Experimental report

13/05/2022

Proposal: 5-41-1060 **Council:** 10/2019

Title: Determination of the magnetic structures of the noncollinear magnet CsCo(NCS)3

Research area: Chemistry

This proposal is a new proposal

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Samples: CsMn(NCS)3
CsCo(NCS)3

Instrument	Requested days	Allocated days	From	To
D19	10	6	12/08/2020 02/07/2021	13/08/2020 07/07/2021

Abstract:

Dense coordination polymers combine the functional properties typical of the traditional inorganic solid state, such as magnetism, with the remarkable tunability and flexibility that arises for the incorporation of molecular components. They therefore offer the opportunity to discover unusual behaviour that arises from the coupling these properties. Thiocyanate compounds have the potential for rich optical and magnetic properties, but both their chemistry and magnetism remain comparatively unexplored.
CsCo(NCS)3 is a non-collinear antiferromagnet which shows significant magnetic hysteresis and multiple magnetic phase transitions. It adopts a layered structure related to the unusual beta-LaYbS3 structure type, with a pseudo 2D-rectangular magnetic lattice, but both its ground state and the intermediate ordered phase remain unknown. This study aims to identify these magnetic structures and, combined with the already determined CsMn(NCS)3 and the proposed CsNi(NCS)3 structure, to rationalise their magnetic behaviour.

Determination of the magnetic structures of the non-collinear magnet $CsCo(NCS)_3$

The largest single crystal we were able to grow of $CsCo(NCS)_3$ obtained measured approximately 0.5 x 0.3 x 0.1 mm^3, which was unfortunately too small for reasonable quality data. In the absence of a suitable single crystal, we requested a modification of the experiment's sample to measure a crystal of the isostructural compound $CsMn(NCS)_3$ instead (6 x 3 x 1 mm^3).

During a previous experiment on the D1b powder diffractometer (5-31-2816) we observed unexpected shifts of the structural peaks of $CsMn(NCS)_3$ in the high Q region between 2 and 20 K, which we were unable to determine the origin of. The objective of this D19 experiment was therefore to investigate any changes in nuclear structure of $CsMn(NCS)_3$ at low temperatures (between 2 and 20 K), using the higher information content of single crystal diffraction to eliminate any ambiguities.

Monochromatic single crystal neutron diffraction data for $CsMn(NCS)_3$ were collected on the four-circle D19 diffractometer, with a wavelength of 1.455 Å. Long acquisition measurements were carried out at 2, 13, 20 and 300 K, with temperatures ramps collected between 2 and 20 K.

NOMAD software from the ILL 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 models were solved using the *SUPERFLIP* program and refined using Jana2006.

We found that the nuclear structure of $CsMn(NCS)_3$ does not significantly change between 2 and 20 K, with only slight deviations in bond length, which can most likely be attributed to its response to temperature.

These improved data allowed us to determine the ground state magnetic structure of $CsMn(NCS)_3$. The additional reflections that appear in the 2 and 13 K measurements (below the ordering temperature 16 K) are most likely described with a propagation vector of (0, ½, ½), where the magnetic unit cell is doubled along the nuclear *b* and *c* axes. These reflections could be indexed to a magnetic space group P_s -1. In this structure there are four unique magnetic manganese atoms, two with a moment size of -5.81($\pm$0.02) μ_B and two, which appear to be partially disordered, with a moment size of 0.81($\pm$0.05) μ_B. The magnetic moments are positioned so that the two-dimensional layers of $[Mn(NCS)_3]^-$ alternate between layers of the two larger moments and two smaller moments, which induce some frustration.

These data, in combination with other experiments carried out at ILL (5-12-344, 5-31-2767, 5-31-2816) will form part of the thesis for a current ILL PhD student and the results are currently being written up to for publication (e.g. Inorganic Chemistry/Chemical Science).

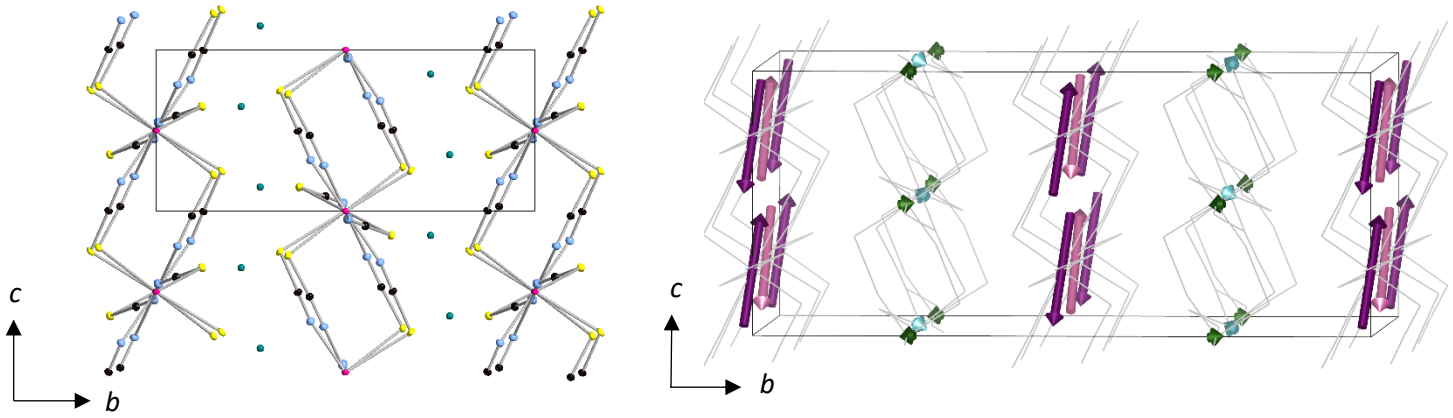

Figure 1. Left: Asymmetric unit cell of $CsMn(NCS)_3$ at 2 K shown with 50 % displacement ellipsoids. Right: Magnetic structure of $CsMn(NCS)_3$ with the four unique magnetic vectors shown with, purple, pink, green and blue arrows.

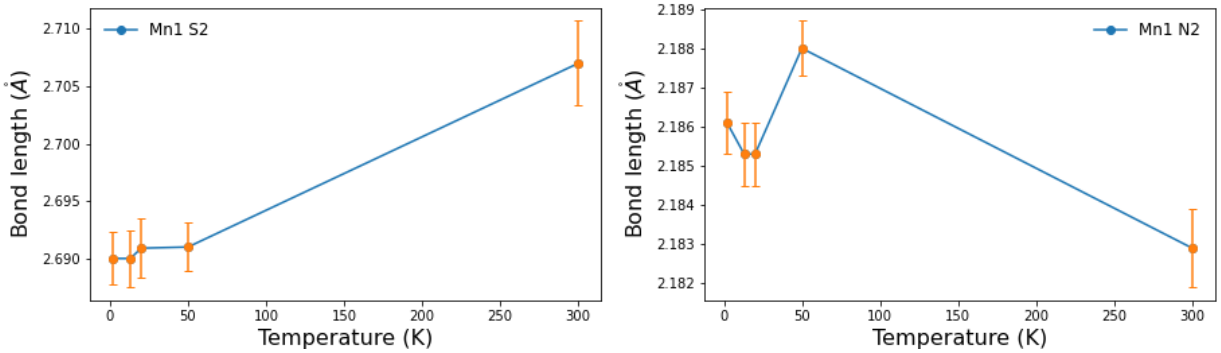

Figure 2. Bond lengths plotted as a function of temperature, values obtained from the structural models at 2, 13, 20, 50 and 300 K. Left: Mn-S bond lengths. Right: Mn-N bond lengths.