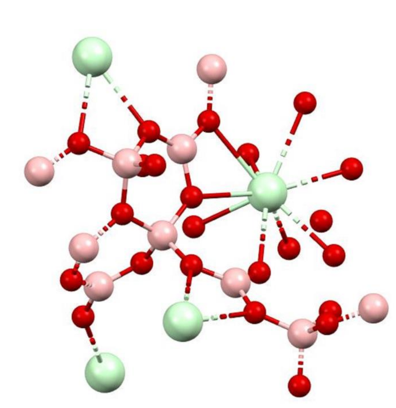


Spin-spin cooperative behavior can be achieved by introducing ligands into the molecular structures of rare-earth elements, which can guide the magnetic spin interactions between atomic centers.

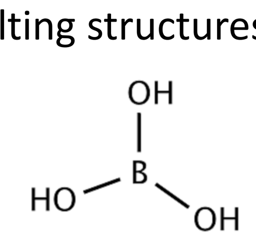
Ligands are atoms, ions, or molecules that can donate electron pairs to a central metal atom or ion, forming a coordination complex. Bridging ligands are ligands that can connect two or more metal centers within a coordination complex. They typically contain two or more coordinating atoms that can simultaneously bind to different metal ions, forming bridging bonds.In molecular magnets, bridging ligands can facilitate the magnetic exchange interaction between metal ions, leading to the formation of magnetic clusters or networks.

Borate ligands in rare-earth molecular structure

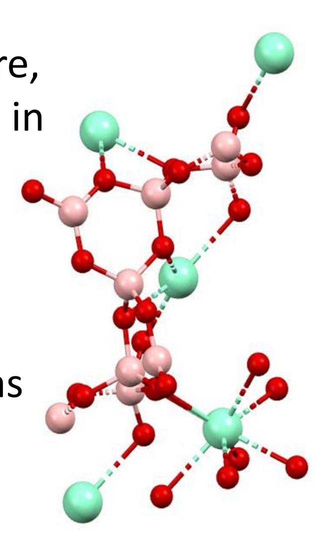
To create borate ligands in the molecular structure, boric acid was used as a borate donor in solution in both ionothermal synthesis environment and hydrothermal synthesis methods. Synthesis was attempted with acetate, nitrate, chlorate and triflate types of rare earths at various temperatures and ratios, but no borate ligand was found in the resulting structures.



Molecule structure of Nd borate Nd=Green,O=red,B=rose



Boric acid



Molecule structure of Sm borate Sm=Blue,O=red,B= rose

Objectives

- Synthesise novel molecular magnets with spin-cooperative behaviour
- Understand the synthesis of molecular cluster magnets
- New synthesis pathways through ionic liquid
- Use the understanding of formation mechanisms and magneto structural property relationships to inform the design of further molecular cluster magnets

References

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Acknowledgement

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