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Dimensionality selection in a molecule-based magnet

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Gaining control of the building blocks of magnetic materials and thereby achieving particular characteristics will make possible the design and growth of bespoke magnetic devices. While progress in the synthesis of molecular materials, and especially coordination polymers, represents a significant step towards this goal, the ability to tune the magnetic interactions within a particular framework remains in its infancy. Here we demonstrate a chemical method which achieves dimensionality selection via preferential inhibition of the magnetic exchange in an $S = 1/2$ antiferromagnet along one crystal direction, switching the system from being quasi-two- to quasi-one-dimensional while effectively maintaining the nearest-neighbour coupling strength.

Coordination polymers are self-organising materials consisting of arrays of metal ions linked via molecular ligands, with non-coordinated counterions supplying charge neutrality. The choice of initial components permits a high level of control over the final product, enabling many different polymeric architectures to be obtained [1]. These materials provide a route to successful crystal engineering, and a number of functionalities are being actively studied, including gas storage [2–4], optoelectronic [5, 6], ferroelectric [7, 8] and magnetic properties [9–14].

Although it is now possible to generate an assortment of disparate magnetic lattices using this method [15, 16], true control of magnetic exchange interactions implies an ability to adjust selected parameters while keeping others constant. To this end, a series of coordination polymers based on Cu(II) ions bridged by pyrazine ($C_4H_4N_2$) molecules have proven to be highly versatile. In these systems it has been shown that it is possible to alter significantly the primary exchange energies via adjustment of the ligands [17] and the counterions [18, 19], or fine-tune the exchange by a few percent via isotopic substitution [20], all the while maintaining the same basic metal–pyrazine network. In this paper we demonstrate the power of this strategy by chemically engineering a reduction in the dimensionality of a magnetic system. After first designing a material based on coordinated planes of Cu(II), we adapt the recipe such that the ligand bridges are broken along a specific crystal direction, resulting in a chain-like compound. Because the ligand mediating the magnetic interactions in both cases is unchanged, the nearest-neighbour exchange energies of the two materials are found to be equal to each other to within 5%. The difference in numbers of nearest-neighbours, however, means that the strength of the combined exchange

interactions acting on each magnetic ion in the quasi-two-dimensional material is twice that of its quasi-one-dimensional cousin.

Figs. 1(a) and (b) show the crystal structure of orthorhombic $[Cu(pyzo)_2(pyO)_2](PF_6)_2$ (where $pyzo =$ pyrazine and $pyO =$ pyridine-*N*-oxide, C_5H_5NO) determined using single-crystal x-ray diffraction [21]. $S = 1/2$ Cu ions are linked by $pyzo$ molecules into nearly square planar arrays, with perpendicular non-bridging pyO ligands keeping the planes well-separated. Because of the separation, as well as the staggered arrangement of adjacent planes shown in Fig. 1(b), magnetic exchange energies are likely to be very small along the c -direction. In contrast, $Cu-pyzo-Cu$ bridges are known to be good mediators of antiferromagnetic superexchange [22, 23] and so the magnetic properties of this material are expected to be quasi-two-dimensional. This is confirmed by the magnetic measurements described below. Sample synthesis involves mixing together of the molecular components in a solution of water and ethanol. Intermolecular self-organisation means that only a small amount of intervention is subsequently required. To achieve the desired planar structure the $pyzo$ and pyO molecules were added in a 3:1 ratio, previous experience suggesting that to account for the potential for pyO to substitute for $pyzo$, the ligands must initially be in a proportion different to that found in the final product. In order to create a similar sample, but one based on $Cu-pyzo$ chains rather than planes, we reduce the $pyzo:pyO$ ratio to 2:1 and proceed with the synthesis in a similar way. The resulting material has the composition $[Cu(pyzo)(pyO)_2(H_2O)_2](PF_6)_2$ and the structure is shown in Figs. 1(c) and (d). Here the $pyzo$ ligands link Cu ions along the b -axis only, the other ligands being non-bridging pyO and water molecules. The alteration in composition has the effect of chang-

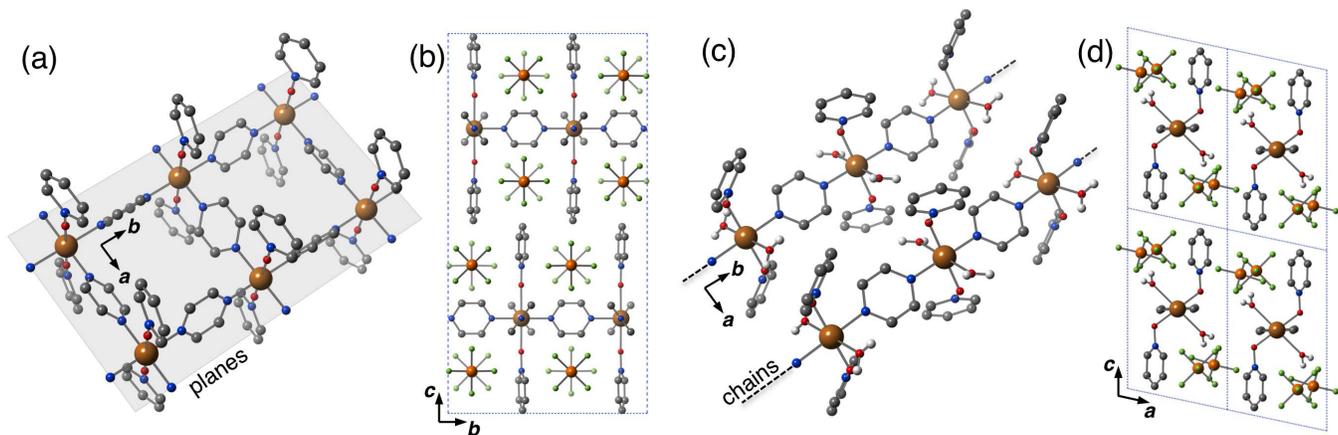


FIG. 1. (a) View of the crystal structure of the planar material $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$ determined using x-ray diffraction showing the 2D Cu—pyrazine network in the ab -plane. (b) a projection of the same structure along the a -axis highlighting the shift between adjacent Cu—pyrazine layers and the arrangement of the PF_6 counterions. (c) Crystal structure of the chain-like material $[\text{Cu}(\text{pyz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ showing the 1D Cu—pyrazine chains in the ab -plane, and (d) a projection along the chains showing the arrangement of the pyO and H_2O ligands and the PF_6 counterions. The dashed lines in (c) and (d) enclose one unit cell. Cu = brown, C = grey, N = blue, O = red, P = orange, F = green. Hydrogens other than those in the water molecules have been omitted for clarity.

ing the symmetry of the crystal from orthorhombic to monoclinic and reducing the number of formula units in the unit cell, but, most importantly for the magnetic exchange, the Cu—pyz—Cu linkages along the a -axis are removed without altering the b -axis Cu—Cu separation by more than a fraction of a percent ($6.914 \pm 0.001 \text{ \AA}$ for the planar material and $6.851 \pm 0.001 \text{ \AA}$ for the chain compound).

Recent heat capacity measurements on the planar material in zero magnetic field see no evidence of a magnetic transition down to the lowest temperatures measured [24]. However, thermodynamic probes are known to be less sensitive to transitions driven by interplanar couplings [25] while local probes such as muon-spin relaxation ($\mu^+\text{SR}$) are much more effective at determining the antiferromagnetic transition temperature, T_N [22]. Our $\mu^+\text{SR}$ data on this compound, shown in Fig. 2(a), exhibits a clear precession signal which develops below $T_N = 1.71 \pm 0.02 \text{ K}$ [26], demonstrating long-range magnetic order throughout the bulk of the sample. In contrast, the $\mu^+\text{SR}$ data for the chain-like compound exhibit no resolvable oscillations, see Fig. 2(b), probably due to a smaller ordered moment, but can be fitted to the expression $A(t) = A_0 e^{-\lambda t} + A_{\parallel}$, where A_{\parallel} represents the non-relaxing part of the signal. Both A_{\parallel} and λ rise markedly below $T = 0.26 \text{ K}$ due to crossover from a regime in which the relaxation is dominated by dynamic magnetic fluctuations to one dominated by quasistatic magnetic order, see Fig. 2(b) insets. From these fits we estimate $T_N = 0.27 \pm 0.01 \text{ K}$ for this material [21].

The type of magnetic order displayed by the two compounds can be deduced from their low-temperature magnetization (see Fig. 3(a)). The form of our pulsed-field

magnetization data up to saturation is in keeping with that expected for low-dimensional antiferromagnets. The slightly concave curve exhibited by the planar material is typical of quasi-two-dimensional (Q2D) antiferromagnetic interactions [18], while the more extreme curvature shown by data from the chain-like sample is indicative of a quasi-one-dimensional (Q1D) magnetic lattice, where, for an ideal system, dM/dB is known to diverge at the saturation field [27]. To support these observations we compare the data with the results of low-temperature quantum Monte Carlo (QMC) simulations based on the Hamiltonian

$$\mathcal{H} = J \sum_{\langle i,j \rangle_{\parallel}} \mathbf{S}_i \cdot \mathbf{S}_j + J_{\perp} \sum_{\langle i,j \rangle_{\perp}} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B B \sum_i S_i^z. \quad (1)$$

Here, for a Q1D (or Q2D) system, J is the strength of the exchange coupling within the magnetic chains (planes), J_{\perp} is the coupling between chains (planes), and the first and second summations refer to summing over unique pairs of nearest neighbours parallel and perpendicular to the chain (plane), respectively. Comparisons of theory and data are shown in Fig. 3(b). Theoretical magnetisation curves were calculated in finite steps of the J_{\perp}/J parameter for both Q1D and Q2D magnetic lattices [18, 21]. For both materials curves corresponding to the quoted values of J_{\perp}/J gave the best matches with experimental data; the Q2D curve with $J_{\perp}/J = 0.00$ for the planar sample, and the Q1D curve with $J_{\perp}/J = 0.02$ for the chain-like material. The predicted curve for a three-dimensional antiferromagnet is also shown for contrast. The deviation of the data from the simulations close to the saturation field is likely due to the finite temperatures at which the experiments were performed.

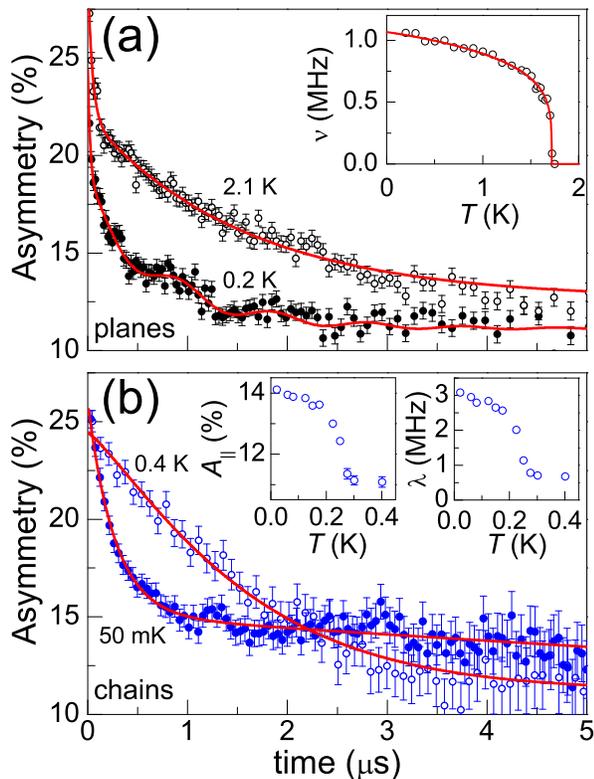


FIG. 2. (a) Example muon-spin relaxation (μ^+ SR) spectra measured on planar $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$. Data at different temperatures are offset for clarity. Inset: Evolution of the precession frequency ν with temperature. Long-range magnetic order is observed below 1.71 K. (b) μ^+ SR spectra measured on chain-like $[\text{Cu}(\text{pyz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$. Insets: The evolution of the amplitude A_{\parallel} (left) and relaxation rate λ (right) with temperature indicates the onset of long-range magnetic order below about 0.27 K. Red lines are fits to functions described in the text and [21].

The saturation field (B_c) can be extracted from the pulsed-field data and is found to be 23.7 ± 0.8 T for the planar material and 12.8 ± 0.4 T for the chain-like material. At saturation, the Hamiltonian above implies that $g\mu_B B_c = nJ + n_{\perp}J_{\perp}$, where, for each spin, n is the number of exchange bonds of interaction strength J ($n = 4$ for Q2D, 2 for Q1D), and n_{\perp} is the number of exchange bonds of interaction strength J_{\perp} ($n_{\perp} = 2$ for Q2D, 4 for Q1D) [18, 20, 26]. From this, by assuming that $J_{\perp}/J \ll 1$ and using the appropriate values for the g -factor determined from electron-spin resonance, we estimate the primary exchange couplings, J , to be 8.1 ± 0.3 K for the planar compound and 8.8 ± 0.2 K for the chain-like compound.

Another estimate of the magnetic dimensionality comes from the temperature dependence of the low-field magnetic susceptibility. Fits of such data for both materials results in estimates of J that are in accord with those derived above from pulsed-field magnetization data [21].

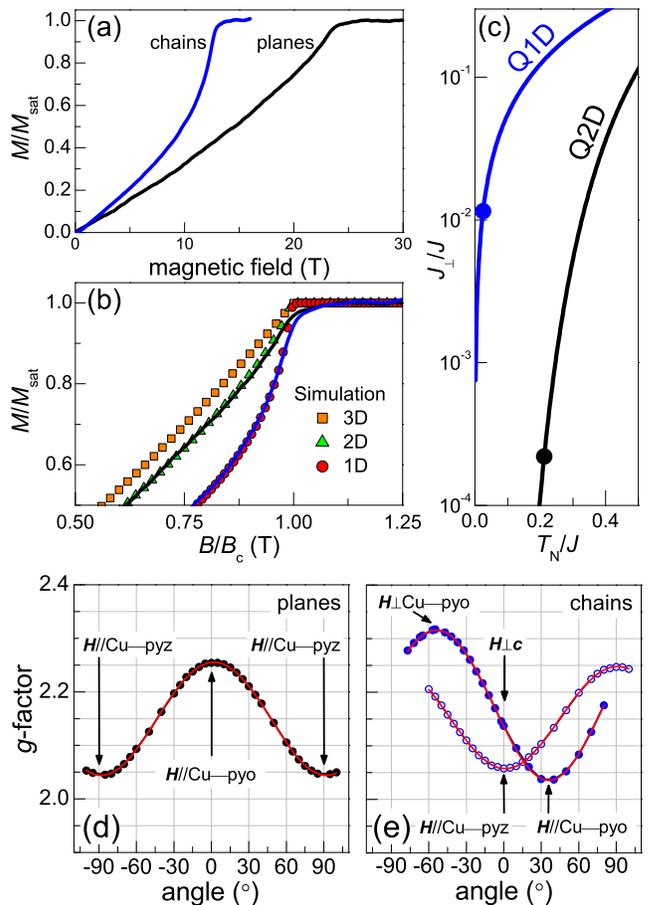


FIG. 3. (a) Normalized pulsed-field magnetization of planar $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$ at $T = 1.5$ K, and chain-like $[\text{Cu}(\text{pyz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ at $T = 0.5$ K. (b) The results of quantum Monte Carlo (QMC) simulations of the low temperature magnetization for 3D ($J_{\perp}/J = 1$), 2D ($J_{\perp}/J = 0$), and 1D ($J_{\perp}/J = 0.02$) antiferromagnets. The lines are the pulsed-field data scaled by the saturation field (B_c). (c) The relation between the exchange anisotropy and the ratio of critical temperature and primary exchange energy in Q1D and Q2D antiferromagnets deduced from QMC simulations [28]. The circles indicate the materials reported here. (d) Anisotropy of the g -factor in the planar and (e) chain-like compounds measured using ESR at 10 K and 1.5K, respectively. Red lines are fits to $g(\theta) = (g_{xy}^2 \sin^2 \theta + g_z^2 \cos^2 \theta)^{1/2}$.

The relative sizes of T_N and J are indicative of the anisotropy of the exchange interactions in a low-dimensional magnetic system. Using quantum Monte Carlo (QMC) calculations Yasuda *et al.* [28] developed empirical relations between these values for $S = 1/2$ Heisenberg antiferromagnets, the results of which are shown in Fig. 3(c). For compounds considered here the exchange anisotropies are found to be $|J_{\perp}/J| \sim 10^{-4}$ in the planar material and 10^{-2} in the chain-like material. These values are in keeping with the comparison between data and simulation shown in Fig. 3(b).

The magnetic lattice in a low-dimensional system is not

always obvious from an inspection of the crystal structure [17, 29]. Verification of the equivalence of the magnetic and structural planes and chains in our materials comes from the angle-dependence of the g -factor as determined by electron-spin resonance. To first approximation, the Cu(II) ions in the planar material have a local octahedral symmetry with a tetragonal distortion along the c -axis. In such situations, the unpaired spin in a d^9 configuration is expected to occupy the $d_{x^2-y^2}$ orbital [30], and the g -factor parallel to the distorted z -axis takes a larger value than those in the xy -plane (see discussion in Ref. 29). Accordingly, the data in Fig. 3(d) show that the g -factor is lowest when the excitation field is applied in the ab -plane, implying that the direction of highest electronic orbital overlap is the Cu—pyz directions, with the strong Q2D exchange interactions being mediated via the molecular orbitals of the pyrazine. For the chain-like material, the distortion is more complicated due to the lower crystal symmetry. Nevertheless, using two rotations, the smallest values of the g -factor are found to be along the Cu—pyz and Cu—pyO bonds, as shown in Fig. 3(e), implying that again the magnetic orbital is $d_{x^2-y^2}$. This allows for the possibility of good exchange coupling along those bonds, but as the pyO molecules are non-bridging ligands, the Q1D magnetism must be mediated along the Cu—pyz chains.

Taken together, these experimental observations paint a complete picture of the two closely-related magnetic systems. From the point of view of magnetic superexchange, the chain direction in the Q1D material looks very similar to the two Cu—pyz directions in the Q2D material and so, despite the compositional differences, the primary nearest-neighbour exchange energies remain largely unaltered. At the same time the critical field in the Q2D material is approximately double that for the Q1D compound because it has twice the number of nearest neighbours. The Q2D compound is strongly anisotropic, comparable to the most 2D materials yet identified [26]. As suggested above, this is likely due to the disconnect and staggering that occurs between successive planes. The extreme anisotropy explains why the zero-field heat capacity was not sensitive to the antiferromagnetic transition observed using μ^+ SR. In the Q1D material the anisotropy is less pronounced (even though the T_N/J ratio is smaller) because the chains are not staggered, there are twice as many next-nearest neighbours, and the shortest distance between chains (along the a -axis) is approximately half the interlayer separation in the Q2D material.

These materials showcase the ability to take deliberate control over the magnetic properties of polymeric systems. The self-organisation of the coordination polymers enables them to spontaneously form crystalline lattices whose structure can be anticipated with a high level of predictability. It is this predictive power, together with the ability to choose the starting ingredients and the

knowledge of the exchange efficiency of various ligands accrued over the past few decades, that permits the preselection of exchange anisotropy. In the Cu—pyz systems we have demonstrated the ability to make this preselection without significantly perturbing the magnitude of the primary interaction strengths, while previous studies of similar materials have highlighted the capacity to tune the exchange couplings without changing the overall dimensionality. Thus these compounds represent a promising approach to magnetic crystal engineering, and in particular raise the possibility of generating systems that exhibit higher ordering temperatures and other cooperative phenomena.

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