Supplementary information:

Magnetic order and enhanced exchange in the quasi-one-dimensional molecule-based antiferromagnet $Cu(NO_3)_2(pyz)_3$

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Experimental details

Single crystal X-ray diffraction.

A crystal was glued on a glass fiber and cooled by an Oxford cryostream N2 flow cryostat at 173.00(10) K up to a resolution of 0.75 Å. The measurement was made on an Oxford Diffraction SuperNova area-detector diffractometer using mirror optics, monochromated, and Al filtered[1] microsource Mo K radiation (λ=0.71073 Å). Data reduction was performed using the CrysalisPro program.[2] The intensities were analytically corrected for Lorentz and polarization effects and for absorption with the Gaussian method based on the crystal shape. The pyrazine H-atoms were placed in positions calculated theoretically and refined using a riding model. The conventional structural refinements were carried out using SHELXL.[3]

Magnetic susceptibility.

Prior to a measurement of the susceptibility, the polycrystalline sample (mass = 16.524 mg) was dispersed in vacuum grease so as to minimize the exposure to air. The samples were placed inside a gelatin capsule, which was fixed inside a plastic drinking straw and attached to the end of a brass rod. The sample magnetic moment (M) was then measured in an applied field of $\mu_0 H = 0.1$ T for temperatures in the range $1.8 \leq T \leq 300$ K, with a Quantum Design SQUID magnetometer. In the linear limit, the magnetic susceptibility (χ) was deduced from this measurement using $\chi = M/H$.

The Hamiltonian for a 1D S=1/2 Heisenberg antiferromagnet is $\widehat{H} = J\sum_i S_i \cdot S_{i+1}$. We fit the susceptibility to a function of the form[3]

$$\chi_{mol}(t) = \frac{N_{\mathrm{A}} g^2 \mu_B^2 S(S+1)}{3k_{\mathrm{B}}T} P_{(6)}^{(5)}(t), \tag{1}$$

where $t = \frac{T}{J}$ and the Padé approximant is

$$P_{(r)}^{(q)}(t) = \frac{1+\sum_{n=1}^{q} N_n/t^n}{1+\sum_{n=1}^{r} D_n/t^n}. \tag{2}$$

The fitting coefficients in $P_{(r)}^{(q)}(t)$ are taken from Johnson et al.[3] and are listed in Table 1.

n	1	2	3	4	5	6
N_n	-0.053837836	0.097401365	0.014467437	0.0013925193	0.00011393434	
D_n	0.44616216	0.32048245	0.13304199	0.037184126	0.00026467628	0.00026467628

Table 1. Fitting coefficients for the Padé approximant in Equation 2.[3]

Pulsed-Field magnetization.

Measurements up to 60 T (rise time to full field ~ 10 ms) were performed at the National High Magnetic Field Laboratory in Los Alamos. Single crystals were mounted in a 1.3 mm diameter PCTFE ampoule that can be moved into and out of a 1500-turn, 1.5 mm bore, 1.5 mm long compensated-coil susceptometer, constructed from 25 µm high-purity copper wire. When the sample is within the coil and the field pulsed, the voltage induced in the coil is proportional to the rate of change of magnetization with time. Accurate values of the magnetization are then obtained by subtraction of the signal from that taken using an empty coil under the same conditions, followed by numerical integration. The magnetic field is measured via the signal induced an adjacent empty 10-turn coil and calibrated via observation of de Haas-van Alphen oscillations arising from the copper coils of the susceptometer.[4] The susceptometer is placed inside a ^{3}He cryostat, which can attain temperatures as low as 0.5 K.

Muon-Spin spectroscopy.

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. In a μ^+SR experiment[5] spin-polarized positive muons are stopped in a target sample, where the muon usually occupies an interstitial position in the crystal. The observed property in the experiment is the time evolution of the muon spin polarization, the behaviour of which depends on the local magnetic field at the muon site. Each muon decays, with an average lifetime of 2.2 µs, into two neutrinos and a positron, the latter particle being emitted preferentially along the instantaneous direction of the muon spin. Recording the time dependence of the positron emission directions therefore allows the determination of the spin-polarization of the ensemble of muons. In our experiments positrons are detected by detectors placed forward (F) and backward (B) of the initial muon polarization direction. Histograms $N_F(t)$ and $N_B(t)$ record the number of positrons detected in the two detectors as a function of time following the muon implantation. The quantity of interest is the decay positron asymmetry function, defined as

$$A(t) = \frac{N_\mathrm{F}(t) - \alpha_\mathrm{exp} N_\mathrm{B}(t)}{N_\mathrm{F}(t) + \alpha_\mathrm{exp} N_\mathrm{B}(t)},$$

where α_exp is an experimental calibration constant. $A(t)$ is proportional to the average spin polarization of the muon ensemble.

Density functional theory calculations.

The intrachain coupling constant J was calculated from the energy difference between high- and low-spin states by use of an Ising Hamiltonian (for both periodic and gas phase DFT). For the gas phase DFT we employed the broken symmetry approach described by Ruiz *et al.*[6]

References

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