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Magnetic structure and properties of the honeycomb antiferromagnet $[Na(OH_2)_3]Mn(NCS)_3$

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1 Experimental

1.1 Synthesis

$Ba(NCS)_2 \cdot 3\,H_2O$ was heated at 50°C until a constant mass of $Ba(NCS)_2$ was obtained (approx. 48 hr). Aqueous solutions of $Ba(NCS)_2$ (4.87 g, 19.2 mmol, approx. 50 mL) and $MnSO_4 \cdot H_2O$ (3.25 g, 19.2 mmol, approx. 15 mL) were combined and stirred. A white precipitate was filtered from a pale pink solution. The solution was heated just below boiling and a dry beige powder of $Mn(NCS)_2$ was collected (2.24 g, 13.1 mmol, 68 %). $Mn(NCS)_2$ was dissolved in distilled H_2O (approx. 15 mL) and NaSCN (1.06 g, 13.1 mmol) was added and dissolved in the solution and stirred overnight. The solution was concentrated *in vacuo*, until a pale green-yellow powder of $[Na(OH_2)_3]Mn(NCS)_3$ was obtained (Fig. 4).

To obtain single crystals, an aqueous solution of $[Na(OH_2)_3]Mn(NCS)_3$ was concentrated *in vacuo* until the solution was pale green. The solution was covered and cooled at 7°C for 24 h, with care not to create vibrations or knock the sample. From the crystals obtained, the largest crystals were removed, whilst the rest of the mixture was redissolved in distilled H_2O. The solution was concentrated *in vacuo* until the solution was a pale green colour. The selected crystal was placed in the solution and the mixture was covered and cooled at 7°C for 24 h. This process was repeated daily for 9 days at which point a green, hexagonal plate-shaped crystal of $[Na(OH_2)_3]Mn(NCS)_3$ was collected ($4 \times 3 \times 1$ mm^3).

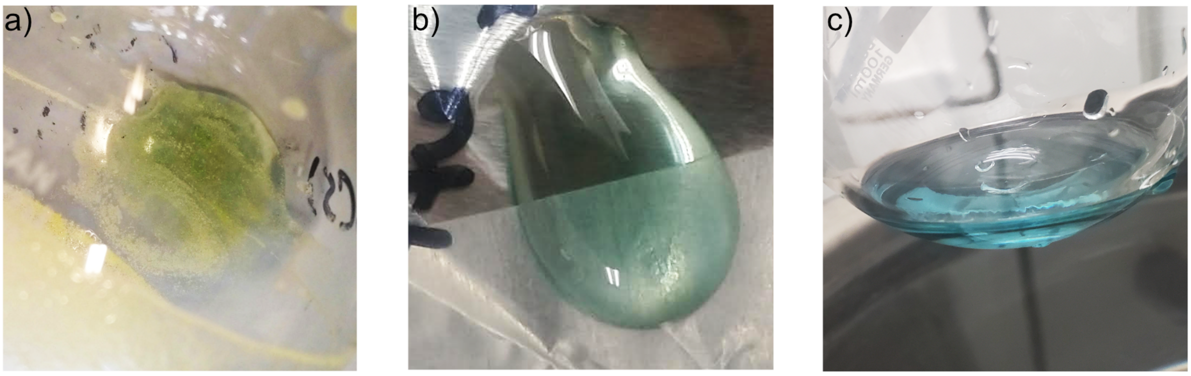
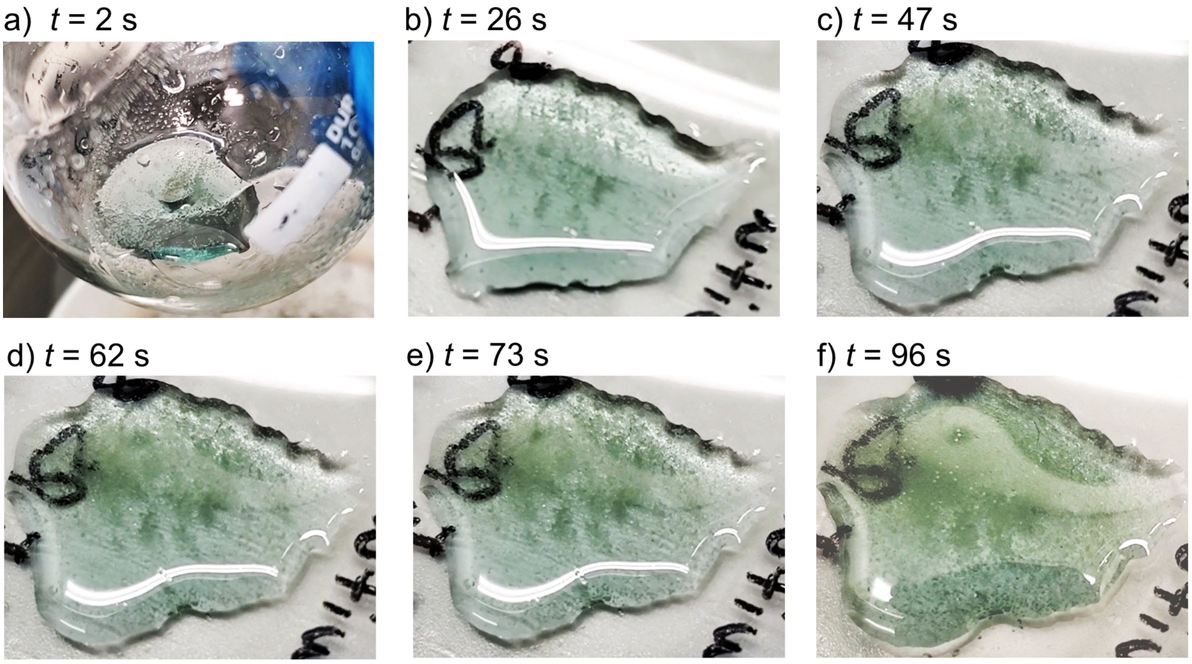


Figure 1: Variations in colour of aqueous $[Na(OH_2)_3]Mn(NCS)_3$ at different concentrations. Comparative concentrations of a) too dilute, b) ideal concentration, and c) too concentrated solutions for ideal crystal growth conditions.



a) $t = 2$ s
b) $t = 26$ s
c) $t = 47$ s
d) $t = 62$ s
e) $t = 73$ s
f) $t = 96$ s

Figure 2: Following an over-concentrated aqueous solution of $[Na(OH_2)_3]Mn(NCS)_3$ with time. The solution becoming more cloudy or opaque is an indication of where the crystals are growing. Images taken at t seconds after removing the vacuum.

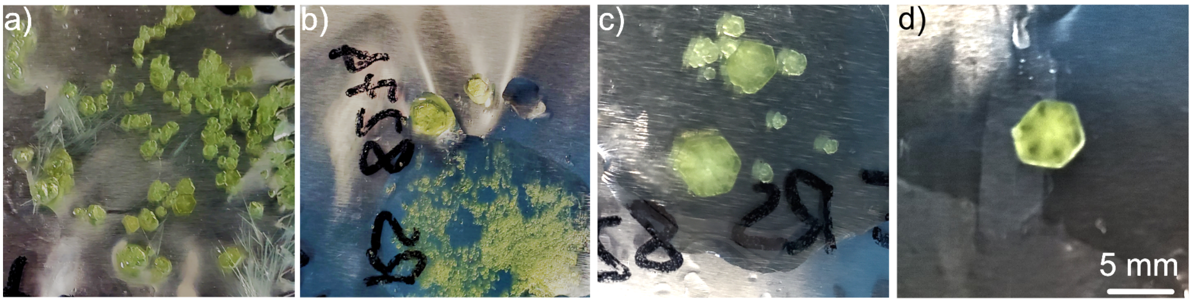


Figure 3: Stages of crystal growth from concentrated aqueous solutions of $[Na(OH_2)_3]Mn(NCS)_3$. Crystals are shown after a) 2 days, b) 5 days and c) 9 days. d) A crystal with a 5 mm scale bar for reference.

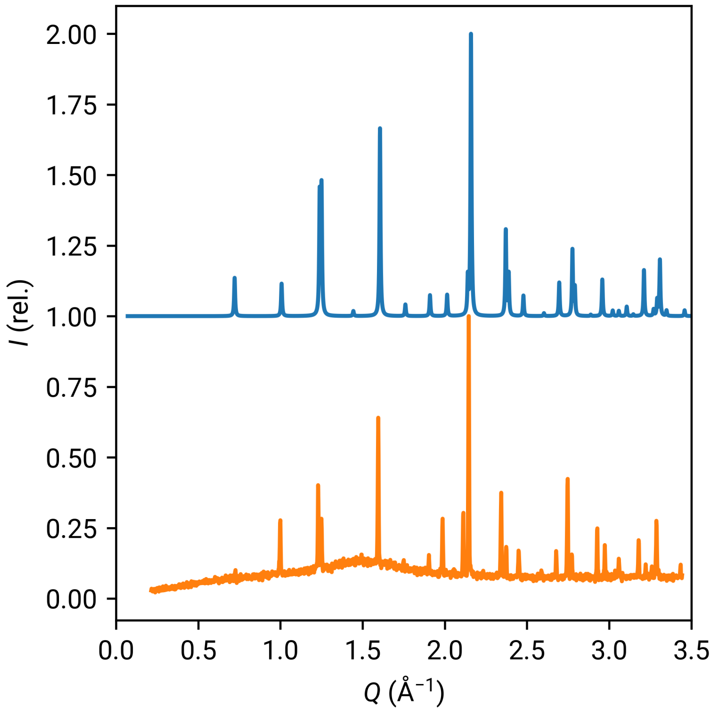


Figure 4: PXRD of $[Na(OH_2)_3]Mn(NCS)_3$ powder sample, measured in reflection geometry using monochromated Cu-Kα1 radiation on a Panalytical X'pert diffractometer.

1.2 Magnetic Measurements

Measurements of the magnetic susceptibility were carried out using a Quantum Design Magnetic Property Measurements System XL (MPMS-XL) Superconducting Quantum Interference Device (SQUID) magnetometer. A polycrystalline sample of [Na(OH$_2$)$_3$]Mn(NCS)$_3$ (9.29 mg) was immobilised in eicosane (9.87 mg). Magnetic susceptibility measurements were performed under field cooled and zero field cooled conditions in an applied direct current field of 0.01 T over the temperature range $2-300$ K. As *M*(H) is linear in this field, the small-field approximation for the susceptibility, $\chi(T) \simeq \frac{M}{H}$, where *M* is the magnetisation and *H* is the magnetic field intensity, was taken to be valid.
Isothermal magnetisation measurements were carried out at 2 K from -5 to $+5$ T. Data were corrected for diamagnetism of the sample using Pascal's constants.[1]

1.3 Single crystal neutron diffraction

Monochromatic single crystal neutron diffraction data of [Na(OH$_2$)$_3$]Mn(NCS)$_3$ ($4 \times 3 \times 1$ mm^3) were collected on the four-circle D19 diffractometer at the Institut Laue Langevin (ILL) Grenoble, France. Neutrons with a wavelength of 1.456 Å were provided by a flat Cu monochromator using the 220 reflection at $2\theta_M = 69.91°$ take-off angle. The sample was placed in a closed-circuit displex cooling device, which was operated following a ramp of 2 K min^{-1}. Measurements were taken at 2 and 25 K. In addition, measurements were taken between 2 and 20 K in 0.25 K steps, and between 20 and 25 K in 1 K steps, following selected reflections. The sample was wrapped in aluminium foil with a small amount of grease before being mounted to avoid direct contact with the glue which can degrade the sample.
NOMAD software from the ILL was used for data collection.[2] Unit cell determinations were performed using PFIND and DIRAX programs, and processing of the raw data was applied using RETREAT, RAFD19 and Int3D programs.[3–6] The data were corrected for the absorption of the low-temperature device using the D19ABS program[7] and for the size and composition of the crystal. Refinements of the nuclear and magnetic model were completed using the FullProf program.[8]

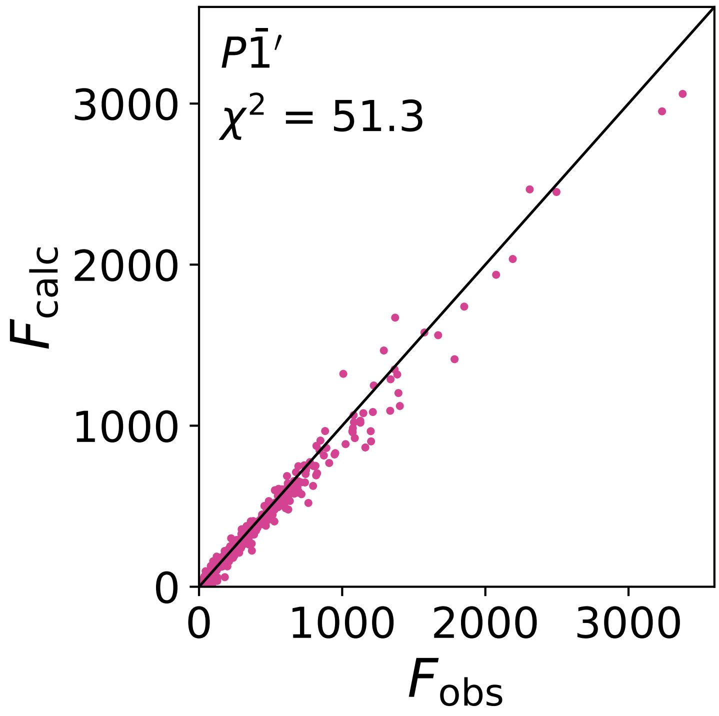


Figure 5: F_{calc} vs. F_{obs} for the structure in $P\bar{1}'$

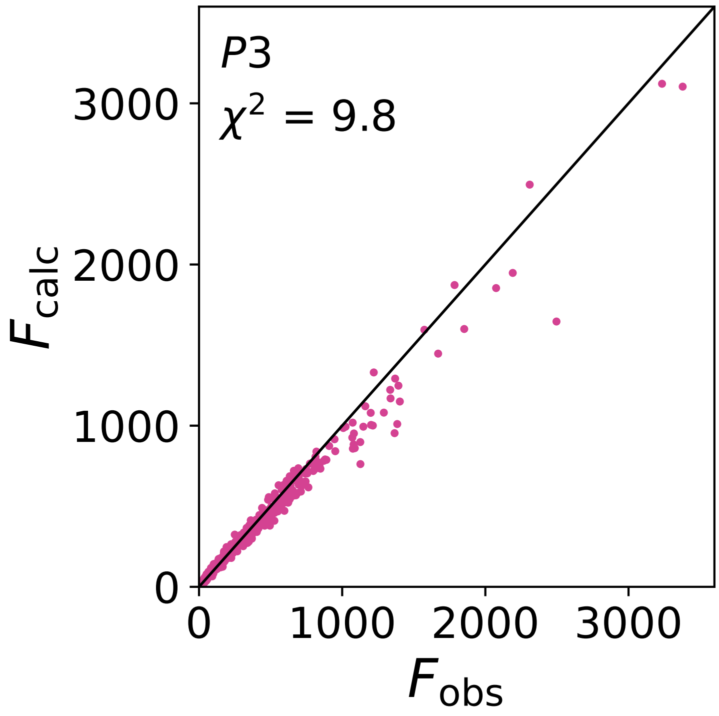


Figure 6: F_{calc} vs. F_{obs} for the structure in $P3$

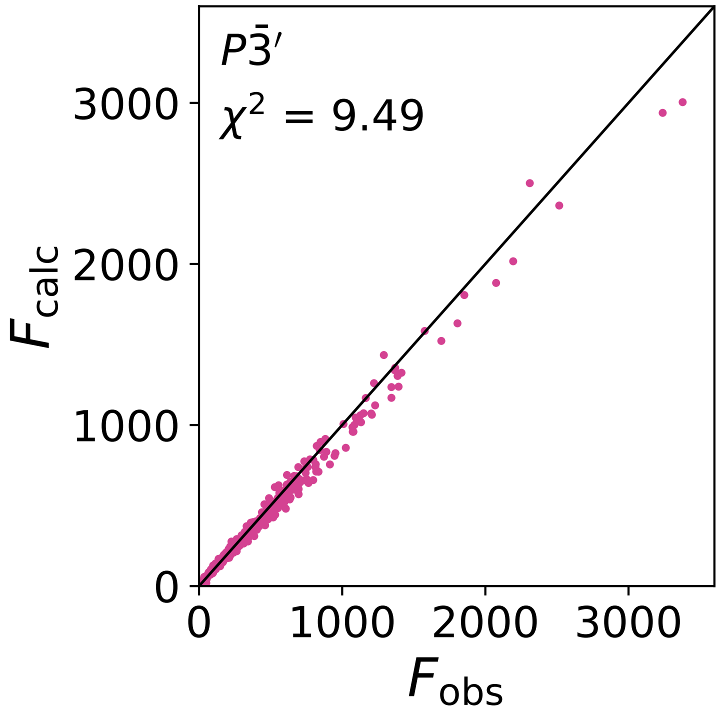


Figure 7: F_{calc} vs. F_{obs} for the structure in $P\bar{3}\prime$

1.4 Second harmonic generation measurements

Second harmonic generation measurements were performed by mounting a crystal of $[Na(OH_2)_3]Mn(NCS)_3$ between two copper plates with an aperture slightly smaller than the dimensions of the crystal, which were in turn clamped onto a copper cold finger. It was then placed into an Oxford Instruments Microstat-He with TPX windows and cooled to 4 K. An incident laser of λ = 800 nm (40 fs pulses, 1 kHz rep. rate) was generated by a Spectra-Physics Spitfire Ace PA system. A λ/2 waveplate was placed in the beam to allow for polarisation rotation before the beam was focused onto the sample with a lens. The average power of the 800 nm beam used ranged from 1 mW – 1 W which was limited by the damage threshold of the micostat windows. Detection was performed using an Ocean Optics HR400CG-UV-NIR spectrometer with a ThorLabs shortpass and bandpass filter placed in front of the detection fibre to block light outside of the 390hg – 410 nm range. Additional measurements were carried out at λ = 400 nm, generated by a type-I β-barium borate (BBO) crystal placed between the lens and cryostat. For these measurements, the shortpass and bandpass filters were removed from in front of the detection fibre and placed between the BBO crystal and the cryostat. Average optical power of the generated 400 nm was in the range of 0.3 – 600 mW (30% SHG efficiency with 800 nm incident light with an average power ranging from 1 mW to 2 W).

2 Magnetisation measurements

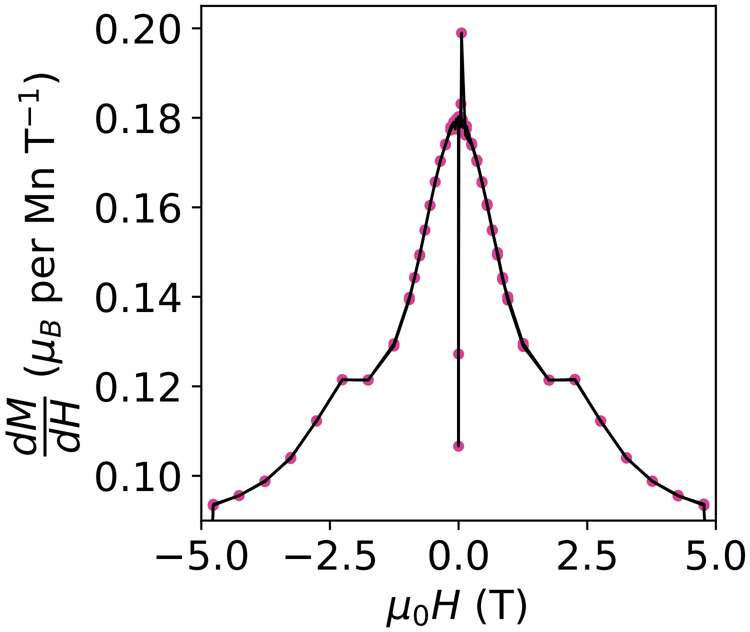


Figure 8: The derivative of the isothermal magnetisation of [Na(OH_2)$_3$]Mn(NCS)$_3$, measured between $+5.00(1)$ and $-5.00(1)$ T at 2 K.

3 Neutron diffraction

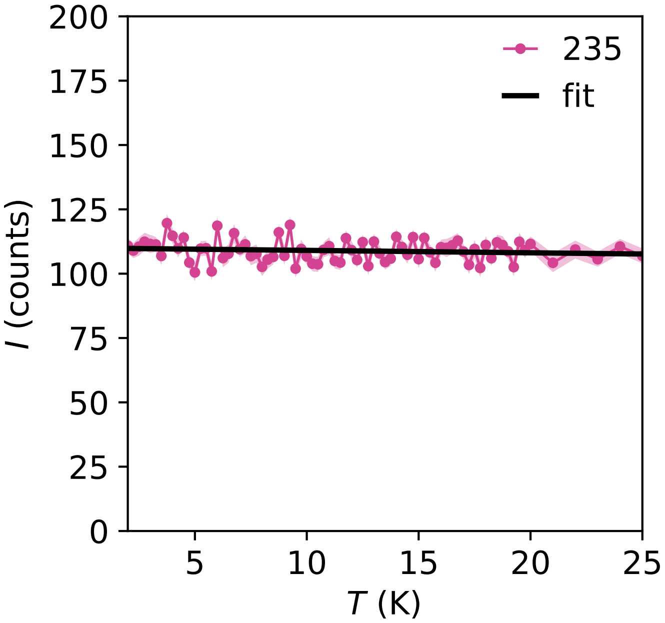


Figure 9: The temperature dependence for the 235 Bragg reflection measured between 2 and 25 K (D19, ILL), fitted with a linear equation (black line) $I = 0(1)T + 109.9(3)$, showing, within error, no temperature dependence above and below the magnetic orering temperature, $T_{\mathrm{N}} = 18.1(6)$ K. The shaded regions denotes the errors.

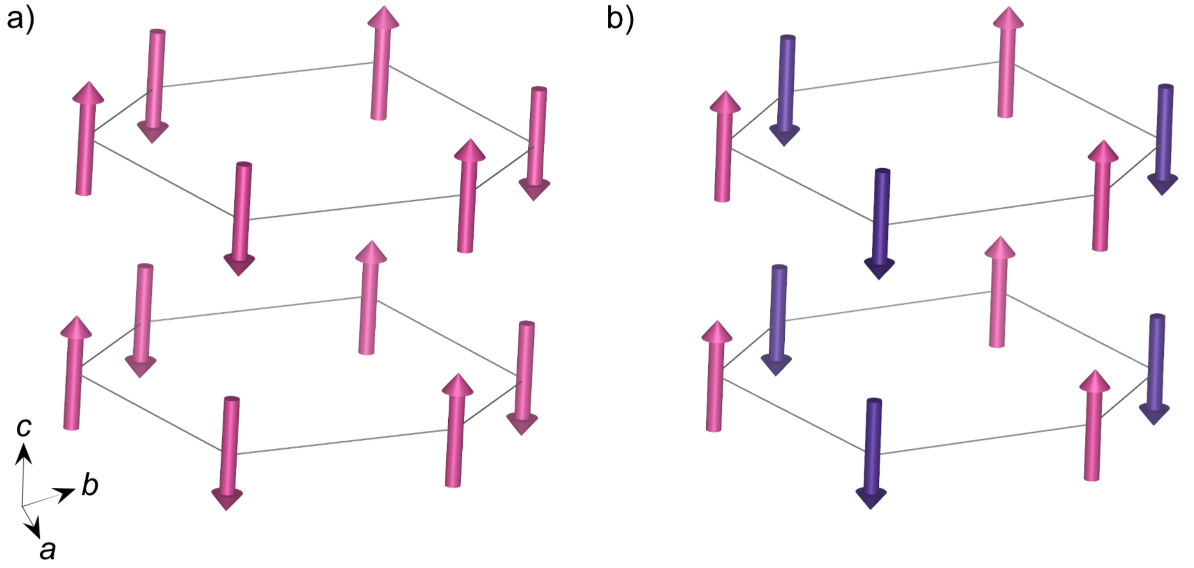


Figure 10: The arrangement of the magnetic moments in the a) $P\bar{3}'$ magnetic space group with one symmetry distinct moment (pink), and b) $P3$ magnetic space group with two symmetry distinct Mn sites (pink and purple). The connection between Mn atoms (through two NCS$^-$ anions) is shown by the light grey line.

Table 1: Comparison of integration and refinement parameters for [Na(OH$_2$)$_3$]Mn(NCS)$_3$ using the $P\bar{3}'$, $P\bar{3}$ and $P\bar{1}'$ models at 2 K (D19, ILL). θ and ϕ are the angles of the moments in spherical coordinates (radians), where θ describes the inclination with respect to the c axis and ϕ describes the rotation around c. In the trigonal space groups, θ and ϕ are restricted by symmetry to be zero.

	$P\bar{3}'$	$P\bar{3}$	$P\bar{1}'$
a (Å)	$10.0361(3)$	$10.0361(3)$	$10.084(3)$
b (Å)	$10.0361(3)$	$10.0361(3)$	$10.083(3)$
c (Å)	$6.2315(2)$	$6.2315(2)$	$6.258(2)$
α (°)	90	90	$89.97(2)$
β (°)	90	90	$90.03(2)$
γ (°)	120	120	$120.04(4)$
χ^2	9.49	9.83	51.3
Moment (μ_B)	$4.9(2)$	$3.9(2)$, $-4.0(2)$	$4.1(2)$
θ (rad)	0	0	$4(5)$
ϕ (rad)	0	0	$-40(70)$

Table 2: Single crystal experimental details for [Na(OH$_2$)$_3$]Mn(NCS)$_3$ determined from neutron diffraction at 25 K (D19, ILL) using the FullProf program.

Crystal data	[Na(OH$_2$)$_3$]Mn(NCS)$_3$
Chemical formula	$C_3MnN_3S_3H_6NaO_3$
M_r	306.22
Temperature (K)	25
λ (Å)	1.456
Radiation type	Neutron
Crystal system	Trigonal
Space group	$P\bar{3}$
a (Å)	$10.0384(3)$
b (Å)	$10.0384(3)$
c (Å)	$6.2313(2)$
V (Å^3)	$543.79(8)$
Z	2
μ (mm^{-1})	0.029
Crystal size (mm)	$4 \times 3 \times 1$
Data collection	
Diffractometer	D19, ILL
No. of measured reflections	1942
No. of independent reflections	631
No. of observed reflections $[I > 2\sigma(I)]$	628
R_{int}	0.0534
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.5992
Data completeness	0.959
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $\omega R(F^2)$	0.090, 0.094
No. of reflections	1942
No. of parameters	65

References

[1] G. A. Bain *et al.*, *Journal of Chemical Education*, 2008, **85**, 532.
[2] P. Mutti *et al.*, Proc. ICALEPCS, 2011.
[3] A. J. M. Duisenberg, *Journal of Applied Crystallography*, 1992, **25**, 92–96.
[4] G. J. McIntyre *et al.*, *Acta Crystallographica Section A Foundations of Crystallography*, 1988, **44**, 257–262.
[5] C. Wilkinson *et al.*, *Journal of Applied Crystallography*, 1988, **21**, 471–478.
[6] N. A. Katcho *et al.*, *Crystals*, 2021, **11**, 897.
[7] J. C. Matthewman *et al.*, *Journal of Applied Crystallography*, 1982, **15**, 167–173.
[8] J. Rodríguez-Carvajal, *Physica B: Condensed Matter*, 1993, **192**, 55–69.