Magnetic order and enhanced exchange in the quasi-one-dimensional molecule-based antiferromagnet Cu(NO$_3$)$_2$(pyz)$_3$†

Benjamin M. Huddart, Jamie Brambleby, Tom Lancaster, Paul A. Goddard, Fan Xiao, Stephen J. Blundell, Francis L. Pratt, John Singleton, Piero Macchi, Rebecca Scatena, Alyssa M. Barton and Jamie L. Manson

The quasi-one-dimensional molecule-based Heisenberg antiferromagnet Cu(NO$_3$)$_2$(pyz)$_3$ has an intrachain coupling $J = 13.7(1)$ K ($\mathcal{H} = J \sum_i S_i \cdot S_{i+1}$) 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 low-dimensional magnetic properties. In some notable cases, large intermolecular spacing and pseudo Jahn–Teller (JT) distortions result in exchange interactions between transition metal ions being facilitated by bridging ligands such as pyrazine (=pyz=C$_4$H$_4$N$_2$). This allows for the construction of polymeric networks whose primary exchange occurs along one, two or three dimensions. The manipulation of these building blocks, combined with further ingredients such as counterions and additional ligands, 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-dimensional and two-dimensional quantum Heisenberg antiferromagnets.

Additional information about density functional theory calculations. CCDC 1879250. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cp07160h. For muon-spin spectroscopy measurements. Additional information about density functional theory calculations. CCDC 1879250. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cp07160h.
We prepared deep blue rods of 2 following the procedure previously described by Parkin et al.‡ 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 NO₃⁻ ligands and four N-donor atoms belonging to pyz [Cu–N(1) = 2.0719(14) and Cu–N(3) = 2.0149(16) Å]. The local coordination geometry of the Cu²⁺ ion in 2 is elongated due to a JT distortion along the O–Cu–O axis [Cu–O(1) = 2.3808(11) Å]. 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(2) forms a bifurcated interaction with the two non-coordinated oxygen atoms from NO₃⁻ on an adjacent chain, O(2) and O(3), at distances of 2.5959(15) Å and 2.5548(14) Å, respectively. As a result of these weak interchain interactions we anticipate small magnetic coupling between chains as well.

The measured molar susceptibility, χₘol, of 2 [Fig. 2(a)] 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.† 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 |θcw| = 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 several temperatures is shown in Fig. 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. 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-temperature value of J can be estimated from the saturation field Bₛ via the expression gμBBₛ = 2J. From the T = 0.6 K magnetization data it is found that Bₛ = 19.9(1) T and so, using the g-factor determined from the Curie–Weiss fit, J is found to
measurements of $J$ and $T_N$. Substituting $|J|/k_B = 13.7$ K and $T_N = 0.105(1)$ K we obtain $|J'|/k_B = 0.045$ K and $|J'| = 3.3 \times 10^{-3}$. These values are very similar to those obtained for 1. Furthermore, we can obtain an estimate of the magnetic moment of Cu$^{2+}$ in this system through $m \approx 1.017 |J'|^{1/2}$ 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. It is worth noting that the ratio of larger muon precession frequency observed for 1 and the corresponding frequency for 2 is similar to the ratio of the Cu$^{2+}$ magnetic moments in these two systems. This suggests that the muon site in 2 is similar to the higher frequency site in 1, but with a smaller local field as a result of the slightly smaller Cu$^{2+}$ moment.

Periodic DFT calculations were carried out using the CRYSTAL14 software. The functional B3LYP was used with basis set 86-411G(41d) for the Cu and 6-311G(2d,2p) for all the other atoms. Gas-phase DFT calculations on a dimeric unit were carried out with Gaussian09 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 a dimer fragment approach respectively, supporting the experimentally observed trend. The calculated spin density distribution through the pyz ligand is shown in Fig. 4. The largest part of the spin density is located at the Cu atoms, with some delocalization to the adjacent N atoms.

Considering the DFT results, we can rationalize the computed $J$ in terms of symmetry, orbital overlap and structural comparisons. In both 1 and 2, a JT distortion places lobes of the magnetic Cu $d_{x^2-y^2}$ orbitals along the Cu–N bonds. The primary exchange pathway between Cu$^{2+}$ ions is through the bridging pyz ligands along the 1D chain resulting in similar magnetic properties for 1 and 2. However, the enhanced magnetic exchange observed in 2 requires careful analyses of the local environment surrounding the Cu$^{2+}$ ions. Aside from the shared inversion symmetry of the Cu$^{2+}$ ion in 1 and 2, the enhanced spin exchange in 2 results

![Figure 3](1016 | Phys. Chem. Chem. Phys., 2019, 21, 1014--1018)  
**Fig. 3** Temperature dependence of the muon precession frequency $\nu$ for the fits described in the text. Inset: Example $\mu^+\mathrm{SR}$ spectra for 2 measured above and below the magnetic ordering temperature.

![Figure 4](1016 | Phys. Chem. Chem. Phys., 2019, 21, 1014--1018)  
**Fig. 4** Spin density distribution through the pyrazine ligand in 2 calculated using density functional theory.
from the particular bonds and angles making up the coordination sphere. In 1 the d_{x^2-y^2} orbital lies in the plane containing the Cu–N bonds (=1.976 Å) and the two shorter Cu–O(1) bonds (=2.002 Å). Nitrate coordination in 1 is quite different wherein it chelates to the Cu^{2+} ion resulting in a O(1)–Cu–O(2) bite angle of 56.3°, far from the ideal 90° observed for purely octahedral symmetry [see Fig. 1(a)]. For 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 [see Fig. 1(b)]. The net result is a higher symmetry environment for the Cu^{2+} in 2 relative to 1. In terms of the electronic structure, the lower symmetry environment of Cu in 1 can be expected to result in splittings of the d orbitals, altering the energy differences between the various Cu d orbitals and the sp^2-hybridized orbital at N responsible for supereexchange. For example, we expect the repulsion between O(2) and the magnetic Cu d_{x^2-y^2} orbital (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, thus reducing the contribution of this supereexchange pathway to J.

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-overlap. This is consistent with an X-ray charge-density study on 1 and the 3D coordination polymer [Cu(NO$_3$)$_2$(pyz)$_3$]NO$_3$H$_2$O (3). Bond ellipticity profiles ruled out π-type exchange between the Cu d$_{xy}$ and d$_{z^2}$ orbitals and the pyz π orbitals, favouring a σ-only exchange mechanism. This places emphasis on the Cu–N interactions and these are most important factor in driving the topology of the spin density.

Finally, 3 is structurally similar to 1 and 2, with pyz ligands providing the primary exchange pathway between Cu$^{2+}$. The intrachain Cu–N bonds and the Cu–N bonds of the terminal pyz ligands in 2 are both shorter than the Cu–N bonds in 3. The shorter intrachain Cu–N bonds in 2 concentrate electron density along these bonds, enhancing exchange along the chain. By analogy, the shorter apical Cu–O bond in 3 (2.337 Å) than in 2 (2.381 Å) results in a greater depletion of the spin density in the CuN$_4$ plane, reducing the effectiveness of the magnetic exchange through pyz. The magnitude of J in 1 is intermediate between 2 and 3 owing to ligand variation in the Cu equatorial plane. Oxygen is more electronegative than N and this likely plays a role in depleting spin density away from the intrachain Cu–N bond axis in 1.

In conclusion, the spin-1/2 chain compound Cu(NO$_3$)$_2$(pyz)$_3$ exhibits a larger intrachain coupling J = 13.7 K and a lower magnetic ordering temperature $T_N$ = 0.105 K than Cu(NO$_3$)$_2$(pyz), making it a more successful realization of a 1DQHAFM. The slightly enhanced J is likely due to the details of the local Cu$^{2+}$ environment, while effective chain isolation is maintained by non-bridging pyz branches.

Conflicts of interest
There are no conflicts to declare.

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Notes and references
‡ Further increasing the amount of pyrazine in the chemical reaction yields square plates of [Cu(NO$_3$)$_2$(pyz)$_3$]NO$_3$H$_2$O recently reported by some of us.9


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