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Magnetic order and enhanced exchange in the quasi-one-dimensional molecule-based antiferromagnet $\text{Cu}(\text{NO}_3)_2(\text{pyz})_3$ [†]

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The quasi-one-dimensional molecule-based antiferromagnet $\text{Cu}(\text{NO}_3)_2(\text{pyz})_3$ has an intrachain coupling $J = 13.7(1)$ K and exhibits a state of long-range magnetic order below $T_N = 0.105(1)$ K. The ratio of interchain to intrachain coupling is estimated to be $|J'/J| = 3.3 \times 10^{-3}$, demonstrating a high degree of isolation for the Cu chains.

Recent progress in the field of molecular magnetism has shown the clear potential for gaining control over the structural building blocks of molecular materials in order to engineer desirable magnetic properties. Bridging ligands such as pyrazine ($=\text{pyz}=\text{C}_4\text{H}_4\text{N}_2$) facilitate exchange interactions between transition metal ions and allow for the construction of polymeric networks whose primary exchange occurs along one, two or three dimensions^{1–3}. The manipulation of these building blocks, combined with further ingredients such as counterions^{4,5} and additional ligands⁶, enables the synthesis of materials with a wide range of magnetic properties. Furthermore, such systems

act as experimental realizations of simple and well-studied model systems, such as the one-dimensional⁷ and two-dimensional⁸ $S = 1/2$ quantum Heisenberg antiferromagnet.

The molecule-based antiferromagnet $\text{Cu}(\text{NO}_3)_2(\text{pyz})$ (**1**) represents a highly-ideal experimental realization of the one-dimensional quantum Heisenberg antiferromagnet (1DQHAFM)⁹. Antiferromagnetic coupling between Cu^{2+} ions is facilitated by pyz ligands [see Fig.1(a)] with an exchange constant $J = 10.5$ K determined from measurements of magnetic susceptibility, specific heat and neutron scattering⁹. Weak inter-chain coupling J' results in a state of 3D long range magnetic order at $T = 0.107$ K, which was detected using muon-spin relaxation¹⁰. These measurements give an estimate $|J'/J| = 4.4 \times 10^{-3}$ for the ratio of interchain to intrachain coupling¹⁰.

In this paper, we report the magnetic properties of the Heisenberg antiferromagnetic chain system $\text{Cu}(\text{NO}_3)_2(\text{pyz})_3$ (**2**)¹¹. Like **1**, **2** comprises Heisenberg $S = 1/2$ Cu^{2+} ions connected via pyrazine ligands to form a chain along the *a*-axis [Fig. 1(b)]. Different from **1**, each metal centre has two further trans-coordinated non-bridging pyrazine ligands extending perpendicular to the chains, keeping them well separated [Fig. 1(b)]. This results in a regular octahedral environment for the Cu^{2+} ions in **2**, which has a much higher degree of symmetry than the distorted octahedral environment for Cu^{2+} in **1** [Fig. 1(a)]. For **2**, we obtain an intrachain coupling of $J = 13.7(1)$ K (30% larger than in **1**) from measurements of magnetic susceptibility and pulsed-field magnetization and we argue that different local environments for the Cu^{2+} ions is the main factor responsible for this higher intrachain coupling. Muon-spin spectroscopy reveals a state of long range magnetic order below $T_N = 0.105(1)$ K. The ratio of interchain to interchain coupling is lower than that obtained for **2**, suggesting that this system is an even more successful realization of a 1DQHAFM.

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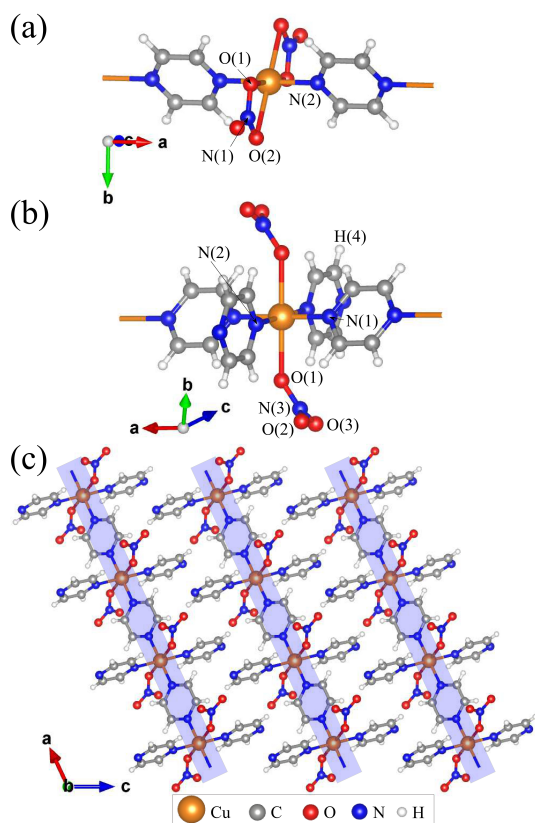


Fig. 1 Local environments of the Cu^{2+} ions in (a) **1** and (b) **2**. (c) Structure of **2** demonstrating the packing of chains.

We prepared deep blue rods of **2** following the procedure previously described by Parkin et al.^{11§}. We re-determined the X-ray crystal structure of **2** as it is relevant to our interpretation of its magnetic properties (see ESI[†]). Different to **1**, which contains four oxygen donor atoms (from chelated nitrate ligands) and two N-donor atoms from pyz, **2** contains two oxygen donor atoms from coordinated NO_3^- ligands and four N-donor atoms belonging to pyz [Cu-N(1) = 2.069(2) and Cu-N(3) = 2.020(2) Å]. The Cu^{2+} ion in **2** is elongated due to Jahn-Teller distortion along the O-Cu-O axis [Cu-O(1) = 2.400(2) Å]. Importantly, this places the magnetic $d_{x^2-y^2}$ orbital in the CuN_4 plane such that it can interact with two other Cu^{2+} ions along the chain through pyz-bonds. The resulting structure is that of a polymeric linear chain [Fig. 1(c)] which propagates along the crystallographic *a*-axis. Successive chains stagger along the *c*-direction and pack to form pseudo two-dimensional sheets in the *ab*-plane [Fig. 1(c)]. Supramolecular interactions within these sheets are weak whereas H(4) forms a bifurcated interaction with the two non-coordinated oxygen atoms from NO_3^- , O(2) and O(3), at distances of 2.579 Å and 2.530 Å, respectively. As a result of these weak interchain interactions we anticipate negligible magnetic coupling between them as well.

The measured molar susceptibility, χ_{mol} , of **2** [Figure 2(a)]

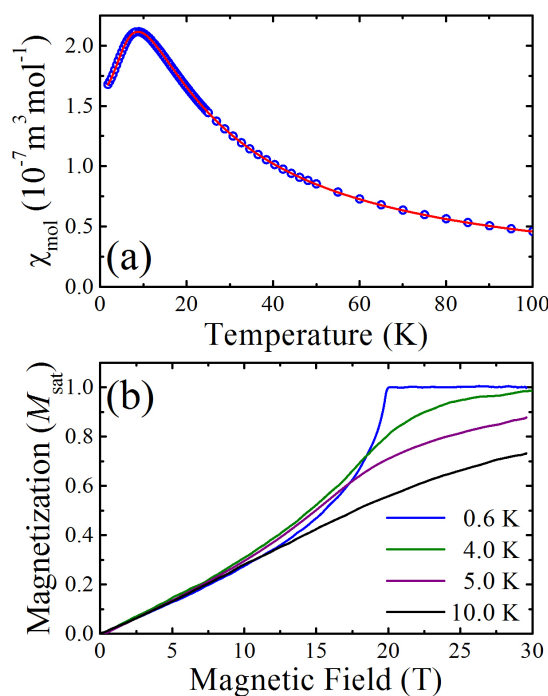


Fig. 2 (a) Molar susceptibility (χ_{mol}) vs. temperature for a polycrystalline sample of $\text{Cu}(\text{NO}_3)_2(\text{pyz})_3$ (circles) shows a broad maximum at 9 K. The data have been fitted to a model of spin-1/2 Heisenberg moments connected in a 1D chain with nearest-neighbour exchange J ¹³ (line), yielding $g = 2.04$ and $J = 13.7$ K. (b) Magnetization in units of the saturation magnetization (M_{sat}) vs magnetic field provided by a short-pulse magnet. Down sweeps of the magnetic field at various temperatures are shown. The data at the lowest temperature are typical of highly isolated $S = 1/2$ antiferromagnetic chains.

shows a broad maximum at 9 K indicative of the individual copper moments becoming correlated along the chains and the onset of low-dimensional behaviour below this temperature. Motivated by the structural analysis, the data are fitted to a model of $S = 1/2$ Heisenberg spins connected in a 1D chain with a single nearest-neighbour interaction J ¹³. The resultant fitted parameters are $g = 2.04(1)$ and $J = 13.7(1)$ K. A Curie-Weiss analysis of the inverse susceptibility data for temperatures above 100 K returned fitted values $g = 2.03(1)$ and an antiferromagnetic Curie-Weiss temperature $|\theta_{\text{CW}}| = 5.4(5)$ K, which is consistent with the energy scale and nature of the intrachain Heisenberg exchange constant.

Pulsed-field magnetization measurements up to 60 T (rise time to full field ~ 10 ms) were carried out at the National High Magnetic Field Laboratory in Los Alamos. The magnetization measured at various temperatures is shown in Figure 2(b) as a fraction of the saturated value. The concave rise observed at the lowest temperature and the sharp change in gradient at saturation is characteristic of highly isolated $S = 1/2$ antiferromagnetic chains, where, for the ideal system, dM/dB is known to diverge at the saturation field¹⁴. As the temperature increases the magnetization exhibits a more gradual approach to saturation.

The structural, susceptibility and magnetization data all imply that the interchain interactions are orders of magnitude smaller than the intrachain exchange (J). In this case, the low-

§ Further increasing the amount of pyrazine in the chemical reaction yields square plates of $[\text{Cu}(\text{NO}_3)_2(\text{pyz})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ recently reported by some of us¹².

temperature value of J can be estimated from the saturation field B_C ⁴ via the expression $g\mu_B B_C = 2J$. From the $T = 0.6$ K magnetization data it is found that $B_C = 19.9(1)$ T and so, using the g -factor determined from the Curie-Weiss fit, the exchange energy is found to be 13.6(1) K, in agreement with the result of fitting the magnetic susceptibility.

Implanted muons are very sensitive to small magnetic fields and were therefore used to probe the low-temperature magnetic behaviour. Zero-field muon-spin relaxation (ZF μ^+ SR) measurements were made on a polycrystalline sample using the low temperature facility (LTF) spectrometer at the Swiss Muon Source. Example μ^+ SR spectra are shown in Figure 3. For $T < 0.105$ K we can resolve oscillations at a single frequency in the asymmetry, $A(t)$, characteristic of quasistatic long range magnetic order (LRO) at one magnetically distinct muon site. We note that, in an earlier work on **1**, oscillations in the μ^+ SR spectra were observed at two distinct frequencies¹⁰; the additional pyz branches in **2** may block muons from occupying one of the candidate muon sites. We fit the spectra to the functional form

$$A(t) = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t} \cos(2\pi\nu t + \phi) + A_{bg}, \quad (1)$$

where the components with amplitudes A_1 and A_2 , due to muons stopping in the sample, have relaxation rates λ_1 and λ_2 respectively and the component with amplitude A_2 oscillates with a frequency ν . A_{bg} is the constant background asymmetry due to muons in the sample holder or those with their spins aligned parallel to the internal field. Above $T = 0.105$ K the spectra change shape and we instead fit the data to the sum of a Gaussian and an exponential relaxation. The temperature dependence of ν is shown in Figure 3. The oscillation frequency ν is related to the magnitude of the magnetic field at the muon site through $\nu = \gamma_\mu B / 2\pi$ where γ_μ is the muon gyromagnetic ratio ($= 2\pi \times 135.5 \text{ MHz T}^{-1}$) and serves as effective order parameter for the system. A fit to the phenomenological function $\nu(T) = \nu(0)[1 - (T/T_N)^\alpha]^\beta$ with $\alpha = 3$ (fixed) yields $\nu(0) = 1.59(1)$ MHz, $\beta = 0.12(2)$ and $T_N = 0.105(1)$ K [see Figure 3(a)]. A critical exponent $\beta = 0.18(5)$ was previously obtained for **1**, which is consistent with 2D Ising or 2D XY models¹⁰. The value of β obtained for **2** is even smaller and closer to that of a 2D Ising model, for which one expects $\beta = 1/8$. This might suggest that the fluctuations that destroy the LRO are two dimensional, most likely occurring along the chains and along the strongest exchange pathway between chains.

Periodic DFT Calculations were carried out using the software CRYSTAL14¹⁵. The functional B3LYP was used with basis set 86-411G(41d)¹⁶ for the Cu and pob-TZVP¹⁷ for all the other atoms. Gas-phase DFT calculations on a dimeric unit were carried out with Gaussian09¹⁸ using again the B3LYP functional and the basis set 6-311G(2d,2p). We have calculated the exchange couplings J using both periodic DFT and gas phase DFT on a single dimer and find $J = 14.88$ K and $J = 11.49$ K respectively. Our calculations indicate antiferromagnetic coupling between Cu spins and show reasonable agreement with the values of J obtained experimentally. These values are larger than the coupling constants $J = 10.70$ K and $J = 11.02$ K obtained for **1** using periodic DFT and

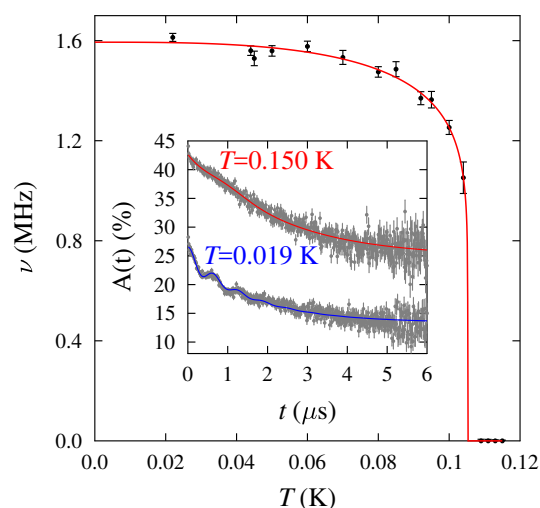


Fig. 3 Temperature dependence of (a) the frequency and (b) the relaxation parameter λ_2 in equation 1. Inset: example μ^+ SR spectra for $\text{Cu}(\text{NO}_3)_2(\text{pyz})_3$ measured above and below the magnetic ordering temperature.

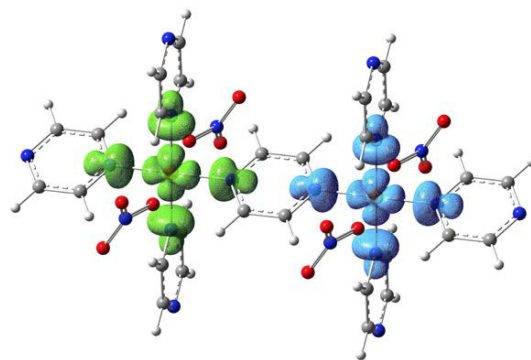


Fig. 4 Spin density distribution through pyrazine ligand calculated using density functional theory.

a dimer fragment approach respectively¹², supporting the experimentally observed trend. The calculated spin density distribution through the pyrazine ligand is shown in Figure 4. The largest part of the spin density is located at the copper atoms, with some delocalisation to the adjacent N atoms.

The combination of our measurements of the intrachain coupling J (from magnetic susceptibility) and the ordering temperature T_N (from μ^+ SR) allows us to estimate the interchain coupling J' through

$$|J'|/k_B = \frac{T_N}{4c \sqrt{\ln\left(\frac{\lambda|J|}{k_B T_N}\right) + \frac{1}{2} \ln\left(\frac{\lambda|J|}{k_B T_N}\right)}}, \quad (2)$$

where $\lambda = 2.6$ and $c = 0.223$ ¹⁹. Substituting $|J|/k_B = 13.7$ K and $T_N = 0.105(1)$ K we obtain $|J'|/k_B = 0.045$ K and $|J'/J| = 3.3 \times 10^{-3}$. These values are very similar to those obtained for **1**¹⁰. Furthermore, we can obtain an estimate of the magnetic moment of Cu^{2+} in this system through $m \approx 1.017 |J'/J|^{1/2}$ ²⁰ and obtain $m \approx 0.059 \mu_B$. The moment is very small, highlighting the effect

of quantum fluctuations in suppressing the ordered moment in this low-dimensional system.

In both **1** and **2**, a Jahn-Teller distortion places lobes of the Cu $d_{x^2-y^2}$ orbitals along the Cu-N bonds. The primary exchange pathway between Cu²⁺ ions is through the bridging pyz ligands along a 1D chain in both compounds and results in them having similar magnetic properties. However, the precise environments of the Cu²⁺ ions in the two cases are quite different. In **1** the $d_{x^2-y^2}$ orbital lies in the plane containing the Cu-N bonds and the two shorter Cu-O(1) bonds. The Cu ion forms bonds to both two of the O atoms in the nitrate ligand and the inherent rigidity of the nitrate group results in an O(1)-Cu-O(2) angle of 57°, far from the ideal 90° for octahedral symmetry [see Fig.1(a)]. The Cu²⁺ ion therefore sits in a highly distorted octahedral environment. In **2**, the $d_{x^2-y^2}$ orbital lies in the plane containing four Cu-N bonds with the Cu-O bonds lying perpendicular to this plane, completing the octahedral coordination [see Fig.1(b)]. This results in a higher symmetry environment for Cu²⁺ in **2** than in **1**.

In superexchange processes the exchange coupling $J \approx \sum |H_{fi}|^2 / \Delta E$ depends on the orbital overlap H_{fi} between the orbitals involved in virtual hopping processes and the difference ΔE between energy levels on the magnetic ion and the non-magnetic intermediary. Given that in both **1** and **2** superexchange occurs through magnetic $d_{x^2-y^2}$ orbitals which can interact with other Cu²⁺ ions through pyz bonds, we expect the orbital overlap to be similar, explaining the similarity in values of J . However, J also depends on higher order virtual processes which may be affected by the different environments for Cu in the two cases. We expect the lower symmetry environment of Cu in **1** to result in splittings of the d orbitals. In particular, we expect the repulsion between O(2) and the $d_{x^2-y^2}$ (which would be smaller if O(2) was occupying the ideal octahedral position) to raise the energy of electrons in the $d_{x^2-y^2}$ orbital and thus increase ΔE . Processes like these could explain the fact that J is larger in **1** than in **2**.

In **1** and **2** the angles between pyz and the plane containing the $d_{x^2-y^2}$ orbitals are similar (51° and 55° respectively) and we find that J in **1** is smaller despite the tilt angle being closer to the theoretically ideal value of 45° which would be expected to maximize π -overlap²¹. This is consistent with a study on **1** and the quasi-2D/3D antiferromagnet [Cu(NO₃)(pyz)₂]NO₃·H₂O (**3**)¹² where bond ellipticity profiles of the related compounds **1** and **3** were taken to rule out a mechanism driven by the π -overlap between the d_{yz} and d_{xy} orbitals of Cu and the π orbitals at the pyrazine in favour of a mechanism based on σ -exchange only.

The quasi-two-dimensional Cu-based antiferromagnet **3** is structurally similar to **1** and **2**, with pyz ligands again allowing coupling between Cu²⁺ ions¹². Despite the dimeric unit of **3** and its associated spin density¹² being nearly identical to that for **2**, the lack of staggering between chains (present for **1** and **2**) results in significant overlap between trans-coordinated pyz orbitals and the Cu²⁺ ions in adjacent chains. This additional exchange pathway results in a quasi-two-dimensional system with a reduced exchange constant $J = 7.3$ K.

In conclusion, the spin-1/2 chain compound Cu(NO₃)₂(pyz)₃ exhibits a larger intrachain coupling $J = 13.7$ K and a lower magnetic ordering temperature $T_N = 0.105$ K than Cu(NO₃)₂(pyz),

making it a more successful realization of a 1DQHAFM. Its success as a quasi-one-dimensional system is likely due a more symmetrical environment for the Cu²⁺ ion that enhances J and the presence of non-bridging pyz branches that assist to maintain effective chain isolation.

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Conflicts of interest

There are no conflicts to declare.

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