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Magnetic order in a metal thiocyanate perovskite-analogue

This study showed that the coordination framework $\text{Cr}[\text{Bi}(\text{SCN})_6]_x\text{H}_2\text{O}$ undergoes long-range magnetic order, despite the long distance between the two metal sites, a through-bond distance of 15 Å (via eight-bonds). Rietveld refinement of neutron diffraction data measured at the Institut Laue Langevin uncovered that this compound has a Type-II antiferromagnetic order, analogous to that of MnO .

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Magnetic order in a metal thiocyanate perovskite-analogue†

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Metal thiocyanate perovskite-analogues are a growing class of materials, but although they contain paramagnetic cations there have been no reports of their magnetic properties. Due to the large separations between the paramagnetic cations, with a shortest through-bond distance of 15.1 Å, these materials might be expected to be good examples of paramagnets. In this communication we investigate the magnetic properties of a metal thiocyanate framework $\text{Cr}[\text{Bi}(\text{SCN})_6] \cdot x\text{H}_2\text{O}$. We find that $\text{Cr}[\text{Bi}(\text{SCN})_6] \cdot x\text{H}_2\text{O}$ undergoes long-range magnetic order at $T_N = 4.0(2)$ K. We use neutron powder diffraction to determine that $\text{Cr}[\text{Bi}(\text{SCN})_6] \cdot x\text{H}_2\text{O}$ has a MnO-type $\{111\}_{\text{cubic}}$ -ordering as its ground state, consistent with frustrated nearest- and next-nearest-neighbour antiferromagnetic interactions. This suggests that appropriate design of metal thiocyanate perovskite-analogue structures may reveal a rich vein of frustrated magnetism.

Molecule-based perovskite-analogues, framework compounds built from corner-sharing octahedra with a general formula A_xMX_3 where at least one of A, M or X is a molecular ion, offer a diverse range of new chemistries and functionality to the solid state scientist.^{1,2} In particular, including molecular components generates additional degrees of freedom, which permits orderings impossible in conventional atomic analogues—for example, ordering of the electric dipole of MeNH_3^+ as an A-site guest can generate electrical polarisation.^{3,4} This polar ordering could, if combined with

magnetic order generated by M-site cations, generate multiferroic materials possessing simultaneous electric and magnetic order.^{3,5} The magnetism of molecule-based perovskites has therefore been intensively investigated, particularly focussing on metal formates due to the diversity of A-site ammonium and M-site transition metal cations which can be incorporated. A wide range of magnetic formates have now been investigated, with particular excitement found in the wide-range of non-collinear magnets, including the perovskite $\text{A}[\text{M}(\text{CHOO})_3]^{6-8}$ and niccolite mixed-metal formates $\text{A}\{\text{M}[\text{M}'(\text{CHOO})_6]\}^{9-11}$.

A major challenge for molecular magnetism has been the weakness of the magnetic interactions between paramagnetic ions, especially compared to the pure elements and simple oxides, where strong exchange can be produced through direct overlap of the magnetic orbitals, or a single intervening anion. Developing our understanding of how crystal chemistry determines magnetic interactions will aid us realising both in producing practical magnetism, and, critically, in targeting exotic magnetic phases requiring careful balance of interactions. The cyanide Prussian Blue analogues provide an outstanding example of how crystal engineering can be used to optimise magnetic properties, with the enhancement of magnetic Curie temperatures T_C from 5.6(1) K for Prussian Blue itself, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$,¹³ up to 376 K, $\text{KV}[\text{Cr}(\text{CN})_6]$.¹⁴

Thiocyanate as a pseudohalide ligand is well-known for its optical properties,^{12,15} but control over its magnetism is much less developed, with most focus either on either the two dimensional pseudobinaries¹⁶⁻¹⁹ or frameworks incorporating additional organic coligands.^{17,20-22} Recently, some of us showed that the magnetism of the layered pseudobinary $\text{M}(\text{NCS})_2$, $\text{M} = \text{Cu}, \text{Ni}, \text{Co}, \text{Fe}$ and Mn , can be qualitatively explained on the basis of changing orbital occupation and size, leading to enhancement of interactions and uncovering layered antiferromagnetism.^{18,19} Three dimensionally connected, perovskite-analogue structured materials would be of particular interest as magnets, but thus

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far no frameworks containing only paramagnetic metals on the M-site has been synthesised, as the sulfur terminus requires a softer metal such as Cd^{2+} ,²³ Bi^{3+} ,¹² or Pt^{4+} ,²⁴ leading to the “double perovskite” structure. These sulfur-bonding metals are all diamagnetic, which suggests that the paramagnetic ions in thiocyanate Prussian Blue analogues would be magnetically isolated. However, were these paramagnetic metal ions to be magnetically connected through superexchange pathways, these frameworks would be examples of magnets with the $J_1 - J_2$ face-centered cubic model [Fig. 1(b)], which is both the source of exotic frustrated states,^{25,26} and shared by both rock-salt structured oxides^{27,28} and double perovskites.^{29–31}

Here, we report the magnetic properties of a metal double-perovskite framework, $\text{Cr}[\text{Bi}(\text{SCN})_6] \cdot x\text{H}_2\text{O}$ [Fig. 1], using a combination of bulk magnetometry and neutron powder diffraction. We show that despite the large distances (>8 Å) between paramagnetic ions, there is significant superexchange coupling between these ions: indeed, we find that it has long-range magnetic order below 4.0(2) K. We then go on to solve the magnetic structure of $\text{Cr}[\text{Bi}(\text{SCN})_6] \cdot x\text{H}_2\text{O}$, demonstrating that it orders with ferromagnetically correlated close-packed $\{111\}_{\text{cubic}}$ type planes, antiferromagnetically coupled, like MnO .^{27,32} This finding suggests that by using the extensive range of chemistry available in perovskite-analogue metal thiocyanates we could tune the magnetic interactions to realise exotic quantum states.

A multigram sample of $\text{Cr}[\text{Bi}(\text{SCN})_6] \cdot x\text{H}_2\text{O}$ was prepared *via* solution precipitation, in which an aqueous solution of $\text{K}_3\text{Cr}(\text{NCS})_6 \cdot 4\text{H}_2\text{O}$ (5.89 g, 10 mmol) was added to a solution of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4.85 g, 10 mmol) in 2 M HNO_3 , stirred for 2 hours, filtered, washed with water and dried.¹² We confirmed the structure of this compound using powder diffraction, and from the lattice parameters we determined that this sample was hydrated ($x \approx 1$) [ESI† Fig. S3].¹² We measured the magnetisation in a 100 Oe applied field using

an MPMS-3 magnetometer on warming from a sample cooled in zero field, calculating the susceptibility using the small field approximation.

The susceptibility showed a sharp cusp at 4.0 K and Curie Weiss fitting to the high temperature susceptibility (20–300 K, including a temperature independent paramagnetism term) gave a Weiss temperature, θ , of $-7.8(2)$ K, and an effective moment of $3.27(0.06) \mu_{\text{B}}$, reduced from the spin-only value of $3.87 \mu_{\text{B}}$ [Fig. 2]. Isothermal magnetisation measurements at 2 K and 5 K showed no evidence of hysteresis, with a field-induced transition at around 1.4(1) T observed in the data measured at 2 K [ESI† Fig. S4 and S5]. Together, this suggests that $\text{Cr}[\text{Bi}(\text{SCN})_6] \cdot \text{H}_2\text{O}$ is an antiferromagnet, with mildly frustrated ratio of $f = |\theta|/T_{\text{N}} = 1.9$.

To confirm that the ground state was indeed long-range magnetic antiferromagnetic order, we carried constant wavelength powder neutron diffraction measurements on the high-intensity medium resolution D1B diffractometer at ILL, Grenoble [Fig. 3, ESI† S1 and S2].³³ The incident wavelength was $\lambda = 2.52$ Å and the scattering was measured over an angular range of $2 < 2\theta < 128^\circ$. We measured high quality long-acquisition time diffraction patterns at 10 K and 2 K, supplemented by shorter measurements at intermediate temperatures of 5, 4.5, 4, 3.5, 3 and 2.5 K. By subtracting the 10 K dataset from the lower temperature data we were able to confirm that additional magnetic Bragg peaks emerged between 4 and 4.5 K [Fig. 3], demonstrating that the cusp identified in bulk magnetic susceptibility was due to antiferromagnetic order. We first refined the structural model against the previously determined room temperature

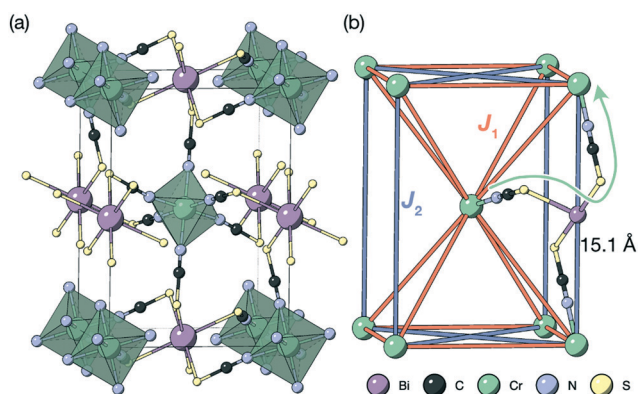


Fig. 1 (a) Crystal structure of the $\text{Cr}[\text{Bi}(\text{SCN})_6]$ framework. Disordered guest water omitted for clarity.¹² (b) The structure showing only the magnetic Cr^{3+} ions and the nearest- (J_1) and next-nearest-neighbour (J_2) superexchange pathways, together with the through-bond distance.

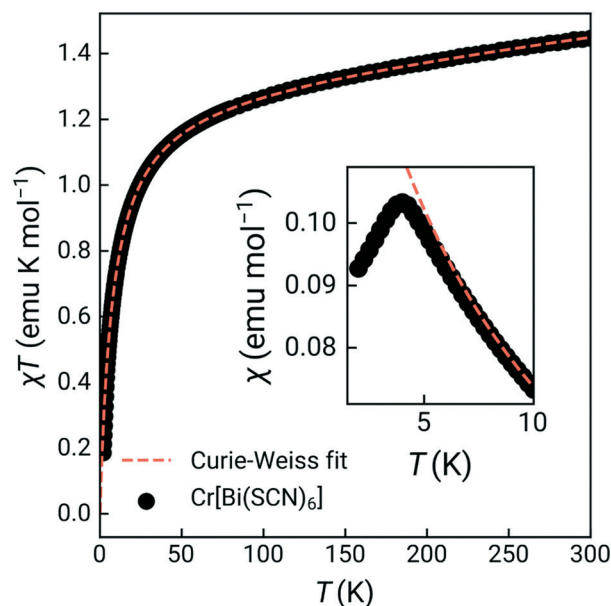


Fig. 2 Variable temperature magnetic susceptibility product measured over the range 2–300 K (zero field cooled). Inset shows the magnetic susceptibility measured over 2–10 K, highlighting magnetic order. Orange dashed line indicates the Curie-Weiss fit, carried out over the range 20 to 300 K.



Using the ISODISTORT tool from the ISOTROPY software suite,³⁵ we were able to identify the three distinct possible

The diagram illustrates the crystal structure of $\text{Na}_2\text{Fe}_2\text{P}_2\text{O}_7$. It features a 3D arrangement of octahedra, with green and dark green colors highlighting different structural components. The 'nuclear cell' is indicated by a dashed box with axes a and c . The 'magnetic cell' is indicated by a solid box with axes a and c , showing a larger unit that encompasses multiple nuclear cells.

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the magnetic structure but as yet single crystals of sufficient size are unavailable.

The most striking feature of this order is that it occurs at such accessible temperatures. The shortest through space distance between Cr atoms is $d = 8.32 \text{ \AA}$, and the shortest through-bond distance is $d = 15.1 \text{ \AA}$, and occurs through 8-bond superexchange, Cr–N–C–S–Bi–S–C–N–Cr. This can be compared to the iron cyanide Prussian Blue, which orders ferromagnetically at $5.6(1) \text{ K}^{13}$ with the magnetic Fe^{3+} ions separated by 7.2 \AA , where magnetic superexchange occurs through a six-bond Fe^{3+} –N–C– Fe^{2+} –C–N– Fe^{3+} pathway 10.2 \AA long. In Prussian Blue, charge and spin delocalisation onto Fe^{2+} (approximately 5% of an electron) through a mixed-valence mechanism are critical to the generation of long-range order.^{37,38} Mixed valency is not likely in this case as the adjacent oxidation states for both Cr and Bi are not easily accessible, and the antiferromagnetic interactions we observe rule out the ferromagnetic ‘double exchange’ found in Prussian Blue. One possible explanation would be facilitation of this comparatively strong superexchange through the accessible NCS redox states—as can be seen in the relatively dispersive conduction band in our previously reported DFT band-structure calculations of $\text{Cr}[\text{Bi}(\text{SCN})_6]$.¹²

The importance of effective superexchange can be seen by comparison to paramagnetic salts of Cr^{3+} , e.g. $[\text{Cr}(\text{CN})_6][\text{Co}(\text{NH}_3)_6]$, where $|\theta| < 0.05 \text{ K}$ and $d_{\text{Cr–Cr}} = 7.4 \text{ \AA}$.³⁹ These comparisons also allow us to eliminate through-space dipolar coupling as a significant contributor to the observed order. Indeed, even in molecular cluster nanomagnets with similar magnet–magnet spacing but much larger total spin it is clear that superexchange rather than dipolar order drives the transition to magnetic long-range order, e.g. the $S = 35/2$ $[\text{Fe}_{19}(\text{metheidi})_{10}(\text{OH})_{14}\text{O}_6(\text{H}_2\text{O})_{12}]\text{NO}_3 \cdot 24\text{H}_2\text{O}$ has a shortest Fe–Fe distance of 8.3 \AA and orders at 1.2 K due to superexchange interactions.⁴⁰

The Cr ions form a face-centered cubic lattice, with only small chemical differences between different crystallographic directions. The interactions are likely to be primarily through-bond rather than through space, and as such the nearest neighbour (J_1) and next nearest neighbour (J_2) interactions are likely to be comparable in magnitude [Fig. 1(b)]. This is directly analogous to what has been found in both rocksalt transition metal monoxides, e.g. the canonical MnO ,^{27,32} and the oxide double perovskites.²⁹ The $\{111\}_{\text{cubic}}$ AFM order observed (Type II) occurs for $J_2 > 0.5J_1$ for an ideal $J_1 - J_2$ face-centered cubic magnet with antiferromagnetic interactions. The combination of this with the observed mild frustration, $|\theta|/T_N = 1.9$, and the presumed weakness of both further-neighbour superexchange (due to the long distances) and of non-Heisenberg effects due to the Cr^{3+} ion presence suggests that suggests that $J_2 < J_1$, and thus that a small (20%) reduction in J_1/J_2 might induce a transition into a highly frustrated state.^{41,42} Like other perovskites, $\text{Cr}[\text{Bi}(\text{SCN})_6]$ has a wide-range of potential chemical possibilities for tuning its magnetic function: not only through substitution of the magnetic Cr,¹² but also of

the non-magnetic Bi,^{23,24} and the anionic ligand⁴³ or the inclusion of A-site cations.⁴⁴ This, together with the moderate exchange strength found in this material, comparable with the Zeeman splitting accessible through superconducting magnets, suggests that NCS double perovskites are ideal platforms to engineer the complex, chiral, multi- k magnetic orderings of current interest for their potential use in magnetic computation.^{26,45}

Author contributions

M. J. C. synthesized the samples. M. J. C., O. F., and L. C. D. carried out the neutron diffraction experiment and analysed the neutron diffraction data. M. J. C. carried out and analysed the bulk magnetic measurements. M. J. C. wrote the paper, with input from all other authors.

Conflicts of interest

There are no conflicts to declare.

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