Experimental report

29/06/2022

Proposal: 5-41-1167 **Council:** 4/2021

Title: Exploring the magnetic structure of Manganese(II) thiocyanate, Mn(SCN)2

Research area: Physics

This proposal is a new proposal

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Samples: Na.3H2O[Mn(NCS)3]

Instrument	Requested days	Allocated days	From	To
D19	7	6	21/09/2021	27/09/2021

Abstract:

The study of two-dimensional magnetic compounds is a contemporary addition to the ever-growing field of magnetic materials. Layered molecular structures are enticing as a result of their inherent chemical diversity, however, identified 2D magnetic molecular structures are remain uncommon. Binary transition metal thiocyanates, M(SCN)2 are a series of isomorphic materials adopting layered structures, which exhibit long range order at low temperatures. Despite the appeal of these frameworks, structural and magnetic data thus far has only been collected through powder diffraction data. Recently we have managed, for the first time, to obtain single crystal samples, Mn(SCN)2, of up to 8x5x3 mm3 in volume. Here, we propose a deeper exploration of Mn(SCN)2 to determine its magnetic structure using single crystal neutron diffraction. The experiment aims to understand the conflicting magnetic pathways within the framework and will help the design of future families of low-dimensional magnetic molecular frameworks.

Exploring the magnetic structure of Manganese(II) thiocyanate, $Mn(SCN)_2$

$Mn(NCS)_2$, a two-dimensional polymeric framework compound, is sensitive to moisture and as a result is deliquescent, which lead to the original crystal (8x5x3 mm^3) not being available to use in the experiment. In the absence of obtaining further crystals of $Mn(NCS)_2$, the experiment sample was modified to measure a crystal of the related compound $[Na(OH_2)_3][Mn(NCS)_3]$ (4x3x1 mm^3).

Monochromatic single crystal neutron diffraction was carried out on the four-circle diffractometer D19. Data were collected at 2 K, 25 K and 70 K with a wavelength of 1.455 Å; and, in addition, at 2 K with a wavelength of 0.950 Å. Due to the hygroscopic nature of the crystal, the crystal was wrapped in aluminium foil with a small amount of grease before being mounted.

NOMAD software was used for data collection. Unit cell determinations were performed using PFIND and DIRAX programs, and processing of the raw data was applied using RETREAT and RAFD19 programs. Structural and magnetic refinements of the data were carried out using the FullProf program.

The 2 K data set, below the magnetic ordering temperature of 18 K, revealed that the magnetic structure has a propagation vector of (0, 0, 0). The possible magnetic models that fit this propagation vector with the compound's nuclear structure of *P*-3 are the trigonal space groups *P*-3', *P*-3 and *P*3; and the triclinic space groups *P*-1', *P*-1 and *P*1.

The data measured at 2 K with the shorter wavelength (0.950 Å) allows reflections to be collected to a higher Q range, making it ideal to determine a high quality nuclear structure of the compound. At 2 K the data suggested that the compound crystallises in the trigonal crystal system, rather than lowering its symmetry to a triclinic structure. This meant the triclinic magnetic space group could be eliminated from consideration.

The magnetic susceptibility data suggest that the dominating magnetic interactions present in the compound are antiferromagnetic, which cannot be achieved by ordering in the *P*-3 space group, leaving the *P*-3' and *P*3 models as the potential magnetic space group. Refinements were carried out for both the *P*-3' and *P*3 models with the 2 K data collected with the longer wavelength (1.455 Å). These gave similar refinement statistics of χ^2 of 11.83 % (*P*-3') and 9.84 % (*P*3). The size of the magnetic moment in *P*-3' is 4.11(±0.22) μ_B per Mn, and orders as an antiferromagnet. In the *P*3 model the moment sizes are −3.98(±0.23) and +3.97(±0.23) μ_B per Mn, resulting in a net magnetisation of 0.01(±0.33) μ_B per Mn along the *c* axis.

It is likely that the magnetic ground state of $[Na(OH_2)_3][Mn(NCS)_3]$ is *P*-3', given that the two moment sizes in the *P*3 model are within error the same value. To confirm if the interactions are purely antiferromagnetic, or if there is a small ferromagnetic contribution further magnetic susceptibility measurements will be carried out to complement the neutron data.

The results of this experiment will form part of the thesis for a current ILL PhD student and will be written up to for publication (e.g. Inorganic Chemistry/Chemical Science).

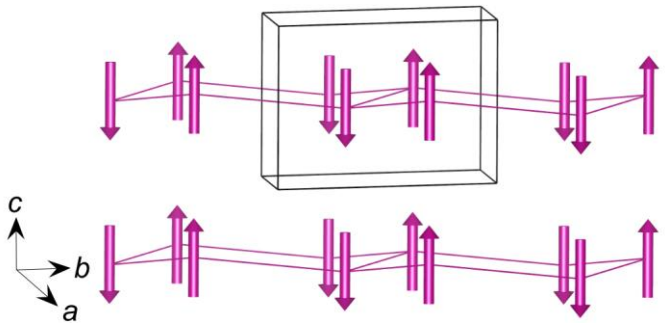

Figure 1. The P-3' magnetic model for $[Na(OH_2)_3][Mn(NCS)_3]$. All non-magnetic atoms have been removed for clarity and the manganese atoms have been joined with straight purple lines to highlight the nearest neighbour superexchange pathways.

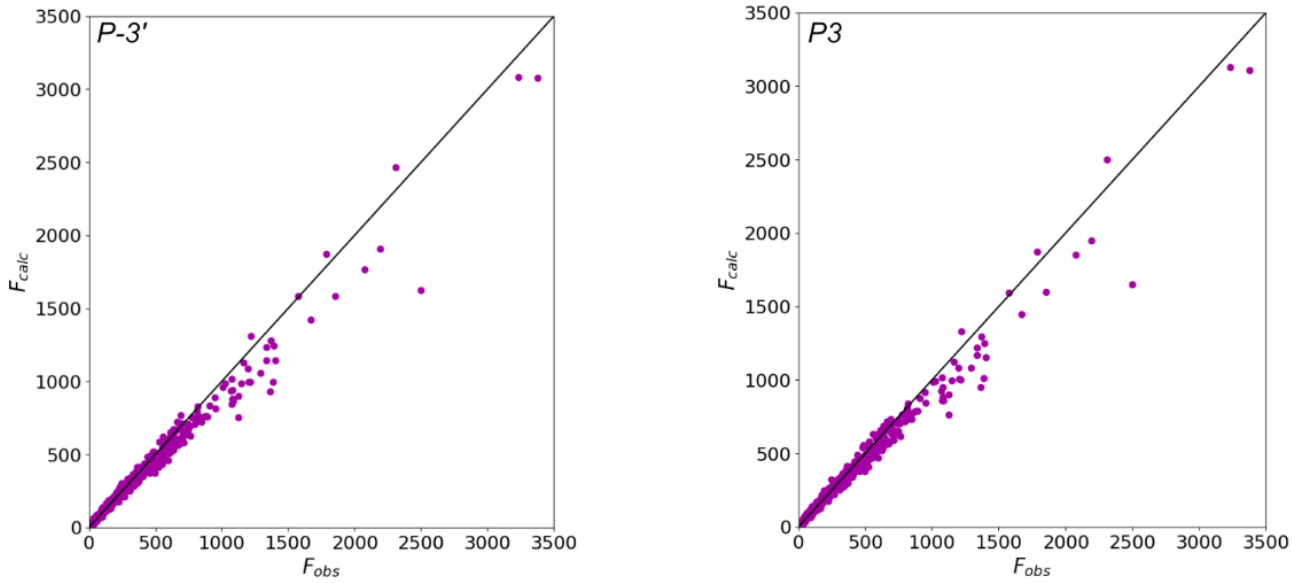

Figure 2. Plots of F_{obs} against F_{calc} for the refinements against the trigonal magnetic space groups P-3' (left) and P3 (right) with λ=1.55 Å.