Spin dynamics of molecular nanomagnets unravelled at atomic scale by four-dimensional inelastic neutron scattering

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Molecular nanomagnets are among the first examples of finite-size spin systems and have been test beds for addressing several phenomena in quantum dynamics. In fact, for short-enough timescales the spin wavefunctions evolve coherently according to the Schrödinger equation for an appropriate spin Hamiltonian. It is difficult to probe this evolution directly because of its small characteristic length- and timescales, typically of the order of a few ångströms and 0.1 ps, respectively. The most powerful technique to investigate the spin dynamics in bulk samples is inelastic neutron scattering (INS). In MNMs, the dynamics are usually extrapolated by fitting INS spectra to a spin Hamiltonian and by performing calculations within the framework set by this model. However, this indirect approach does not work in many interesting cases when the Hilbert space dimension is too large or when a large number of model parameters makes the fit non-univocal. Here we show that measurements of the scattering function over a large solid angle of wave vectors in high-quality single crystals of MNMs permit us to directly determine real-space dynamical two-spin correlations without assuming any underlying model Hamiltonian. These correlations are the key quantities characterizing the magnetic dynamics. For instance, they determine the linear response of the system to an arbitrary magnetic field varying in space and time. We exploit Cr8, a prototype antiferromagnetic ring8,9,20,21, as a benchmark to demonstrate the potential of this approach for the determination of the spin dynamics in MNMs. The so-obtained correlation functions allow a model-free picture of the quantum dynamics of the ring. For example, the way a quantum fluctuation propagates along the ring or the degree of validity of a NVT description20,21,34 are determined.

The Cr8 prototype antiferromagnetic ring

The Cr8 molecule contains eight Cr3+ ions (s = 3/2) forming a nearly regular octagon33,35. It is one of the most studied MNMs, both for its intrinsic interest and for being the precursor of a large family of heterometallic molecules and supramolecular complexes that are interesting for a number of fundamental and applicative

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The spin Hamiltonian of Cr₈ contains a dominating nearest-neighbour Heisenberg antiferromagnetic exchange and small axial anisotropic terms:

\[ H = J \sum_{i=1}^{8} \mathbf{s}(i) \cdot \mathbf{s}(i+1) + D \sum_{i=1}^{8} \mathbf{z}(i)^2 \]  

(1)

where \( \mathbf{s}(9) = s(1) \), \( J = 1.46 \) meV, \( D = -0.038 \) meV and the anisotropy axis \( \mathbf{z} \) is perpendicular to the ring plane. The ground state of equation (1) is a non-magnetic singlet (total spin \( S = 0 \)), and the low-lying excited levels are arranged into rotational bands (Fig. 1). The lowest one (called the L-band) contains the ground state and approximately follows the Landé rule \( E(S) = 2JS(S+1)/N \) (ref. 39). The second set of levels belongs to the so-called E-bands, which are also parabolic with respect to \( S \) but shifted to higher energies. Owing to their internal structure, L-band states can be excited by neutrons practically only to L- or E-band states. Hence, at low temperature, where only the \( S = 0 \) ground state is populated, three peaks are expected and observed in INS spectra (transitions marked by arrows in Fig. 1). Anisotropy produces small splittings of the otherwise degenerate \( S \)-multiplets and a tiny second-order mixing of different multiplets. For instance, the L-band \( S = 1 \) triplet is split into an \( |S = 1, M = 0 \rangle \) singlet and an \( |S = 1, M = \pm 1 \rangle \) doublet that are resolved by high-resolution INS measurements (inset of Fig. 1b). Splittings of the E-band triplets are smaller and not experimentally resolved.

**INS and dynamical correlation functions**

The INS spectra in Fig. 1b have been obtained on a polycrystalline sample and are integrated over a wide range of momentum transfer \( Q \); hence, they contain no direct information on the spatial structure of wavefunctions. This is usually indirectly inferred by fitting the spectra to a specific model Hamiltonian such as equation (1) or by analysing the dependence of peak intensities on the modulus of the momentum transfer \( Q \). In powder INS measurements, however, the resulting angular-averaged cross-section does not in general allow one to extract dynamical spin correlations directly. Indeed, in the corresponding cross-section formula (see refs 34, 41) all anisotropic correlation coefficients multiply the same \( Q \)-dependent function and therefore cannot be extracted separately. Even in the isotropic case, the fact that the powder cross-section depends only on scalar distances between magnetic ions and not on their vector positions in space poses severe limitations. For instance, correlations in the simple but important case of a heterometallic ring cannot be determined if only powder data are available, because this case cannot be distinguished from that of a homometallic ring with averaged correlations.

If single-crystal samples are used, only limited and partially integrated information on the \( Q \)-dependence of the scattering function \( S(Q, \omega) \) (where \( \hbar \omega \) is the transferred energy, see ref. 42 and equation (2)) can be obtained by traditional time-of-flight neutron spectrometers, which carry unitary detectors fitted on Debye–Scherrer rings. The implementation of large arrays of position-sensitive detectors in cold-neutron time-of-flight spectrometers, which carry unitary detectors fitted on Debye–Scherrer rings. The implementation of large arrays of position-sensitive detectors in cold-neutron time-of-flight spectrometers, which carry unitary detectors fitted on Debye–Scherrer rings. The implementation of large arrays of position-sensitive detectors in cold-neutron time-of-flight spectrometers, which carry unitary detectors fitted on Debye–Scherrer rings. The implementation of large arrays of position-sensitive detectors in cold-neutron time-of-flight spectrometers, which carry unitary detectors fitted on Debye–Scherrer rings. The implementation of large arrays of position-sensitive detectors in cold-neutron time-of-flight spectrometers, which carry unitary detectors fitted on Debye–Scherrer rings. The implementation of large arrays of position-sensitive detectors in cold-neutron time-of-flight spectrometers, which carry unitary detectors fitted on Debye–Scherrer rings. The implementation of large arrays of position-sensitive detectors in cold-neutron time-of-flight spectrometers, which carry unitary detectors fitted on Debye–Scherrer rings. The implementation of large arrays of position-sensitive detectors in cold-neutron time-of-flight spectrometers, which carry unitary detectors fitted on Debye–Scherrer rings.

![Figure 1](image-url) **Figure 1** | Magnetic energy spectrum of Cr₈ and zero-temperature INS transitions. a, Low-lying energy multiplets as a function of their total spin for the isotropic exchange Hamiltonian of Cr₈ (equation (1) with \( D = 0 \)). The arrows indicate the three transitions seen by INS at zero temperature. All other transitions have negligible cross-section. The blue and red symbols indicate L- and E-band states, respectively; grey symbols indicate states not belonging to these bands. The inset shows the core of Cr₈ (Cr₈Cr₄Fe₃D₄O₈; green, Cr; yellow, F; red, O; dark grey, C; D omitted). b, Measured low-\( T \) INS spectra for a powder Cr₈ sample, with an incident neutron wavelength \( \lambda = 3.1 \) Å. The labels indicate the three peaks corresponding to the transitions reported in a. The \( p = 1 \) transition is partially hidden by the elastic signal. The inset reports higher-resolution measurements with \( \lambda = 5 \) Å showing the \( p = 1 \) transition split by magnetic anisotropy.
where \( E_p(Q) \) is the form factor for the \( d \)th ion, \( |0\rangle \) and \(|p\rangle \) are ground and excited eigenstates, respectively, \( E_p \) are eigenenergies and \( \mathbf{R}_{a}^\text{M} \) are the relative positions of the \( N \) magnetic ions within a molecule. As is well known, this formula can be rewritten in terms of \( T = 0 \) dynamical correlation functions

\[
(s_{0d}(d), t)s_{0d}(d'), 0) = \sum_{p} (0|s_{0d}(d)|p)(p|s_{0d}(d')|0)e^{-i\omega_{dp}t} \tag{3}
\]

where \( \omega_{dp} = E_p/\hbar \). In fact, the Fourier coefficients \( c^{d}_{0d}(\omega_p) = \langle 0|s_{0d}(d)|p\rangle\langle p|s_{0d}(d')|0\rangle \) in equation (3) coincide with the coefficients in equation (2). Whereas the values of \( \omega_p \) are directly read out from the energies of the peaks in the INS spectrum, the \( c^{d}_{0d}(\omega_p) \) can be extracted from the data by fitting equation (2) to the observed \( q \)-dependence of each peak. Indeed, for each value of \( E_p \) these coefficients are the only unknown quantities in equation (2). To fix the scale-factor in equation (2) we have exploited the sum rule

\[
(0|s^{2}(d)|0) = \sum_{\omega} c^{d}_{0d}(\omega_p) = s(s+1)
\]

with \( s(s+1) = 3.75 \).

The Fourier coefficients \( c^{d}_{0d}(\omega_p) \) extracted by the fits of data integrated over the anisotropy splittings are given in Table 1. They do not depend significantly on \( \omega \) within experimental uncertainty, consistently with the first-order-perturbation effect of anisotropy in \( \text{Cr}_x \). Figure 3d–f shows calculated \( q \)-dependencies corresponding to the best-fit Fourier coefficients \( c^{d}_{0d}(\omega_p) \). The agreement with experimental maps is excellent. The \( d \)-dependence of \( c^{d}_{0d}(\omega_p) \), which determines the spatial pattern of correlations at the various frequencies, strongly varies with \( \omega_p \). This is in line with the behavior expected from the model of equation (1) (see Table 1).

The information on the low-\( T \) spin dynamics embedded in the dynamical correlation functions (equation (3)) can be visualized by exploiting the well-known link between these correlations and linear response functions\(^2\). The building blocks of such functions are the set of susceptibilities \( \chi_{a',d'}^{a,d}(t) \), which provide the response of \( s_{a}(d) \) at time \( t \) to a delta-pulse perturbation produced by a field \( b \) of direction \( a' \) applied on spin \( d' \) at time zero:

\[
\delta \mathbf{H}(t) = -b s_{a}(d') \delta(t) \rightarrow \langle s_{a}(d) \rangle(t) - \langle s_{a}(d) \rangle_{eq} = b \chi_{a',d'}^{a,d}(t) \tag{4}
\]

with

\[
\chi_{a',d'}^{a,d}(t) = \frac{i}{\hbar} \Theta(t) \left[ \left\langle s_{a}(d), t \right| s_{a'}(d') \right\rangle \right] = \delta_{a,a'} \frac{2}{\hbar} \Theta(t) \sum_{p} c^{d}_{a}(\omega_p) \sin(\omega_p t) \tag{5}
\]
Table 1 | Fourier components of two-spin dynamical correlations \(c^\text{Exp}_s(\omega_p) = c^\text{Heis}_s(\omega_p)\) extracted from the present data (Exp column), and calculated by the isotropic Heisenberg model (equation (1) with \(D = 0\)).

| \(p\) | \(E = 0.7\) meV | \(E = 0.9\) meV |
|------|-----------------|-----------------|
| \(d = 1\) | 0.78 0.772 0.28 0.336 0.19 0.125 | 0.93 0.82 0.76 0.02 |
| \(d = 2\) | -0.77 -0.772 -0.15 -0.173 0.01 0.0 | -0.84 -0.75 0.00 |
| \(d = 3\) | 0.78 0.772 0.0 0.0 -0.14 -0.125 | 0.81 0.72 -0.02 |
| \(d = 4\) | -0.80 -0.772 0.18 0.173 -0.01 0.0 | -0.94 -0.76 0.00 |
| \(d = 5\) | 0.81 0.772 -0.32 -0.336 0.1 0.125 | 0.95 0.85 -0.06 |

The uncertainty on the experimental coefficients is of the order of 0.04 for \(d = 1\) and of 0.06 for \(d = 5\). Coefficients for \(d = 6, 7, 8\) are equivalent by symmetry to \(d = 3, 2, 1\), respectively.

\(\Theta\) being the step function and \(\langle \delta_s(d) \rangle_{\text{eq}}\) being the equilibrium average (vanishing in the present case). The response is diagonal \((\delta_{s,\alpha \alpha'})\) because of axial symmetry. As an example, we show in Fig. 4 how a fluctuation on a given site at \(t = 0\) (produced by a delta-pulse field on site 1) propagates in subsequent times along the ring. The three-frequency spectrum in Table 1 produces a wave-like motion of the magnetization, which propagates forth and back along the ring with a pattern determined by the precise values of the Fourier coefficients. After the pulse is applied on site 1, waves propagating clockwise and anticlockwise interfere constructively at the opposite site (\(d = 5\)). No interference is produced on site 1, where the fluctuation was applied.

The measurement of the whole set of low-\(T\) Fourier coefficients also allows us to extract equal-time correlation functions (that is, equation (3) with \(t = 0\)), which are important quantities widely used to characterize the ground state. The advantage here is that one can isolate the weak magnetic signal by integrating over the inelastic response. Such information would be extremely challenging to obtain by other techniques such as diffuse scattering, even with polarization analysis. The pattern of equal-time correlations (see Supplementary Fig. 5) has an envelope slowly decreasing with distance as expected for the one-dimensional antiferromagnetic Heisenberg model with \(s = 3/2\), which has a quantum critical ground state with power-law correlations\(^{16}\).

Anisotropy

As discussed above, magnetic anisotropy in \(\text{Cr}_8\) is small and its main effect is to cause a splitting of the \(S = 1\) triplet into a \(|M = 0\rangle\) singlet and a \(|M = \pm 1\rangle\) doublet, with \(M\) being the magnetic quantum number. This splitting is witness by the presence of two separate peaks at 0.7 and 0.9 meV in the high-resolution INS spectrum (see the inset of Fig. 1b). We have investigated the effects of magnetic anisotropy on the spin dynamics by measuring the \(Q\)-dependence of the neutron scattering intensity separately for the two low-energy peaks. The results are shown in the two upper panels of Supplementary Fig. S4. The positions of the maxima are the same for both peaks but the relative intensities of the various maxima are different. In particular, the two \(Q_i = 0\) maxima are the most intense for the 0.7 meV transition but the weakest for the 0.9 meV one. We have followed the same procedure as before to fit separately the \(Q\)-dependencies of the two peaks. The so-extracted Fourier coefficients are reported in Table 2 and the corresponding calculated maps are shown in the two lower panels of Supplementary Fig. S4. Table 2 shows that \(c^\text{Exp}_s(\omega_p)\) are non-negligible only for \(\alpha = z\) for the first peak and for \(\alpha = x, y\) for the second peak. This is exactly the behaviour expected for the axial Hamiltonian of equation (1), and means that the low-frequency oscillations of \(\langle \delta_s(d_i) \delta_s(d_j) \rangle\) occur at a smaller frequency than those of \(\langle \delta_s(d_i) \delta_s(d_j) \rangle\) and \(\langle \delta_s(d_i) \delta_s(d_j) \rangle\). We find a slightly larger weight of the \(zz\) coefficients (first peak) with respect to the \(xx\) and \(yy\) ones (second peak), consistent with the asymmetry expected from the model of equation (1) in the presence of \(S\)-mixing\(^{33}\).

Figure 4 | Propagation of a local disturbance deduced from the present INS spectra and in a NVT regime. The frames show the time evolution of \(\langle \delta_s(d) \rangle\) in an eight-spin ring after a delta-pulse perturbation \(-b_\text{eq}(0)\delta(0)\) applied on the red \((d = 1)\) spin. Note that as the ground state is a singlet, \(\langle \delta_s(d) \rangle = 0\) just before \(t = 0\) (frame not shown). a, Dynamics deduced from equations (4) and (5) using the present experimental Fourier coefficients (Tables 1 and 2) and frequencies. The delay between two frames is 1.85 \(\times 10^{-13}\) s, that is, 1/32 of the longest oscillation period 2\(\pi h/\Delta\), with \(\Delta = 0.7\) meV. b, Results for a hypothetical ring in a NVT regime, that is, \(D/J = -0.2\) corresponding to a tunnel action \(\Delta_0 \simeq 7.6\). The delay between two frames is 1/32 of the tunnelling oscillation period 2\(\pi h/\Delta\), with \(\Delta\) being the tunnelling gap.
NVT has been proposed\(^\text{20}\) that the low-temperature dynamics of antiferromagnetic rings could be characterized by the coherent tunnelling of the Neel vector \(\mathbf{n} = \sum_d (-1)^d s(d)\) between the two classically degenerate configurations. This phenomenon is the antiferromagnetic counterpart of the tunnelling of the magnetization (quantum tunnelling of magnetization, QTM) observed in single-molecule magnets\(^\text{21}\). Interestingly, whereas for QTM the tunnelling time is usually so long that the dynamics becomes overdamped owing to interaction with the nuclear-spins subsystem, the timescale of NVT in antiferromagnetic rings could be much shorter than the decoherence time. Within the semiclassical framework, the condition for the occurrence of NVT is that the action \(S_N = N \sqrt{2D/T}\) be much larger than unity. Hence, NVT is expected to occur in long antiferromagnetic rings with large anisotropy. Whereas QTM can be directly probed by macroscopic magnetization measurements, NVT is elusive and a direct experimental demonstration of its occurrence is lacking. NVT has recently been shown to occur in a Fe\(_{13}\) ring\(^\text{21}\), but only indirectly through powder INS and bulk thermodynamic measurements.

The possible occurrence of the NVT scenario in the low-\(T\) dynamics of antiferromagnetic rings can be assessed by extracting dynamical correlation functions with the method presented in the paper. Indeed, in the case of NVT the two lowest eigenstates are close to the symmetric and antisymmetric superpositions of the two Neel states \(|1\ 1\ 1\ . . .\rangle\) and \(|1\ 1\ 1\ . . .\rangle\). This implies that all of the spins are rigidly locked into a two-sublattice pattern. If a local perturbing field is applied along \(z\) on a single spin as discussed before, the expectation values of all the spins jointly increase in modulus (with an alternating pattern) with a practically instantaneous propagation of the perturbation. This behaviour, which already emerges for rather low \(D/J\) ratios (see Fig.\(4b\)), is completely different from the one we have experimentally found in Cr\(_8\) (Fig.\(4a\)). Hence, these results demonstrate that the low-\(T\) dynamics of Cr\(_8\) is not characterized by NVT. Figure \(4\) shows that even for \(|D/J|\ < 1\) (but larger than in the case of Cr\(_8\)) NVT dynamics occurs. The present method could be applied to Fe\(_{13}\) to deeply investigate its spin dynamics and show that it exhibits NVT, circumventing also the fact that the huge expectation values of all the spins jointly increase in modulus (with an alternating pattern) with a practically instantaneous propagation of the perturbation. The project was collected by filtration, washed with acetone, dried and then was extracted with hexane (50 ml), and finally purified on a silica gel column using toluene as the eluent. The first fraction from the column was collected and the solution was evaporated to dryness. Yield: 3.15 g (65%).

Electronic (spectroscopy) analysis calculated for Cr\(_8\)F\(_6\)D\(_2\)O\(_8\): Cr 17.80, C 40.99. ES-MS (sample dissolved in THF; spectra run in CH\(_3\)OH): 2352 [M+Na\(^+\)], 2348 [M+CH\(_3\)OH+Na\(^-\)].

Large crystals of Cr\(_8\) were obtained by very slow evaporation of hexane solution of compound 2 at ambient condition. The crystal structure is tetragonal (space group \(P4_212\)) with \(a = b = 20.093(2)\) Å and \(c = 16.801(2)\) Å.

INS experiments were performed on the INS time-of-flight inelastic neutron spectrometer\(^\text{14}\) at the high-flux reactor of the Institute Laue–Langevin. The INS instrument has a 30 m² position-sensitive detector divided into 10⁹ pixels, covering 147° of azimuthal angle and ±20° out-of-plane. A 0.24 g Cr\(_8\) single crystal was aligned as in Supplementary Fig. S1 and measurements were taken by rotating the crystal in steps of 1° about the vertical \(z\) axis. Incident neutron wavelengths of 5.0 and 3.1 Å were selected to probe measured excitations with energy resolutions, at zero energy transfers, of 0.079 and 0.38 meV respectively. The uniformity of the detector sensitivity was ensured by measurement of a standard vanadium sample.

Measurements for different rotation angles were combined using the HORACE analysis suite\(^\text{16}\). S(Q,\(\omega\)) was rotated by 37.8° about the \(Q_2\) axis to analyse the data in the \(x, y, z\) molecular reference frame. The two molecules in the unit cell were included in the calculation of the scattering function and fitting of equation (2) to the \(Q\) dependence of the observed transitions was performed using HORACE. Some compensation for inhomogeneity in the scattering intensity due to self-shielding is performed, based on the variation of incoherent scattering intensity with sample orientation.

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References

1. Krause, S., Berbil-Bautista, L., Herzog, G., Bode, M. & Wiesendanger, R. Current-induced magnetization switching with a spin-polarized scanning tunneling microscope. Science 317, 1537–1540 (2007).

2. Mannini, M. et al. Magnetic memory of a single-molecule quantum magnet wired to a gold surface. Nature Mater. 8, 194–197 (2009).

3. Bogani, L. & Wernsdorfer, W. Molecular spintronics using single-molecule magnets. Nature Mater. 7, 186–198 (2008).

4. Loth, S. et al. Controlling the state of quantum spins with electric currents. Nature Phys. 6, 340–344 (2010).

5. Sanvito, S. Molecular spintronics. Chem. Soc. Rev. 40, 3336–3355 (2011).

6. Khajetoorians, A. A., Wiebe, J., Chilian, B. & Wiesendanger, R. Realizing all-spin-based logic operations atom by atom. Science 330, 1062–1064 (2011).

7. Candelier, A., Klyatskaya, S., Ruben, M., Wernsdorfer, W. & Affronte, M. Graphene spintronic devices with molecular nanomagnets. Nano Lett. 11, 2634–2639 (2011).

8. Leuenberger, M. N. & Loss, D. Quantum computing in molecular magnets. Nature 410, 789–793 (2001).

9. Troiani, F. et al. Molecular engineering of antiferromagnetic rings for quantum computation. Phys. Rev. Lett. 94, 207208 (2005).

10. Hirjibehedin, C. F., Lutz, C. P. & Heinrich, A. J. Spin coupling in engineered atomic structures. Science 312, 1021–1024 (2006).

11. Khajetoorians, A. A. et al. Atom-by-atom engineering and magnetometry of aligned nanomagnets. Nano Lett. 8, 497–503 (2008).

12. Loth, S., Baumann, S., Lutz, C. P., Eigler, D. M. & Heinrich, A. J. Rastabilty in atomic-scale antiferromagnets. Science 335, 196–199 (2012).
13. Gatteschi, D., Sessoli, R. & Villain, J. Molecular Nanomagnets (Oxford Univ. Press, 2006).
14. Mannini, M. et al. Quantum tunnelling of the magnetization in a monolayer of oriented single-molecule magnets. *Nature* **468**, 417–421 (2010).
15. Corradini, V. et al. Magnetic anisotropy of Cr-Ni spin clusters on surfaces. *Adv. Funct. Mater.* **22**, 3706–3713 (2012).
16. Friedman, J. R., Sarachik, M. R., Tejada, J. & Ziolo, R. Macroscopic measurement of resonant magnetization tunneling in high-spin molecules. *Phys. Rev. Lett.* **76**, 3830–3833 (1996).
17. Thomas, L. et al. Macroscopic quantum tunnelling of magnetization in a single crystal of nanomagnets. *Nature* **383**, 145–148 (1996).
18. Wernsdorfer, W. & Sessoli, R. Quantum phase interference and parity effects in magnetic molecular clusters. *Science* **284**, 133–135 (1999).
19. Schnack, J. Effects of frustration on magnetic molecules: A survey from Olivier Kahn until today. *Dalton Trans.* **39**, 4677–4686 (2010).
20. Chioleto, A. & Loss, D. Macroscopic quantum coherence in molecular magnets. *Phys. Rev. Lett.* **80**, 169–172 (1998).
21. Waldmann, O. Quantum phase interference and Néel-vector tunneling in antiferromagnetic molecular wheels. *Phys. Rev. Lett.* **102**, 157202 (2009).
22. Lehmann, J., Gaita-Ario, A., Coronado, E. & Loss, D. Spin qubits with electrically gated polynuclear molecules. *Nature Nanotech.* **2**, 312–317 (2007).
23. Trif, M., Troiani, F., Stepanenko, D. & Loss, D. Spin-electric coupling in molecular magnets. *Phys. Rev. Lett.* **101**, 217201 (2008).
24. Santini, P., Carretta, S., Troiani, F. & Amoretti, G. Molecular nanomagnets as quantum simulators. *Phys. Rev. Lett.* **107**, 230502 (2011).
25. Wernsdorfer, W., Aliaga-Alcalde, N. & Hendrickson, D. N. & Christou, G. Exchange-biased quantum tunneling in a supramolecular dimer of single-molecule magnets. *Nature* **416**, 406–409 (2002).
26. Hill, S., Edwards, R. S., Aliaga-Alcalde, N. & Christou, G. Quantum coherence in an exchange-coupled dimer of single-molecule magnets. *Science* **302**, 1013–1018 (2003).
27. Timco, G. et al. Engineering the coupling between molecular spin qubits by coordination chemistry. *Nature Nanotech.* **4**, 173–178 (2009).
28. Candini, A. et al. Entanglement in supramolecular spin systems of two weakly coupled antiferromagnetic rings (purple-Cr-Ni). *Phys. Rev. Lett.* **104**, 037203 (2010).
29. Ardavan, A. et al. Will spin-relaxation times in molecular magnets permit quantum information processing? *Phys. Rev. Lett.* **98**, 057201 (2007).
30. Schlegel, C., van Slageren, J., Manoli, M., Brechin, E. K. & Dressel, M. Direct observation of quantum coherence in single-molecule magnets. *Phys. Rev. Lett.* **101**, 147203 (2008).
31. Bertaina, S. et al. Quantum oscillations in a molecular magnet. *Nature* **453**, 203–206 (2008).
32. Wedge, C. J. et al. Chemical engineering of molecular qubits. *Phys. Rev. Lett.* **108**, 107204 (2012).
33. Van Slageren, J. et al. Magnetic anisotropy of the antiferromagnetic ring [Cr2F2(CO)4]. *Chem. Eur. J.* **8**, 277–285 (2002).
34. Santini, P. et al. Spin dynamics and tunneling of the Néel vector in the Fe3+ magnetic wheel. *Phys. Rev. B* **71**, 184405 (2005).
35. Carretta, S. et al. Microscopic spin Hamiltonian of a Cr3+ antiferromagnetic ring from inelastic neutron scattering. *Phys. Rev. B* **67**, 094405 (2003).
36. Meier, F. & Loss, D. Thermodynamics and spin-tunneling dynamics in ferric wheels with excess spin. *Phys. Rev. B* **64**, 224411 (2001).
37. Carretta, S. et al. Topology and spin dynamics in molecular magnets. *Phys. Rev. B* **72**, 060403 (2005).
38. Waldmann, O., Guidi, T., Carretta, S., Mondelli, C. & Dearden, A. L. Elementary excitations in the cyclic molecular nanomagnet Ca6, *Phys. Rev. Lett.* **91**, 237202 (2003).
39. Schnack, J. & Luban, M. Rotational modes in molecular magnets with antiferromagnetic Heisenberg exchange. *Phys. Rev. B* **63**, 014418 (2000).
40. Waldmann, O. Spin dynamics of finite antiferromagnetic Heisenberg spin rings. *Phys. Rev. B* **65**, 024424 (2001).
41. Waldmann, O. et al. Exchange-coupling constants, spin density map, and Q dependence of the inelastic neutron scattering intensity in single-molecule magnets. *Phys. Rev. B* **75**, 174438 (2007).
42. Marshall, W. & Loveyse, S. W. *Theory of Thermal Neutron Scattering* (Oxford Univ. Press, 1971).
43. Ollivier, J. & Mutka, H. INS cold neutron time-of-flight spectrometer, prepared to tackle single crystal spectroscopy. *J. Phys. Soc. Jpn* **80**, SB003 (2011).
44. Bewley, R. J., Taylor, J. W. & Bennington, S. M. LET, a cold neutron multi-disk chopper spectrometer at ISIS. *Nucl. Instrum. Meth. Phys. Rev. A* **637**, 128–134 (2011).
45. Pelting, T. G., Ewings, R. A. & Dujin, S. J. Horace: Visualising and manipulating S(q, ω) measured in all four dimensions. http://horace.isis.rl.ac.uk. (2009).
46. Hallberg, K., Wang, X. G., Horsch, P. & Moreo, A. Critical behavior of the $S=3/2$ antiferromagnetic Heisenberg chain. *Phys. Rev. Lett.* **76**, 4955–4958 (1996).
47. Cador, O. et al. The magnetic Möbius strip: Synthesis, structure, and magnetic studies of odd-numbered antiferromagnetically coupled wheels. *Angew. Chem.* **116**, 5308–5312 (2004).
48. Schröder, C. et al. Competing spin phases in geometrically frustrated magnetic molecules. *Phys. Rev. Lett.* **94**, 017205 (2005).
49. Furukawa, Y. et al. Evidence of spin singlet ground state in the frustrated antiferromagnetic ring Cr8Ni. *Phys. Rev. B* **79**, 134416 (2009).
50. Kenzelmann, M. et al. Structure of end states for a haldane spin chain. *Phys. Rev. Lett.* **90**, 087202 (2003).
51. Gerbelein, N. V. et al. Octanuclear chromium(III) fluoro-trimethylacetate—a macroyclic complex. *Dokl. Akad. Nauk.* **313**, 1459–1462 (1990).