

MUSHROOM Science Case Study 1

Immediate impact – Magnetochemistry

Over the past 10 years, LET has established itself as the pre-eminent cold neutron time-of-flight spectrometer – worldwide. This reputation is based largely on its adaptable resolution capabilities, the availability of neutron polarization analysis, and extremely low background – even with complex sample environments. The flux on LET means that experiments on small samples (~1g) can be attempted – and often, this mass is appropriate for many inorganic compounds (mainly oxides) and metallic crystals. However, in the burgeoning field of organic molecular magnetism, crystals of this size are rare, and crystal co-alignment is difficult to achieve. With MUSHROOM, order-of-magnitude increases in flux (concentrated into a small beam area) will be compatible with single crystal masses of < 100 mg – compatible with many organic magnets and effectively providing an “LET for chemists”¹.

Organic magnets often exhibit a variety of interesting electronic and magnetic states. So-called MMX chain complexes (M=metal, X=halide) for example, host 1d-metallic, charge-density wave and dimerised magnetic phases. There is a large coupling between electron-localisation at the M sites and the M-M, M-X bond lengths, which is why the lattice dynamics of this family – essentially unexplored – are of particular potential interest. The addition of

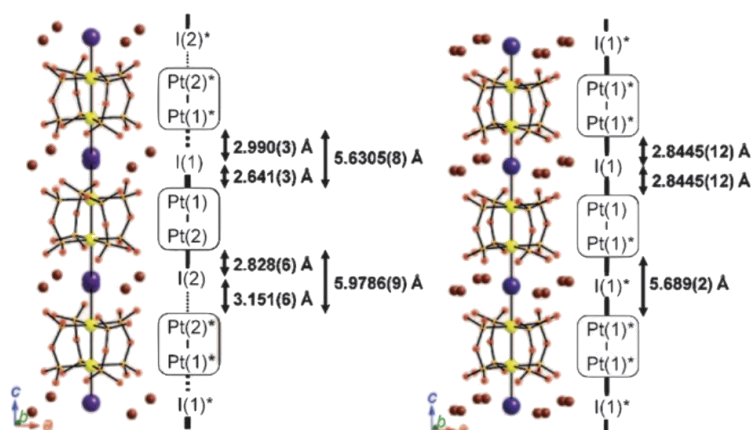


Fig. 1. Crystal structure of the MMX chain $[M_2(pop)_4X] \cdot nH_2O$ with $M=Pt$ and $X=I$ – for two levels of hydration, $n=2.4$ (left) and $n=2$ (right) – showing strong dependence on n of both Pt-Pt and Pt-I bonds [1]

guest water molecules to the complex on hydration in the MMX chain $[M_2(pop)_4X] \cdot nH_2O$, leads to large changes in bond-length (see Fig. 1) and therefore presumably has a direct effect on the electron-phonon coupling in this system [1]. Yet, there is no direct experimental evidence of this. Inelastic neutron experiments on this system could search for possible Kohn anomalies in the parent material, shed light on lattice dynamics under the hydration-dehydration cycle, and also investigate the nature of the 1d-magnetism.

Recent advances in metal-organic framework (MOF) chemistry have allowed the development of electrically conductive MOFs with tuneable properties associated with the MOF architecture. For example, the layered MOF $CrCl_2(py_2z)_2$ exhibits both high electronic conductivity at room temperature and ferrimagnetic order below 52 K [2]. Conductivity is

¹ A. L Goodwin, 2021

conjectured to proceed via hopping – and is strongly coupled to pyrazine orientations, implying the need for characterisation of these modes and their wavevector dependences. Magnetic moments are found on both Cr³⁺ cations and the pyrazine linkers, which indicates particularly strong spin-phonon coupling – and which would result in phonon anomalies on the development of long-range magnetic order at low temperatures.

In these materials, there is a clear need for investigation into both lattice and magnetic excitations *via* inelastic neutron scattering, and yet, no instrument currently exists worldwide which could hope to yield data of sufficient quality. MUSHROOM will be the first instrument of its type – and will immediately be able to attempt experiments on sub 100 mg organic magnetic crystals. Materials such as these are being widely studied around the world, but perhaps especially in the UK, with active research groups in the Universities of Oxford, Warwick, Birmingham, Manchester, Kent, Nottingham and others. With the addition of MUSHROOM to its instrument suite, and well-established links to these user groups, ISIS would be uniquely well placed to take a lead in INS studies of organic magnets

References

- [1] H Iguchi, *et al.*, Water-Vapor-Induced Reversible Switching of Electronic States in an MMX-Type Chain Complex with Retention of Single Crystallinity, *Angewandte Chemie*, **122**, 562-565 (2010). <https://doi.org/10.1002/ange.200905608>
- [2] K S Pedersen, *et al.*, Formation of the layered conductive magnet CrCl₂(pyrazine)₂ through redox-active coordination chemistry, *Nature Chem* **10**, 1056 (2018). <https://doi.org/10.1038/s41557-018-0107-7>