



Control of the third dimension in copper-based square-lattice antiferromagnets

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Using a mixed-ligand synthetic scheme, we create a family of quasi-two-dimensional antiferromagnets, namely, $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ [$\text{pyz} = \text{pyrazine}$], $[\text{Cu}L_2(\text{pyz})_2](\text{ClO}_4)_2$ [$L = \text{pyO} = \text{pyridine-N-oxide}$ and $4\text{-phpy-O} = 4\text{-phenylpyridine-N-oxide}$]. These materials are shown to possess equivalent two-dimensional $[\text{Cu}(\text{pyz})_2]^{2+}$ nearly square layers, but exhibit interlayer spacings that vary from 6.5713 to 16.777 Å, as dictated by the axial ligands. We present the structural and magnetic properties of this family as determined via x-ray diffraction, electron-spin resonance, pulsed- and quasistatic-field magnetometry and muon-spin rotation, and compare them to those of the prototypical two-dimensional magnetic polymer $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$. We find that, within the limits of the experimental error, the two-dimensional, *intralayer* exchange coupling in our family of materials remains largely unaffected by the axial ligand substitution, while the observed magnetic ordering temperature (1.91 K for the material with the HF_2 axial ligand, 1.70 K for the pyO and 1.63 K for the 4-phpy-O) decreases slowly with increasing layer separation. Despite the structural motifs common to this family and $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$, the latter has significantly stronger two-dimensional exchange interactions and hence a higher ordering temperature. We discuss these results, as well as the mechanisms that might drive the long-range order in these materials, in terms of departures from the ideal $S = 1/2$ two-dimensional square-lattice Heisenberg antiferromagnet. In particular, we find that both spin-exchange anisotropy in the intralayer interaction and interlayer couplings (exchange, dipolar, or both) are needed to account for the observed ordering temperatures, with the intralayer anisotropy becoming more important as the layers are pulled further apart.

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I. INTRODUCTION

As a quintessentially quantum-mechanical model and because of its relevance to the unsolved problem of high-temperature superconductivity, the $S = 1/2$ two-dimensional (2D) square-lattice Heisenberg antiferromagnet (SLHAFM) remains one of the most actively studied systems in condensed matter physics [1–5]. It is described by the Hamiltonian $J \sum_{ij} S_i \cdot S_j$ (where J is the strength of the nearest-neighbor exchange interaction) and, because of strong thermal and quantum fluctuations, is resistant to long-range order for temperatures $T > 0$ K [6]. Considerable theoretical attention has

been paid to additions to this ideal model, including external magnetic fields, next-nearest-neighbor coupling, or departures from isotropy in the interactions. Predicted consequences of such deviations include alterations to the excitation spectra [7], changes in the universality class [8], the emergence of exotic magnetic phases [9], and the promotion of a variety of ordered states [10].

Practical realizations of the SLHAFM involve crystalline materials that are inevitably three-dimensional from a structural standpoint [11]; this introduces possible interlayer magnetic coupling between adjacent square-lattice planes, which, if present, will raise the magnetic ordering temperature to nonzero values and, potentially, obscure the effects of the other perturbations [11]. Reducing the interlayer coupling may allow the above effects to come to the fore, permitting the associated theoretical predictions to be investigated in the laboratory. In this context, the closest experimental approximations to ideal 2D magnets have typically made use of copper-oxygen superexchange bonds [12]. However, crystal-engineering efforts have given rise to a number of reduced-dimensionality molecular candidates [13–15] in which the interlayer coupling

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is reduced to levels seen in the best inorganic materials. In this way it has been possible to show evidence of changes in universality class as a function of magnetic field in a molecular SLHAFM [16,17]. An added advantage of molecular systems is the ability to make controlled adjustments to the crystal structure, thereby tuning interaction strengths and better testing the predictions of the SLHAFM and associated models. To this end, we and others have previously shown that it is possible to gain a degree of control over the primary exchange energy in low-dimensional molecular antiferromagnets via constitutional changes that include deuteration [18], anion substitution [11,19], exchange of halide ligands [20,21], and the application of high pressures [22,23].

In this paper, we examine a family of materials based on 2D arrays of magnetic Cu(II) ions linked by pyrazine ($C_4H_4N_2$) ligands in order to investigate the effects of tuning the interlayer coupling strength. By varying the layer separation through the interchange of axial ligands, we study to what extent the antiferromagnetic ordering temperature can be manipulated, and whether it is possible to approach the ideal 2D limit. The four coordination polymers chosen are (1) $[Cu(HF_2)(pyz)_2]ClO_4$, (2) $[Cu(pyO)_2(pyz)_2](ClO_4)_2$, (3) $[Cu(4-phpy-O)_2(pyz)_2](ClO_4)_2$, and (4) $Cu(pyO)_2(ClO_4)_2$. Here, pyz = pyrazine, pyO = pyridine-*N*-oxide (C_5H_5NO), and 4- $phpy-O$ = 4-phenyl-pyridine-*N*-oxide ($C_{11}H_9NO$). These materials have interlayer spacings that range from 6.5713 to 16.777 Å at low temperatures. Number 4 is the prototypical example of a molecular SLHAFM [12,19,24] and is used here as a yardstick by which to judge the other compounds.

This paper is organized as follows. After outlining the synthesis procedures, experimental details and calculations in the next two sections, we describe the crystal structure of the materials as determined using x-ray diffraction. Next, we present the results of electron spin-resonance and pulsed-field magnetization experiments to determine the anisotropic g -factors and effective nearest-neighbor exchange energies, respectively. We describe how the exchange energies compare with those found from previous measurements on structurally related materials and examine possible reasons for their variation across the family using density-functional theory. Then we present the determination of the magnetic ordering temperatures from muon-spin rotation measurements, followed by a discussion of the nature of the magnetic interactions between the layers, as well as the mechanism that drives these systems to long-range order at low temperatures.

II. EXPERIMENTAL DETAILS

A. Sample synthesis

All chemical reagents were obtained from commercial sources and used as received. $Cu(ClO_4)_2 \cdot 6H_2O$ served as the Cu(II) source in all syntheses. For No. 1, Cu(II) ions were slowly mixed with an aqueous solution containing stoichiometric amounts of NH_4HF_2 (0.0627 g, 1.10 mmol) and pyrazine (0.1762 g, 2.20 mmol) to afford a blue solution. For Nos. 2 and 3, an aqueous solution of Cu(II) was combined with an ethanolic solution containing a mixture of pyrazine (0.500 g, 2.11 mmol) and pyridine-*N*-oxide (0.401 g, 4.20

mmol) or 4-phenylpyridine-*N*-oxide (0.7190 g, 4.20 mmol). Compound No. 4 was synthesized as described in the literature [19]. Deep-blue (Nos. 1 and 4) or blue-green (Nos. 2 and 3) solutions were obtained and, when allowed to evaporate slowly at room temperature, x-ray quality blue plates (Nos. 1 and 4) or dark green plates (No. 2) $\sim 0.5 \times 0.5 \times 0.2$ mm³ were recovered, whereas No. 3 yielded dark green microcrystals $\sim 0.03 \times 0.03 \times 0.01$ mm³. The relative amounts of $pyz:pyO$ (No. 2) or $pyz:4-phpy-O$ (No. 3) were optimized in order to prevent formation of byproducts such as $Cu(ClO_4)_2(pyz)_2$, $[Cu(pyO)_6](ClO_4)_2$, or $[Cu(4-phpy-O)_6](ClO_4)_2$.

B. X-ray diffraction studies

Crystals of each compound except $[Cu(pyO)_2(4-phpy-O)_2](ClO_4)_2$ were carefully selected, attached to a glass fiber and data collected at several temperatures between 100 and 297 K using a Bruker APEX II CCD x-ray diffractometer (Mo- K_α radiation, $\lambda = 0.071073$ nm) equipped with a low-temperature device. Measurements employed omega scans and a full sphere of data was collected. Cell parameters were retrieved using SMART software [25], and data were refined using SAINTPLUS [26] based on all observed reflections. Data reduction and correction for Lorentz polarization and decay were performed using the SAINTPLUS software. Absorption corrections were applied using SADABS [27]. Structures were solved directly and refined by the least-squares method on F^2 using the SHELXTL program package [28]. All nonhydrogen atoms were refined anisotropically. No decomposition was observed during data collection.

High-resolution synchrotron x-ray powder diffraction patterns were collected on $[Cu(pyO)_2(4-phpy-O)_2](ClO_4)_2$ at 297 K using the 11-BM-B beamline located at the Advanced Photon Source, Argonne National Laboratory. X rays were selected using a Si(111) channel cut monochromator. After the sample, the diffracted beams were analyzed using a Ge(111) crystal and detected by a NaI scintillation counter. The wavelength and diffractometer zero were calibrated using a sample of NIST Standard Reference Material 1976, a sintered plate of Al_2O_3 . The sample was loaded into a 1.0 mm diameter Kapton tube and mounted in a sample automation robot. Data were collected for approximately 1 hour. To improve particle statistics, the capillary was spun at several radians per second. Results of the data refinement for all four materials are given in Table I below.

C. Electron-spin resonance

Electron-spin resonance spectra were measured on single-crystal samples of Nos. 1 and 2, and fine powders of Nos. 3 and 4 in the frequency range 10 to 110 GHz using cavity perturbation techniques. For single-crystal g -factor anisotropy measurements, a monomoded cavity, resonating at a frequency of around 71 GHz and mounted on a cryogenic goniometer was employed [29]. This allows the crystal to be rotated with respect to the applied magnetic field without thermal cycling. For powder samples, and to examine the frequency-field scaling for single crystals, over-moded cylindrical and con-focal resonators were used. Temperature control was provided by a standard ⁴He flow cryostat and/or a single shot ³He

TABLE I. Space groups and lattice parameters of the compounds in Fig. 1. The 300-K data for No. 4 are taken from Ref. [19]; the rest are from this study.

	T (K)	space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
(1) [Cu(HF ₂)(pyz) ₂]ClO ₄	300	$P4/nmm$	9.7054(6)	9.7054(6)	6.6894(9)	90.00	90.00	90.00
	50	$P\bar{1}$	6.5943(1)	9.6300(1)	9.7089(2)	90.0006(4)	94.791(1)	91.720(1)
(2) [Cu(pyO) ₂ (pyz) ₂](ClO ₄) ₂	300	$C2/m$	13.7154(2)	13.7014(2)	13.1926(2)	90.00	108.637(1)	90.00
	100	$C2/m$	13.6676(2)	13.6699(2)	13.1910(2)	90.00	111.572(1)	90.00
(3) [Cu(4-phpy-O) ₂ (pyz) ₂](ClO ₄) ₂	300	$C2/c$	34.566(2)	9.4850(3)	9.8863(3)	90.00	102.763(3)	90.00
	100	$C2/c$	35.6195(4)	9.44905(9)	9.83656(7)	90.00	109.606(1)	90.00
(4) Cu(pyz) ₂ (ClO ₄) ₂	300	$C2/m$	9.734(2)	9.729(2)	8.132(2)	90.00	120.855(4)	90.00
	100	$C2/c$	13.9276(3)	9.7438(2)	9.7871(2)	90.00	96.924(1)	90.00

refrigerator. Quasistatic magnetic fields were applied using a 17 T superconductive solenoid; a Millimetre-wave Vector Network Analyzer (MVNA), manufactured by AB-Millimetre, was used as both the microwave source and detector [29].

D. Magnetometry

Pulsed-field magnetization measurements were performed at the National High Magnetic Field Laboratory in Los Alamos; fields of up to 65 T with typical rise times ≈ 10 ms were used. Single crystals are mounted in 1.3 mm diameter PCTFE ampoules (inner diameter 1.0 mm) that can be moved into and out of a 1500-turn, 1.5 mm bore, 1.5 mm long compensated-coil susceptometer, constructed from 50 gauge high-purity copper wire [11]. 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, (dM/dt) . Accurate values of the magnetization are obtained by numerical integration of the signal with respect to time, followed by subtraction of the integrated signal recorded using an empty coil under the same conditions [11]. The magnetic field is measured via the signal induced within a coaxial 10-turn coil and calibrated via observation of de Haas–van Alphen oscillations arising from the copper coils of the susceptometer [11]. The susceptometer is placed inside a ³He cryostat, which can attain temperatures as low as 500 mK. During each experiment, the size and sign of dH/dt of the field pulses was varied. No evidence of a hysteresis caused by slow relaxation of the sample moment was observed in any of measurements.

Low-field magnetization at temperatures ≈ 500 mK was measured using an iQuantum low-temperature insert for the Quantum Design Magnetic Property Measurement System (MPMS) XL SQUID magnetometer. Zero-field cooled magnetic-moment measurements in the field range $0 \leq \mu_0 H \leq 0.3$ T were performed on 76.007-, 47.326-, and 28.717-mg polycrystalline samples of Nos. 1, 2, and 3, respectively. To make the measurements, the sample is placed inside a polycarbonate capsule with a small amount of cotton wool to prevent it from moving. The capsule is wrapped in a thermally conducting sheath, containing copper wires arranged parallel to the magnetic field, and fixed inside a plastic drinking straw. The temperature is monitored via a thermometer positioned approximately 1 cm above the sample inside the straw. The straw is then mounted to the end of a rod which is lowered into the ³He cryostat. With the ⁴He chamber of the MPMS cooled to 1.6 K, the cryostat is evacuated and

liquid ³He is allowed to condense inside, such that the sample is submerged. Temperatures down to 500 mK are achieved by combined use of a turbo molecular pump and a charcoal sorption pump.

E. Muon-spin rotation

Zero-field muon-spin rotation measurements were performed on powder samples of Nos. 2 and 3. Sample No. 2 was covered by a 25- μ m silver foil and mounted on the cold finger of the dilution refrigerator on the LTF instrument at the Swiss Muon Source, Paul Scherrer Institut, Switzerland. Sample No. 3 was covered by a 12.5- μ m silver foil and mounted in a ³He cryostat on the ARGUS instrument at the ISIS facility, Rutherford Appleton Laboratory, UK. Further details of muon-spin rotation experiments on Nos. 1 and 4 can be found in Refs. [12,14], respectively.

III. CALCULATIONS

A. Density functional theory

The broken-symmetry approach of Noodleman [30] as implemented in the ORCA version 2.8 suite of programs [31–33] was employed to evaluate the exchange couplings. The quoted coupling constants are based on formalism of Yamaguchi, which employs calculated expectation values $\langle S^2 \rangle$ for both high-spin and broken-symmetry states [34,35]. Calculations employed the PBE0 functional, which has previously been demonstrated to yield reliable values for magnetic couplings in analogous systems [21,36]. The Ahlrichs-VTZ basis function set was used [37]. For compound No. 3, SCF convergence was facilitated by using a nonstandard value (10) for the DIISMaxEq parameter in ORCA.

B. Dipole-field calculations

The dipolar interaction of a spin with magnetic moment \mathbf{m}_0 at position \mathbf{r}_0 with the magnetic moment \mathbf{m}_i (assumed to be completely localized) of ion i at position \mathbf{r}_i is given by

$$B_{\text{dip}}^k(\mathbf{r}_0) = \sum_i D_i^{jk}(\mathbf{r}_0) m_i^k, \quad (1)$$

where

$$D_i^{jk} = \frac{\mu_0}{4\pi R_i^3} \left(\frac{3R_i^j R_i^k}{R_i^2} - \delta^{jk} \right) \quad (2)$$

is the dipolar tensor with indices jk and $\mathbf{R}_i = (R_i^x, R_i^y, R_i^z) = \mathbf{r}_0 - \mathbf{r}_i$.

The dipolar tensor is evaluated for the bulk crystal inside a Lorentz sphere of radius $r_L = 100 \text{ \AA}$. The results are well converged due to the relatively short-range nature of the dipolar interaction. The interlayer dipolar interaction was estimated by calculating the intralayer dipolar interaction inside a Lorentz circle of radius $r_L = 100 \text{ \AA}$ and subtracting the result from the bulk 3D dipolar interaction. The dipolar energy of a chosen moment \mathbf{m}_0 is then given by

$$E_{\text{dip}} = -\mathbf{m}_0 \cdot \mathbf{B}_{\text{dip}} \quad (3)$$

and scales with the square of the ordered moment size \mathbf{m}_i^2 .

This calculation was performed by assuming certain collinear magnetic structures (see below) and the energy in Eq. (3) was then calculated for many different directions of the magnetic moments. We define $E_d = (E_{\text{dip}}^{\text{max}} - E_{\text{dip}}^{\text{min}})/2$, where $E_{\text{dip}}^{\text{min}}$ ($E_{\text{dip}}^{\text{max}}$) is the minimum (maximum) dipolar energy given the considered magnetic structure.

IV. CRYSTAL STRUCTURES

The low-temperature crystal structures of all four compounds viewed along the copper-pyrazine planes are shown in Fig. 1; complete data sets are available at the Cambridge Crystallographic Data Centre (CCDC) [38]. Table I collects the lattice parameters at both high and low temperatures,

while Table II offers a comparison of some low-temperature structural parameters relevant to the discussion of the magnetic properties.

[Cu(HF₂)(pyz)₂]ClO₄ (No. 1) crystallizes at room temperature in the tetragonal space group $P4/nmm$, with each copper(II) ion equatorially ligated to four pyrazine nitrogen atoms at a distance of 2.039(3) Å and axially ligated to the fluorines from HF₂⁻ at a distance of 2.228(3) Å. This coordination gives rise to square-lattice copper-pyrazine layers separated by strong hydrogen-bonded HF₂⁻ pillars. Intralayer and interlayer copper separations are 6.863(1) and 6.689(1) Å, respectively, with the noncoordinated ClO₄⁻ counterions located close to the centre of these copper-cornered cuboids. The pyrazine molecule is tilted 64.2° out of the copper-pyrazine planes and counter-rotates relative to its closest neighbor within the plane. This room-temperature structure has been reported previously [11]. On cooling to 50 K the structure transforms into the triclinic space group $P\bar{1}$. The Cu–N bond lengths are no longer equal, varying between 2.064(5) and 2.089 Å. This leads to a slight departure from perfect copper-pyrazine square planes, the shortest in-plane Cu ··· Cu distance being 6.824(1) and the longest 6.850(1) Å (see Table II). The pyrazine molecules are still counter-rotated relative to their neighbors, but now there are four different tilt angles, ranging from 52.8° to 67.7°. In addition, while the N ··· N axis of each pyrazine

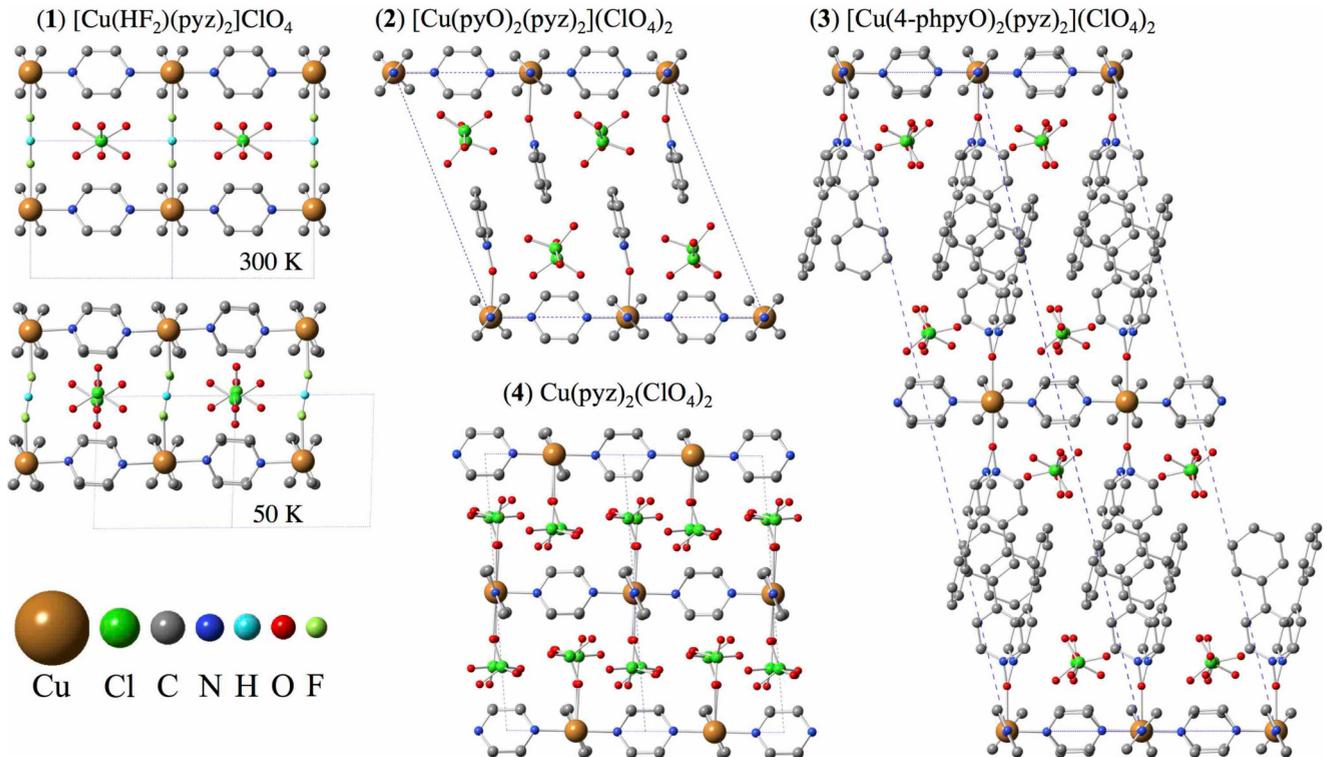


FIG. 1. Experimentally determined crystal structures viewed along the copper-pyrazine planes. All structures shown were determined via single-crystal x-ray diffraction at 100 K, except for No. 1 for which both 300 and 50 K structures are presented. Here, pyz = pyrazine, pyO = pyridine-N-oxide, 4-phpyO = 4-phenyl-pyridine-N-oxide; as shown in the inset key, Cu = brown, Cl = green, C = gray, N = blue, H = cyan, O = red, and F = light green. All hydrogens from organic molecules are omitted for clarity. Broken lines denote a single unit cell. All four systems are based on two-dimensional arrays of Cu-pyz in which pyz orbitals mediate the dominant exchange interactions. In No. 1, the triclinic structure is supported by strong F ··· H ··· F hydrogen bonds that form bridging ligands separating the layers [11]. The three other systems have nonbridging ligands along the interlayer direction and a monoclinic structure. The nonbridging ligands in Nos. 2 and 3 are pyO and 4-phpyO, respectively. While the ClO₄ molecules are noncoordinating anions in Nos. 1, 2, and 3, they coordinate to the Cu ions in No. 4.

TABLE II. Crystallographic parameters of interest for magnetism, measured at 100 K, except for No. 1 for which the data were taken at 50 K. Cu–N represents the equatorial coordination bond length and Cu–L is the axial coordination bond length, i.e., Cu–F for No. 1 and Cu–O otherwise. In all cases the Jahn-Teller axis lies along the axial ligand direction. Intralayer Cu–Cu are the Cu–pyz–Cu distances within the planes. Interlayer Cu–Cu are the shortest interlayer neighbor distances; where more than one value is quoted it is because they are closely spaced due to staggering of adjacent planes. The interlayer spacings are the perpendicular distances between planes. The tilt angle is that between the plane of the pyrazine molecules and the copper-pyrazine layers. The twist angle is that between the N···N axis of the pyrazine molecules and the copper-copper pathways in the two-dimensional planes. The last line shows data measured at 15 K for the related material [Cu(HF₂)(pyz)₂]SbF₆ [11], which is compared to Nos. 1–4 in later discussions.

	equatorial Cu–N (Å)	axial Cu–L (Å)	intralayer Cu–Cu (Å)	interlayer Cu–Cu (Å)	interlayer separation (Å)	pyrazine tilt (°)	pyrazine twist (°)
(1) [Cu(HF ₂)(pyz) ₂]ClO ₄	2.064(5)		6.824(1)			52.8	3.11
	2.075(5)	2.312(4)	6.829(1)	6.5943(1)	6.5713(1)	55.9	3.58
	2.078(5)		6.846(1)			67.1	5.37
	2.089(6)		6.850(1)			67.7	7.41
2.031(1)	6.830(1)		47.3				
(2) [Cu(pyO) ₂ (pyz) ₂](ClO ₄) ₂	2.0315(9)	2.3148(8)	6.834(1)	12.426(2)	12.267(2)	53.4	0.00
	2.0316(9)		6.840(1)	13.191(2)		68.1	0.48
	2.009(5)		6.812(1)			50.6	1.40
(3) [Cu(4-phpy-O) ₂ (pyz) ₂](ClO ₄) ₂	2.019(5)	2.292(2)	6.827(1)	16.81(1)	16.777(9)	64.4	2.31
	2.057(1)		6.904(1)				63.0
(4) Cu(pyz) ₂ (ClO ₄) ₂	2.058(1)	2.356(9)	6.907(1)	8.014(1)	6.913(1)	69.9	1.97
	[Cu(HF ₂)(pyz) ₂]SbF ₆		2.033(1)			2.259(1)	6.836(1)

molecule in the room-temperature structure lies along the path, which connects the copper ions within the planes, at low temperatures the molecules undergo a twist such that the N···N axes make an angle with this pathway that varies between 3.11° to 7.41°.

This material is part of the closely related family [Cu(HF₂)(pyz)₂]X, where the local symmetry of counterion X can be octahedral (e.g., PF₆[−], AsF₆[−], SbF₆[−], NbF₆[−] and TaF₆[−]) or tetrahedral (e.g., ClO₄[−], BF₄[−]) [11]. The main variation in the room temperature structure on moving across this family is in the tilt angle of the pyrazines. For the materials with octahedral anions, this angle is close to 90°, but is significantly smaller for the tetrahedral-anion materials [11]. More differences appear on cooling. In contrast to the 50-K structure of the X = ClO₄[−] material described here, the structure of the X = SbF₆[−] material measured at 15 K indicates that this system remains in a tetragonal space group down to low-temperatures, has a single pyrazine tilt angle of 79.2°, and does not exhibit the twisting of the N···N pyrazine axis mentioned above. In addition, as discussed in more detail below, there is a reduction of nearly a factor of two in the primary exchange constant in this family associated with the change from octahedral to tetrahedral anions [11].

[Cu(pyO)₂(pyz)₂](ClO₄)₂ (No. 2) adopts the monoclinic C2/m space group with no change on cooling to 100 K. There is a similar equatorial ligand arrangement in the low-temperature phase of No. 1, with Cu–N distances ranging from 2.023(3) to 2.040(4) Å at low temperatures and copper-pyrazine plaquettes that deviate slightly from a square arrangement. Each copper(II) site is also coordinated to two oxygens from the axially-ligated pyridine-N-oxide molecules at a distance of 2.331(3) Å and the bond angles within the CuN₄O₂ octahedra that deviate from 90° by up to 2.6°. Adjacent copper-pyrazine planes are shifted with respect to

one another along the *a* axis, leaving each copper close to equidistant from its two nearest neighbors within each adjacent plane. This staggering of layers could give rise to a degree of frustration if any antiferromagnetic interlayer exchange coupling is present, and in principle cause complete cancellation if the copper ions were arranged in a triangular lattice in the interlayer direction. In reality there is a difference in the interlayer Cu–Cu distances, as shown in Table II. As compared to No. 1, No. 2 has twice as many ClO₄[−] anions per formula unit, with the chlorine ion approximately centrally located above and below the copper-pyrazine plaquettes at alternating distances of 3.0 and 3.5 Å.

[Cu(4-phpyO)₂(pyz)₂](ClO₄)₂ (No. 3) also has a monoclinic structure, crystallizing in the C2/m space group. The axial ligand in this material is the larger 4-phenyl-pyridine-N-oxide molecule. The ligand and anion arrangements are akin to that of No. 2 with departures from the ideal square lattice in the copper-pyrazine planes and a similar range of bond angles within the CuN₄O₂ octahedra. Again there are two noncoordinated counterions per formula unit, the chlorines here lying at a distance of approximately 3.5 Å either side of the copper-pyrazine planes.

The structure of Cu(pyz)₂(ClO₄)₂ (No. 4) has been reported by Darriet *et al.* [24] and more recently by Woodward *et al.* [19]. The structure resulting from our x-ray diffraction study is shown in Fig. 1 and is in agreement with the previous measurements. At room temperature the crystal adopts the monoclinic C2/m space group with doubly-staggered square-lattice copper-pyrazine planes and a single pyrazine tilt angle of 65.8°. Below about 180 K a phase change to the C2/c space group occurs. The square layers remain, but there are now two tilt angles, 63.0° and 69.9°, one for each *cis*-coordinated ligand pair [19]. The tilt angles do not counter-rotate within the copper-pyrazine planes. Unlike compounds Nos. 1, 2, and 3,

the ClO_4^- ions are coordinated to the coppers via an oxygen. At temperatures below the phase change, these ligands order such that the chlorines are a perpendicular distance of 3.7 Å away from the planes to which their molecules coordinate and sit in the space above the copper-pyrazine squares of the adjacent plane at a distance of 3.2 Å.

Thus, by changes in the axial coordination of these four materials, a family is realized in which the copper-pyrazine planes are largely maintained while the interlayer structure is significantly altered. In particular, the spacing between adjacent layers at low temperatures varies from 6.5713(1) Å, through 12.267(2) Å, to 16.777(9) Å for the systems with the HF_2 (No. 1), pyO (No. 2), and 4-phpy-O (No. 3) ligands, respectively. System No. 4, with the ClO_4 axial ligands, has an interlayer spacing of 6.913(1) Å.

V. SINGLE-ION PROPERTIES

In all four materials the Jahn-Teller-active copper(II) ion sits at the center of a distorted CuN_4L_2 octahedron, where L is the axially-coordinated ion, namely F in compound No. 1, and O in the other compounds. As shown in Table II, in each case the Cu– L bond length is elongated compared to the intralayer Cu–N coordination bond lengths, an indication that the Jahn-Teller axis points out of the copper-pyrazine planes [39]. For $S = 1/2$ copper in such an environment, the crystal field splits the $3d$ states such that the $d_{x^2-y^2}$ orbital is partially occupied and aligned perpendicular to the axial distortion [39]. The greater overlap of $d_{x^2-y^2}$ with the d_{xy} orbital, than with d_{xz} or d_{yz} , leads to a greater enhancement of the g factor for fields along z (the axial direction) than for those in the xy plane [40]. Similarly, through the spin-orbit interaction, the exchange coupling between neighboring spins will likely also possess spin anisotropy [39]. This spin-exchange anisotropy (as opposed to the spatial exchange anisotropy dictating the dimensionality of the magnetism) is a two-ion anisotropy, which leads to easy-plane or easy-axis deviations from Heisenberg (spin isotropic) antiferromagnetic order. As discussed later, the family of quasi-two-dimensional $3d^9$ copper systems considered here exhibits small levels of spin anisotropy, and which are likely, at least in part, responsible for the long-range order observed in these materials.

For a spin-half system in the absence of interactions between the spins, the electron-spin resonance (ESR) condition (the frequency-field relationship for the ESR line) is a measure of the spectroscopic g factor [41,42]. The ESR condition in the antiferromagnetic state is determined by both the applied magnetic field and the effective internal exchange field [43,44]. This has the largest effect on the frequency-field scaling, and hence the determination of the g factor, for magnetic fields applied perpendicular to the easy plane. In this case, the frequency-field relationship is no longer linear; the applied and internal fields add in quadrature giving rise to a finite frequency intercept for the resonance condition at zero applied field [42]. For conventional three-dimensional antiferromagnets the crossover from paramagnetic resonance to antiferromagnetic resonance (with finite zero-field intercept) occurs close to the magnetic ordering temperature, T_c [41]. By contrast, in antiferromagnets of reduced dimensionality (in which T_c is significantly suppressed relative to

the energy scale of the dominant exchange interaction), a nonlinear frequency-field relationship can become evident at temperatures significantly above those at which long-range order is observed (at $T \simeq 2T_c$) [42,43]. Consequently, the ESR spectra of reduced-dimensional magnetic materials must be interpreted with caution. To obtain the most accurate measure of the paramagnetic g -factor anisotropy, conditions under which the frequency-field relationship becomes strongly nonlinear should be avoided. In practice, this means not employing temperatures or frequencies that are low relative to the energy scales of the exchange anisotropy. Therefore, where possible, for the purpose of this paper, we have derived the spectroscopic g factor from the gradient of linear fits to measurements at multiple high ($\gg 10$ GHz) frequencies at temperatures of at least twice T_c . We have also investigated the temperature dependence to verify minimal influence of the antiferromagnetic order.

Figure 2 contains examples of ESR measurements on the four materials studied in this paper. Figure 2(a) shows the powder spectra of No. 4 measured at a frequency of 71 GHz, while (b) shows similar spectra for No. 3 measured at a frequency of 70.3 GHz. For the latter, a smaller field range is shown to emphasize the small shift of the hard axis ESR line in the vicinity of antiferromagnetic order at 2 K. At temperatures above 10 K the observed asymmetric ESR lines in both cases are consistent with a uniaxial g -factor anisotropy corresponding to $g_z = 2.25(5)$ and $g_{xy} = 2.04(3)$. Note, these are the g factors obtained with the measurement field applied perpendicular and parallel to the Cu–pyz planes, respectively. At a temperature of 2 K the ESR contribution from magnetic fields oriented along the easy axis (g_z) are significantly broadened, in agreement with single-crystal measurements from other members of this family at temperatures approaching that of antiferromagnetic order. Figure 2(c) shows the angle-dependence of the measured g factor in single crystals of No. 2 as field is rotated between perpendicular to (0°) and parallel to (90°) the Cu–pyz planes. Again, the g -factor anisotropy is $g_z = 2.25(5)$ and $g_{xy} = 2.04(3)$. Figure 2(d) shows the frequency-magnetic field scaling of the ESR line measured on a single crystal of No. 1 with the field oriented perpendicular to the planes. At a temperature of 10 K, the linear frequency-field scaling (with the 0,0 intercept) corresponds to a g factor of 2.26(2). The nonlinear frequency-field scaling observed at a temperature of 1.5 K (which is below the ordering temperature of 1.91 K) is well reproduced by adding a zero magnetic-field frequency offset (23 GHz) to the linear frequency-field scaling (given by the g -factor evolution at high temperatures) in quadrature. The frequency-field scaling is consistent with evolution to antiferromagnetic resonance at low temperature indicating an XY-type spin-exchange anisotropy of a few percent [43,44].

The g factors deduced from all of the ESR experiments on compounds No. 1 to No. 4 are reproduced in Table III; to within experimental errors, all compounds exhibit the same range of g factors associated with anisotropy due to crystal-field effects [45]. The material-independence of the g -factor values shows that the microscopic environment of the Cu ions is very similar in all four compounds, as already suggested by the structural data discussed in the previous section.

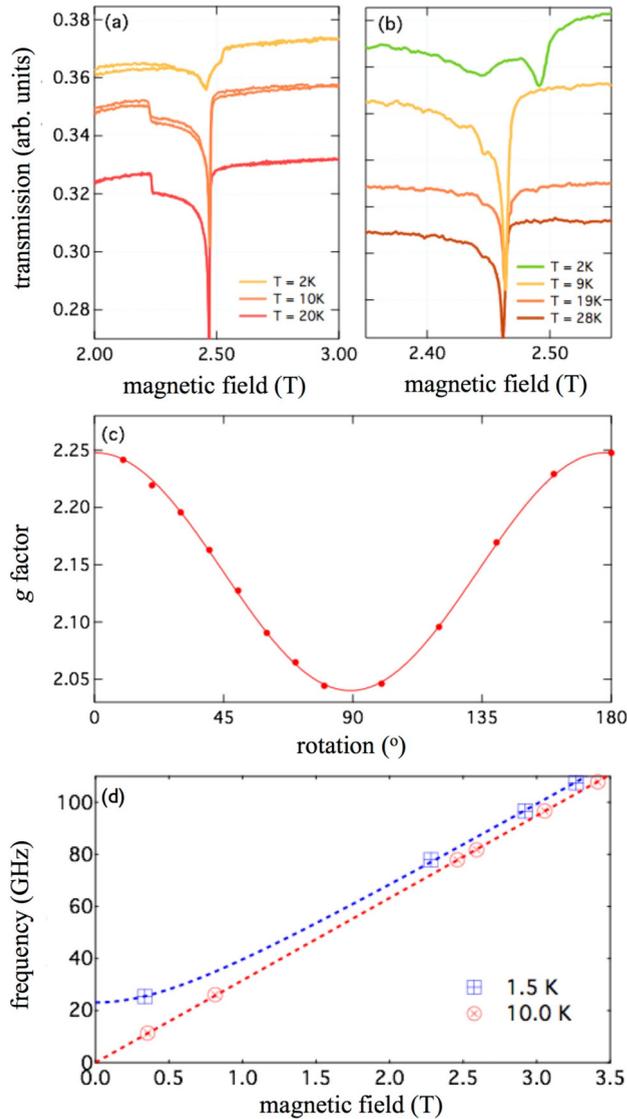


FIG. 2. (a) Powder ESR spectra of $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ (No. 4) measured at a frequency of 71 GHz. (b) Similar powder spectra for $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ (No. 3) measured at a frequency of 70.3 GHz. Above 10 K the g -factor anisotropy in both cases is $g_z = 2.25$ and $g_{xy} = 2.04$. (c) The $\sin(2\theta)$ angle dependance of the g -factor of $[\text{Cu}(\text{pyO})_2(\text{pyz})_2](\text{ClO}_4)_2$ (No. 2) as field is rotated between perpendicular to (0°) and parallel to (90°) the Cu-pyz planes, measured at a temperature of 20 K. Again the g -factor anisotropy is $g_z = 2.25$ and $g_{xy} = 2.04$. (d) The frequency-magnetic field scaling of the ESR line measured on single crystal $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ (No. 1) with the field oriented perpendicular to the planes.

VI. INTRALAYER MAGNETIC EXCHANGE ENERGIES

A. Pulsed magnetic field measurements

Figure 3 shows the magnetization of the four compounds measured in pulsed magnetic fields at temperatures close to 0.60 K. Pulsed-field data have been previously reported for Nos. 1, 2 [11], and 4 [46]. Apart from a low-field hump seen in No. 3, possibly due to a small concentration of paramagnetic impurities, the form of the low-temperature magnetization in all cases is very similar: a gradual concave rise to the

saturation field H_c . This general shape is typical of the $S = 1/2$ SLHAFM with finite interlayer couplings [11] as described by the Hamiltonian

$$\mathcal{H} = J \sum_{\langle i,j \rangle_{\parallel}} S_i \cdot S_j + J_{\perp} \sum_{\langle i,j \rangle_{\perp}} S_i \cdot S_j - g\mu_B B \sum_i S_i^z, \quad (4)$$

where J represents the strength of the effective nearest-neighbor exchange energy within the planes and J_{\perp} the magnetic coupling between the planes [11]. The first and second terms describe summations over unique pairs of nearest neighbors parallel and perpendicular to the planes, respectively, and the last term is the Zeeman energy associated with a uniform magnetic field $B = \mu_0 H$. In particular, previously reported quantum Monte Carlo simulations indicate that data such as those in Fig. 3 are characteristic of systems for which the spatial exchange anisotropy $J_{\perp}/J \ll 1$ and that the curvature of the magnetization increases as this ratio decreases [11]. This concave $M(H)$ curve is a result of the effect of quantum fluctuations on these low-spin systems, which act to reduce the moment at a particular field from its classical value. If the exchange anisotropy were to be reduced and/or the size of the spin quantum number increased the magnetization will approach its classical linear form [11]. In Ref. [11], the difference in saturation fields in single-crystal measurements along different crystallographic axes is attributed to the anisotropy of the g factor. This is also the case for the data shown in Figs. 3(a) and 3(b): saturation along different crystallographic directions in a particular material occurs at the same value of the Zeeman energy once the measured, anisotropic g values have been included. At the saturation field, Eq. (4) reduces to

$$g\mu_B B_c = nJ + n_{\perp}J_{\perp}, \quad (5)$$

where $B_c = \mu_0 H_c$, and for each $S = 1/2$ spin, n is the number of nearest neighbors within the planes and n_{\perp} is the number perpendicular to the planes.

For highly anisotropic, square-lattice systems, $n = 4$ and the final term is small enough to be neglected, allowing the size of the intralayer exchange energy to be deduced from a measurement of B_c . The saturation fields of three of the compounds shown in Fig. 3 are similar; 20.2(2) T (No. 1), 21.9(2) T (No. 2), and 21.1(2) T (No. 3). [Note these values in each case represent a polycrystalline average: $B_c = (B_c^z + 2B_c^{xy})/3$.] Using the above relation and the relevant g factors from the ESR experiments we find that $J = 7.2(2)$ K (No. 1), 7.7(2) K (No. 2), and 7.5(2) K (No. 3). These values are tabulated in Table III.

The size of J for No. 1 is comparable to that of $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]X$ with $X = \text{BF}_4$, but smaller by nearly a factor of two than the members of the same family with octahedral counterions $X = \text{PF}_6$, SbF_6 , and AsF_6 [11]. In contrast, changing the symmetry of the counterion in the $[\text{Cu}(\text{pyO})_2(\text{pyz})_2](X)_2$ family does not appear to have such a significant effect on the exchange energy: the $X = \text{PF}_6$ material has $J = 8.1(3)$ K [47], only slightly larger than found for No. 2.

The similarity in J between compounds Nos. 1, 2, and 3 is not unexpected, given their comparable copper-pyrazine square-lattice configurations. What is more surprising is that, as shown in Fig. 3(c), No. 4 requires the application of a

TABLE III. Magnetic parameters. The anisotropic g -factor is derived from frequency-dependent electron-spin-resonance measurements performed at 24 K (No. 1), 20 K (No. 2), 28 K (No. 3), and 19 K (No. 4). $\mu_0 H_c$ and J are, respectively, the powder-averaged saturation magnetic field and the effective nearest-neighbor exchange energy deduced from pulsed-field-magnetization measurements performed at 600 mK. The antiferromagnetic ordering temperature (T_c) is established via muon-spin relaxation studies. The T_c/J ratios are used to estimate the upper bounds of the interplane coupling (J_\perp) and spatial exchange anisotropy ($|J_\perp/J|$) in the Heisenberg model [48]. Dipole-field calculations are used to estimate the energy scale of the interplane dipolar interaction E_d^\perp for an ordered moment of $1\mu_B$. The anisotropy field $\mu_0 H_A$ is estimated from the position of kinks in the magnetization data at low temperatures. The spin-exchange anisotropy, Δ , is given by the ratio H_A/H_c and the anisotropy energy scale is parameterized by the product of J and Δ .

	g factor	$\mu_0 H_c$ (T)	J (K)	T_c (K)	T_c/J	$ J_\perp/J $	J_\perp (mK)	E_d^\perp (mK)	$\mu_0 H_A$ (T)	$\Delta \times J$ (mK)
(1) [Cu(HF ₂)(pyz) ₂](ClO ₄)	2.25(5) 2.07(3)	20.2(2)	7.2(2)	1.91(1)	0.27	2×10^{-3}	14	4.7	0.08	28
(2) [Cu(pyO) ₂ (pyz) ₂](ClO ₄) ₂	2.25(5) 2.04(3)	21.9(2)	7.7(2)	1.70(1)	0.22	3×10^{-4}	2	0.11	0.11	39
(3) [Cu(4-pphy-O) ₂ (pyz) ₂](ClO ₄) ₂	2.25(5) 2.04(3)	21.1(2)	7.5(2)	1.63(1)	0.22	3×10^{-4}	2	0.02	0.11	39
(4) Cu(pyz) ₂ (ClO ₄) ₂	2.25(5) 2.04(3)	51.1(2)	18.1(4)	4.21(1)	0.23	5×10^{-4}	9	2.6	0.28	100

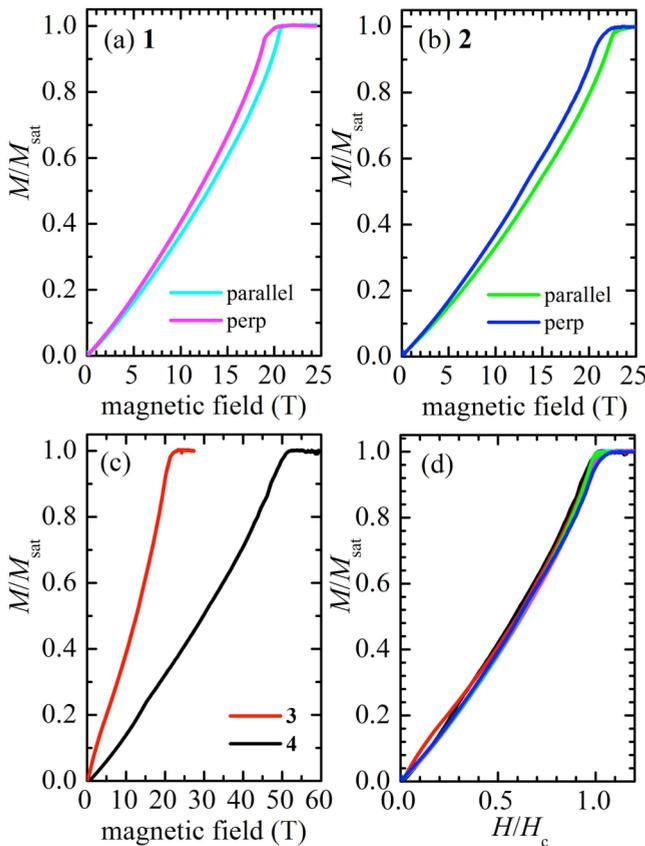


FIG. 3. Pulsed-field magnetization vs field. Data shown are recorded in increasing fields and at a temperature of 0.60 K. (a) and (b) show single-crystal data for [Cu(HF₂)(pyz)₂](ClO₄) (No. 1) and [Cu(pyO)₂(pyz)₂](ClO₄)₂ (No. 2), respectively, with the field applied parallel and perpendicular to the copper-pyrazine planes. (c) Polycrystalline data for [Cu(4-pphy-O)₂(pyz)₂](ClO₄)₂ (No. 3) and Cu(pyz)₂(ClO₄)₂ (No. 4). (d) All of the data vs H/H_c , where H_c is the saturation field.

much bigger field ($B_c = 51.1(2)$ T) to fully align the spins, yielding an effective exchange energy of $J = 18.1(4)$ K, which is in reasonable agreement with previous estimates [19,46]. The square-lattice network in No. 4 is not unlike those in the other compounds; why, then, should this exchange energy be so different? One major structural difference between No. 4 and the other materials considered here is that in the former the ClO₄ molecules are coordinated to the copper-ions rather than adopting noncoordinated positions centrally above the square copper-pyrazine plaquettes. Although the ClO₄ ligands in No. 4 do indeed sit in near-central locations on either side of the squares of the neighboring planes, this contrast in the way the molecule is bonded will likely lead to a difference in the distribution of electron density close to the layers for this compound as compared to the other three.

We recall again that the reduction in J observed on changing the counterion symmetry in the [Cu(HF₂)(pyz)₂] X family from octahedral to tetrahedral is accompanied by a change in the tilt angle of the pyrazines, which could also act to redistribute electron density. Pyrazine tilting has been correlated with changes in J in copper-pyrazine square-lattice materials on several occasions [11,14,24], but a causal relationship has not been established. However, in the context of the current paper, the x-ray measurements discussed above showed that the pyrazine tilt angles are similar for all four of the compounds that are the focus of this paper.

B. Density-functional-theory calculations

The nature of the super-exchange interactions in this class of material has been the subject of attention in the past, with early experimental and theoretical studies at odds as to the relevant importance of the σ orbitals [49] over the pyrazine π orbitals [24,50]. More recent theoretical studies have made use of density-functional theory (DFT) and, in particular, compound No. 4 has been investigated using first-principles calculations by Vela *et al.* [51]. According to their calculations a disparity of about 30% (21.0 K versus 29.6 K) is present at 15 K between the exchange strengths through

the two crystallographically distinct pyrazine molecules in this material [52]. By contrast, using the 165 K structure their calculations show only a very small difference in these exchange energies. Vela *et al.* [51] rule out the tilting of the pyrazines as a contributory factor in the low-temperature disparity and instead attribute it to a combination of three effects, which are, in increasing order of importance: (i) hydrogen bonding between the O atoms of the perchlorates and the H atoms of the pyrazines; (ii) a shearlike distortion of the pyrazine rings; and (iii) the orientation of the ClO_4^- ligands. The authors of Ref. [51] suggest that the role of ClO_4^- molecules is to increase the spin-density along the primary exchange pathway leading to an enhanced interaction strength. By extension, for the other samples considered here, where the ClO_4^- counterions occupy voids between the layers, this enhancement is not expected to occur, which could explain the large disparity in the in-plane exchange energies.

We have performed DFT studies on all four of the compounds using the low-temperature structures shown in Fig. 1. In each case, two distinct exchange strengths were identified along the Cu-pyrazine linkages within the unit cell. These are found to be 4.3 and 10.2 K (No. 1), 4.7 and 8.1 K (No. 2), 14.5 and 17.0 K (No. 3), and 22.8 and 21.3 K (No. 4). We note that the disparity in the two exchange strengths for No. 4 is smaller than that found in Ref. [51]. This is probably because the authors of that work used a 10 K, rather than a 100 K, structure; the disparity develops on cooling. If the predictions are correct it would imply that these materials correspond to a rectangular rather than a square-lattice model. It is not presently possible to experimentally verify such disparities in the exchange parameters from temperature-dependent magnetic susceptibility data owing a lack of analytical fitting expressions that can adequately discriminate between square and rectangular models of antiferromagnetism. We can, however, compare the theoretical results with the exchange energies listed in Table III, obtained by applying the SLHAFM model to the low-temperature pulsed-field magnetization measurements, by calculating an average or effective intralayer exchange strength from the DFT calculations. These are 7.3 K (No. 1), 6.4 K (No. 2), 15.8 K (No. 3), and 22.1 K (No. 4). The correspondence between experiment and calculation is good for Nos. 1 and 4, reasonable for No. 2, but poor for No. 3. The disappointing result for No. 3 may be a consequence of the difficulties of treating the $3d-4s$ mixing in the perchlorate ligand, which is a relatively poor donor [39].

C. Next nearest-neighbor interactions

Finally in this section, we point out that other exchange pathways in the Cu-pyz planes are also possible. A recent neutron-scattering study of No. 4 [53] analyzed the intralayer spin-wave spectrum in this material using the isotropic $J_1 - J_2$ model, which has two intralayer exchange terms in the Hamiltonian: $J_1 \sum S_i \cdot S_j + J_2 \sum S_i \cdot S_k$, where J_1 is nearest-neighbor exchange energy along the Cu-pyz-Cu exchange paths, J_2 is an additional next-nearest-neighbor exchange across the diagonal of the copper-pyrazine squares and the summations are over the unique spin pairs associated with these exchange pathways. If both J_1 and J_2 are antiferromagnetic, then they will act to frustrate one another and the

effective nearest-neighbor exchange energy of Eq. (4) will be given by $J = J_1 - J_2$. Theory predicts that if the J_2 is a significant fraction of J_1 the ground state of this model is no longer the simple Néel state, but transforms first into a disordered spin-liquid phase and, at higher values of J_2 , an ordered collinear state [9,10,54].

However, data described in the next section show that all the materials considered here exhibit a relatively simple phase diagram, with a low-temperature ordered phase. This is in accord with expectations that J_2 is small due to the lack of an effective exchange pathway across the diagonal. The authors of Ref. [53] estimated $J_2 \simeq 0.02J_1$ from their spin-wave data on No. 4. A later neutron spectroscopy study [55] expanded this analysis to conclude a small XY anisotropy in J_1 , which will be discussed in more detail later.

To summarize this section, the intralayer exchange energies in compounds Nos. 1–3 are probably chiefly determined by nearest-neighbor interactions via Cu-pyz-Cu exchange pathways, yielding a dominant $J \approx 7.5$ K in all cases. The almost identical values of the intralayer exchange energies in these three compounds is in accord with the earlier sections of the current paper, in which both the structure of the Cu-pyz planes and the local crystal-field environment of Cu are shown to be very similar in Nos. 1, 2, and 3.

VII. INTERACTIONS DETERMINING THE MAGNETIC ORDERING TEMPERATURES

A. Muon spin-rotation measurements

Reduced-dimensionality magnetic systems accommodate short-range spin correlations that begin to build up at temperatures higher than the transition temperature, affecting the thermodynamic properties of the system [43,56]. This leads to the observation of a broad maximum in both the magnetic susceptibility and the heat capacity at temperatures of the order of the primary exchange energy [11]. At lower temperatures additional interactions force the system into a state of long-range order, but the associated entropy change at the ordering temperature can be rather small, because the spins are already highly correlated. The result is that the feature by which the transition can be identified is often masked by the much larger hump resulting from the spin correlations [56]. Local probes, such as muon-spin rotation (μ^+ SR), do not suffer from the same drawbacks as thermodynamic techniques because they are sensitive to the static, internal magnetic field which only develops once three-dimensional long-range order sets in [11,57]. Thus μ^+ SR can be used to determine the critical temperature in highly anisotropic materials.

In a μ^+ SR experiment, spin-polarized positive muons are implanted in a target sample, where the muon usually occupies an interstitial position in the crystal [57]. In such an experiment, the time evolution of the muon-spin polarization is observed, the behavior 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 a determination of the spin-polarization of the ensemble of muons

as a function of time. Histograms $N_F(t)$ and $N_B(t)$ record the number of positrons detected in detectors placed forward (F) and backward (B) of the initial muon polarization direction. The quantity of interest is the positron-decay asymmetry function, defined as

$$A(t) = \frac{N_F(t) - \gamma N_B(t)}{N_F(t) + \gamma N_B(t)}, \quad (6)$$

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

Example spectra are shown in Fig. 4(a). Below a characteristic temperature, oscillations in the asymmetry are observed in all samples. This is because the local field causes a coherent precession of the spins of those muons for which a component of their spin polarization lies perpendicular to this local field [57]. Thus the observation of oscillations provides clear evidence for long-range magnetic order throughout the bulk of the sample.

For No. 2 at $T \leq 1.7$ K, the spectra were fitted to

$$\begin{aligned} A(t) = & A_1 e^{-\lambda_1 t} \cos(2\pi \nu_1 t + \phi_1) \\ & + A_2 e^{-\lambda_2 t} \cos(2\pi \nu_2 t + \phi_2) \\ & + A_3 e^{-\lambda_3 t} + A_b, \end{aligned} \quad (7)$$

where the first two terms account for muons whose spins precess coherently in a quasistatic magnetic field, the third term is due to muons that depolarize too rapidly for oscillations to be observed and the final term accounts for the muon-spin projection parallel to the local magnetic field and muons that stop in the sample holder or cryostat tail [57]. Nonzero phase angles ϕ_i were found to be necessary; they did not correlate with $\nu_i(T)$. During the fitting process we fixed $\phi_1 = -29^\circ$ and $\phi_2 = 40^\circ$. A zeroth-order Bessel function of the first kind (indicative of spin-density wave order [58]) was found to give a worse fit to the experimental spectra. The ratios A_1/A_2 and ν_2/ν_1 were fixed to 0.864 and 0.378, respectively. Close to the transition it was necessary to also fix $A_2 = 2.91\%$ (and thus $A_1 = 2.51\%$). The asymmetry spectra for No. 3 at $T \leq 1.6$ K were fitted to the same functional form but with $A_b = A_0 \exp(-\Gamma t)$ instead of a constant. The fits to the low-temperature spectra for No. 1 and No. 4 also use Eq. (7) (with the addition of a third precession frequency for No. 4) and have been previously described elsewhere [12,14].

The temperature dependences of the fitted precession frequencies are shown in Fig. 4(b). The oscillation frequencies represent an effective order parameter [57] and were fitted to the phenomenological expression $\nu(T) = \nu(0)[1 - (T/T_c)^\alpha]^\beta$, yielding the parameters listed in Table IV. The extracted values of the β critical parameter are typical of reduced-dimensionality magnetic interactions [14]. The critical temperatures are also tabulated in Table III, and are seen to decrease slowly across Nos. 1, 2, and 3 as the interlayer separation is increased. Compound No. 4 has a significantly higher T_c than Nos. 1–3, the reasons for which will be discussed below.

B. Interlayer exchange interactions

Ideal two-dimensional Heisenberg magnets do not exhibit long-range order at temperatures above zero Kelvin [6].

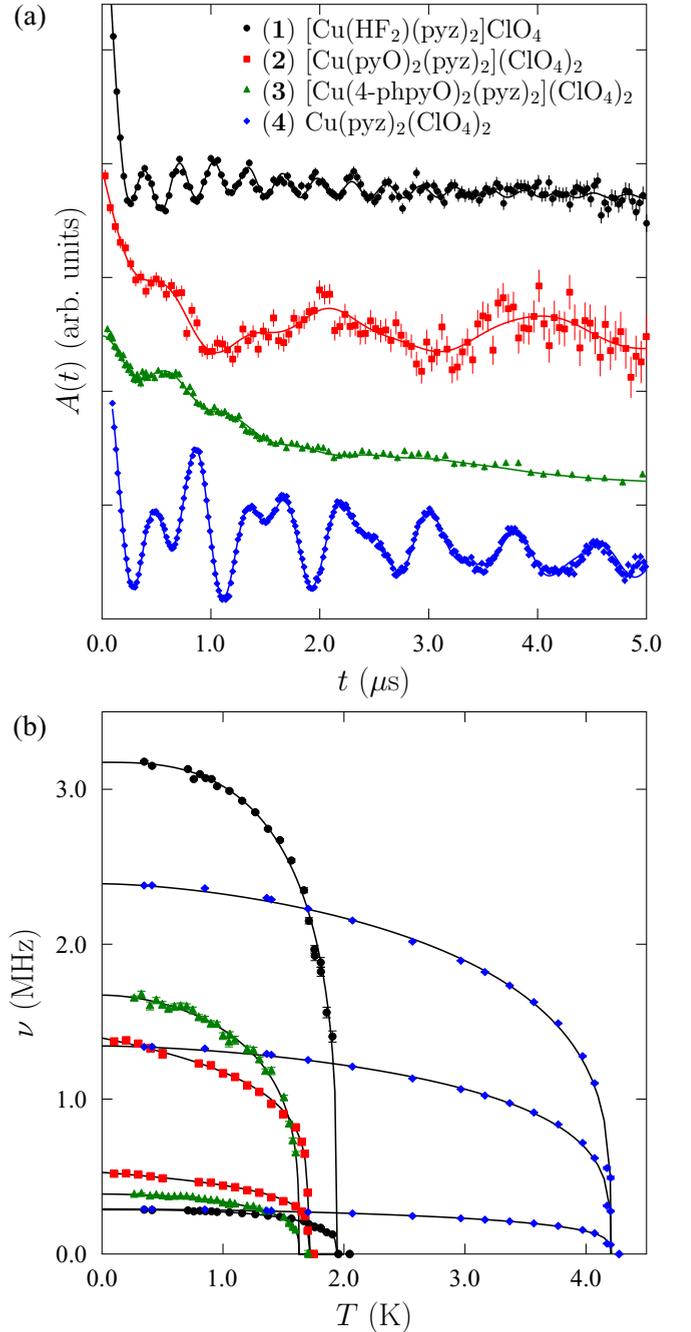


FIG. 4. (a) Muon asymmetry observed at 0.41 K (No. 1), 0.1 K (No. 2), 0.26 K (No. 3), and 0.34 K (No. 4); points are data, while lines represent the fits described in the text. The data for No. 1 and No. 4 are taken from Refs. [14] and [12]. (b) Temperature evolution of the oscillation frequencies ν . The solid lines are fits to the functional form $\nu_i(T) = \nu_i(0)[1 - (T/T_c)^\alpha]^\beta$ as described in the text.

Real systems, however, have additional interactions that act to promote magnetic ordering. In particular, for the quasi-two-dimensional model described by Eq. (4), a finite spatial exchange anisotropy ($|J_\perp/J|$) enhances T_c according to the empirically-derived relation [48]

$$T_c/J = 2.30/(2.43 - \ln |J_\perp/J|), \quad (8)$$

TABLE IV. Parameters extracted from fits to the muon-precession frequencies shown in Figure 4(b) for (No. 1) $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, (No. 2) $[\text{Cu}(\text{pyO})_2(\text{pyz})_2](\text{ClO}_4)_2$, (No. 3) $[\text{Cu}(4\text{-phpyO})_2(\text{pyz})_2](\text{ClO}_4)_2$, and (No. 4) $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$. The parameters for (No. 1) and (No. 4) are taken from Refs. [14] and [12].

	$\nu_1(0)$ (MHz)	$\nu_2(0)$ (MHz)	$\nu_3(0)$ (MHz)	α	β	T_c (K)
(1)	3.2(1)	6.4(1)	–	2.6(3)	0.25(2)	1.91(1)
(2)	1.39(1)	0.53(1)	–	0.8(2)	0.18(1)	1.70(1)
(3)	1.67(2)	0.39(1)	–	1.8(2)	0.27(2)	1.63(1)
(4)	2.38(3)	1.33(2)	0.29(2)	1.8(3)	0.28(2)	4.21(1)

which has been shown to be valid in the absence of strong quantum-critical fluctuations [59,60]. The T_c/J ratios for the compounds considered here are shown in Table III and are seen to be similar across the family, but with compound No. 1 having a slightly higher value than the others. Also shown are the estimates of $|J_\perp/J|$ and $|J_\perp|$ obtained by applying the above formula. According to this calculation all four compounds can be considered to be highly two-dimensional with spatial-exchange anisotropies $\leq 10^{-3}$ (although it should be noted that this requires extrapolation of Eq. (8) somewhat beyond the range for which it was originally derived [48]). By this estimate Nos. 2 and 3 are among the closest approximations to an ideal SLHAFM of any copper-pyrazine system realized so far, having a spatial exchange ratio (0.03%) slightly lower than that of the related compound $[\text{Cu}(2\text{-pyridone})_2(\text{pyz})_2](\text{ClO}_4)_2$ (0.05%) [15], but not as low as the inorganic SLHAFM $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (0.003%) [12], or the $S = 1/2$ coordination polymer $\text{Ag}(\text{pyz})_2(\text{S}_2\text{O}_8)$ (0.0002%) [13].

The estimated interlayer couplings are similar for Nos. 1 and 4, which have comparable interlayer spacings (see Table II); this implies that the difference in ordering temperatures in these two materials arises predominantly from the variation in their intralayer exchange strength described in the previous section.

As the layer separation increases by a factor ≈ 2.5 between compounds Nos. 1 and 3, there is an accompanying sevenfold reduction in the interlayer coupling strength. If we naively attribute the drop in interlayer coupling to a power-law dependence on interlayer separation ($J_\perp \propto R^{-p}$), we find that the exponent $p \simeq 2.1$. In several systems, superexchange energies have empirically been found to vary with interionic spacing with the exponent $p \approx 10$ (see, e.g., [61–63]), a result which has been interpreted to be a consequence of the role of σ bonding in the superexchange process in these materials [64]. Magnetic exchange is contingent on the degree of overlap between neighboring electronic orbitals and its spatial variation will depend upon the nature of the exchange pathways. Unlike the Cu compounds that are the subject of this paper, none of the materials described in Refs. [61–63] involve exchange mediated through aromatic molecules. Therefore the exchange interactions may not necessarily be expected to have the same distance dependence. Nevertheless, as the exponent $p \approx 2.1$ for compounds Nos. 1–3 is much less than that expected for superexchange ($p \approx 10$; see above), in the following section, we consider other types of interaction that might be present and that could drive magnetic order.

The interlayer exchange energies in Table III were derived using the Hamiltonian in Eq. (4). Since, as discussed below, other interactions may contribute to the magnetic order, the

values of the spatial exchange anisotropy quoted in Table III should be considered as upper bounds.

C. Dipolar interactions

Given the small energy scales in these molecular systems, it is important to assess to what extent symmetry-breaking dipolar interactions contribute to the magnetic anisotropy and the propensity of the system to undergo magnetic ordering. This issue provoked early theoretical attention by Luttinger and Tisza [65] as well as more recent experimental work in a rare-earth system [66]. In principle, long-range order in quasi-2D Heisenberg antiferromagnets can be brought about by the dipolar couplings between the layers. The dipole interaction has a R^{-3} distance dependence [67–69], which is similar to the estimate determined above by comparing the upper bounds of the interlayer exchange couplings in Nos. 1 and 3.

We have performed dipole-field calculations given a certain assumed collinear antiferromagnetic structure inspired by the structure suggested for No. 4 on the basis of neutron-diffraction experiments [55]. The calculations leave the direction of each individual moment variable, and hence allow the dipolar anisotropy to be determined for the assumed magnetic structure; results are shown in Table III. The interlayer dipolar coupling E_d^\perp decreases rapidly with interlayer separation and is largest for No. 1. For Nos. 1 and 4, E_d^\perp is found to be similar to the magnitude of interlayer coupling necessary to account for the measured T_c/J ratio, suggesting that dipolar interactions could play a significant role in driving the magnetic ordering in these compounds.

We point out that our dipolar calculations assume an ordered moment size of $1\mu_B$. Quantum fluctuations are expected to reduce the moment in reduced-dimensionality magnets and an ordered moment of $0.62\mu_B$ is expected for the ideal 2D SLHAFM at zero temperature [5]. In such circumstances, the quoted energy scales of the dipolar interactions must hence be reduced by a factor of up to 0.38. However, the ordered moment of $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ has been measured to be as low as $0.47(5)\mu_B$ (see Ref. [53]), so the dipolar interactions could potentially be reduced even further.

D. Spin-exchange anisotropy

The preceding analyses attribute the finite value of T_c entirely to some kind of coupling between the copper-pyrazine planes. However, it has been suggested that the magnetic order in these types of material could be driven by a combination of interlayer coupling and spin-exchange anisotropy within the layers (a departure from a Heisenberg-type interactions) [70].

The g -factor anisotropy determined above shows that the spin-orbit coupling that gives rise to spin-exchange anisotropy is present in the materials considered here. The Hamiltonian relevant to these systems is consequently amended to

$$\mathcal{H} = J_1 \sum_{\langle i,j \rangle_{\parallel}} [S_i^x S_j^x + S_i^y S_j^y + (1 - \Delta) S_i^z S_j^z] \\ + J_2 \sum_{\langle i,k \rangle_{\parallel}} S_i \cdot S_k + J_{\perp} \sum_{\langle i,j \rangle_{\perp}} S_i \cdot S_j - g\mu_B B \sum_i S_i^z, \quad (9)$$

where we have included both nearest-neighbor (J_1) and next-nearest-neighbor (J_2) intralayer interactions, as well as the interlayer coupling (J_{\perp}). Δ is the spin-exchange anisotropy parameter and is expected to be small and positive (XY -like) for quasi-two-dimensional $S = 1/2$ systems. Ignoring the J_2 and J_{\perp} terms, quantum Monte Carlo simulations predict a Berezinskii-Kosterlitz-Thouless-type transition to three-dimensional magnetic order driven by even very small levels of spin-exchange anisotropy [8,71] and obtain T_c/J ratios similar to those measured here arising from $\Delta \sim 10^{-2}$. Reference [70], again neglecting any effects of J_2 , found evidence for spin-exchange anisotropy in low-field magnetization and low-temperature magnetic susceptibility measurements of several quasi-two-dimensional copper-pyrazine polymeric magnets, including compound No. 4. The observation of a change in slope, or kink, in $M(H)$ obtained with the field applied parallel to the planes allowed the authors to conclude $\Delta = 5 \times 10^{-3}$ for No. 4 [72]. Using neutron-spectroscopy measurements on the aforementioned compound, some of the same authors later determined values of $J_2 \simeq 0.02J_1 = 0.4$ K and $\Delta = 2 \times 10^{-3}$ [55]. ESR [74] and heat capacity [16] data were used to estimate $\Delta = 3 \times 10^{-3}$ and 7×10^{-3} for the PF_6^- counterion analogues of Nos. 1 and 2, respectively.

Low-field magnetization data taken using polycrystalline samples of Nos. 1, 2, and 3 are shown in Figs. 5(a)–5(c). These experiments were performed at 500 mK so that the sample is in the magnetically ordered state. Figure 5(d) shows similar data for No. 4 at 1.8 K taken from [70]. In this case, a single crystal was used and the magnetic field aligned both parallel and perpendicular to the Cu–pyz planes. The kink in $M(H)$ arising from the spin-exchange anisotropy is clearly observed with the parallel-field orientation. This kink occurs when the applied in-plane field is increased above the anisotropy field, H_A [70]. At this point the moments can begin to rotate out of the easy plane, leading to an enhancement in the dynamic susceptibility and hence a kink in the magnetization [70]. The equivalent feature in the data for the polycrystalline samples is reduced in clarity by comparison; nevertheless, a change in slope is apparent for all compounds. The fields at which this kink appears, the anisotropy fields $\mu_0 H_A$, are determined from the position of the large peak in d^2M/dH^2 and are found to be 0.08 T (No. 1), 0.11 T (No. 2), and 0.11 T (No. 3). Δ can be found by taking the ratio of H_A and H_c [70] and is found to be similar in magnitude ($\sim 10^{-3}$) for all members of the family. The size of the energy scale associated with this anisotropy is estimated from the product of J and Δ and these values are tabulated in Table III.

If we assume that the polycrystalline compounds also exhibit an XY -type anisotropy, we can determine the effect this has on the magnetic ordering temperature. Figure 5(e)

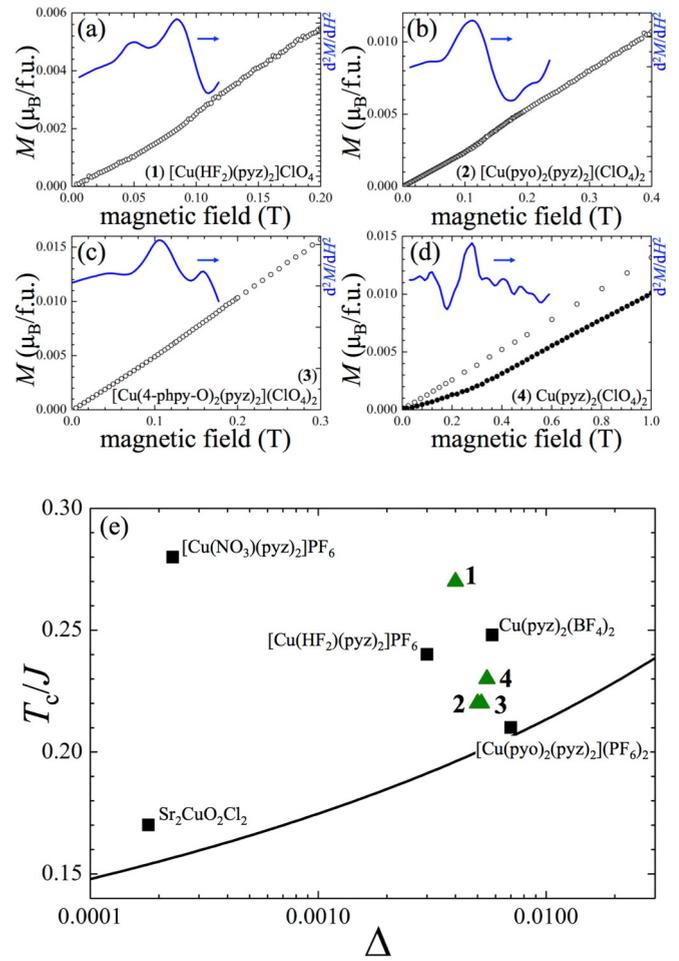


FIG. 5. (a)–(d) Low-field magnetization data (points) for polycrystalline samples for Nos. 1, 2, and 3 taken at 500 mK and a single crystal of compound No. 4. For the latter data, taken from Ref. [70], the magnetic field was applied both parallel (solid circles) and perpendicular (open circles) to the copper-pyrazine planes. The anisotropy fields, H_A , are determined by the peaks in d^2M/dH^2 (solid line). (e) Experimentally determined values of T_c/J and the XY -type spin-exchange anisotropy, $\Delta = H_A/H_c$, for the compounds mentioned in the text (points). Also shown is the theoretical relation (line) determined via quantum Monte Carlo simulations [8].

plots the experimental values of T_c/J against Δ for the four compounds, as well as some other quasi-2D copper-based antiferromagnets. Also shown is the function

$$T_c/J = \frac{2.22}{\ln(330/\Delta)}, \quad (10)$$

which is empirically determined via quantum Monte Carlo calculations [8] and relates the ordering temperature to Δ , assuming that the nearest-neighbor, anisotropic intralayer exchange is the only term in the Hamiltonian [i.e., neglecting J_2 and J_{\perp} in Eq. (9)]. Following Ref. [70], we expect that if an experimental point lies on this line then the ordering temperature can be entirely accounted for by the magnitude of Δ . If, however, the point lies significantly above the theoretical curve, then the long-range ordering is being assisted by another process, such as interlayer coupling. As can be seen, the

experimentally-derived data point for No. 1, which has the shortest interlayer distance of our four materials, lies some way from the theoretical line, while No. 4, with a slightly larger interlayer separation, is much closer. The points for compounds Nos. 2 and 3, with their bulky axial ligands and therefore large separation between planes, lie close together, not far from the theoretical curve. This implies that interlayer coupling appears to become less important in determining the ordering temperature as the copper-pyrazine layers are forced apart.

We can compare our results with those from related materials. As has been mentioned, $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{PF}_6$ has a higher J , T_c , and Δ than $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ (No. 1). As a consequence the data point for this material lies closer to the theoretical prediction in Fig. 5(e) than does compound No. 1. The measured interlayer separation in the PF_6 material is 6.785 Å at 15 K, which is slightly larger than the equivalent distance of 6.594 Å measured in No. 1 at 50 K. Also shown in the graph are the points for $[\text{Cu}(\text{pyO})_2(\text{pyz})_2](\text{PF}_6)_2$ and $\text{Cu}(\text{pyz})_2(\text{BF}_4)_2$ [16,70], but as the structures of these compounds are not known at 100 K or below, a comparison with our materials is difficult. The data point for the former material lies right on the theoretical curve. Its interlayer separation at room temperature is known to be 13.189 Å, compared with 12.471 Å at the same temperature for No. 2, thus reinforcing the trend. However, at low temperatures this separation will certainly not be as big as that for No. 3 with the large 4-phpy-O ligands, suggesting that factors beyond just the interlayer separation are important for understanding how the different interactions determine the magnetic ordering temperature.

New theoretical models will have to be developed in order to achieve an independent estimate of both Δ and J_\perp from the Hamiltonian in Eq. (9). Nevertheless, Fig. 5(e) implies that the magnetic order observed in compounds Nos. 2 and 3 is predominantly driven by the spin-exchange anisotropy. In contrast, in order to account for the transition temperature of compound No. 1, Δ would have to be at least an order of magnitude larger than is measured. Therefore interlayer couplings, probably including dipolar interactions, must play an important role in stabilising the ordered state of this material.

VIII. CONCLUDING REMARKS

We have engineered a family of molecular materials $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ (No. 1), $[\text{Cu}L_2(\text{pyz})_2](\text{ClO}_4)_2$ [$L = \text{pyO}$ (No. 2), and 4-phpy-O (No. 3)] that exhibit highly-2D antiferromagnetism. By changing the axial ligands we have shown that it is possible to vary considerably the interlayer spacings in these materials while at the same time retaining the copper-pyrazine nearly-square-lattice motif to a very good precision. By developing a consistent ESR measurement procedure in conjunction with pulsed-field magnetometry, we have shown that the ligand substitution has only a small effect on the single-ion properties or the magnitude of effective nearest-neighbor exchange interactions within the 2D layers. Long-range magnetic order is observed in all members of the family and the ordering temperatures are found to decrease relatively slowly with increasing interlayer separation, varying at a rate of ~ 10 mK/Å. This slow variation implies

that other mechanisms in addition to or besides interlayer superexchange drive the ordering transition. By determining the anisotropy fields in these materials we conclude that a combination of spin-exchange anisotropy and interlayer coupling (superexchange and/or dipolar interactions) gives rise to the observed transition temperatures in these materials. In particular, the small spin-exchange anisotropy in the intralayer exchange interaction becomes increasingly more dominant in determining the long-range ordering temperature as the layer spacing increases.

$\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ (No. 4) is a well-known molecular antiferromagnet, and has similar copper-pyrazine planes to our family of compounds. Nevertheless, the intralayer exchange energy J , and (hence) the magnetic ordering temperature, are significantly higher for this material, reminiscent of the larger values of J found in some members of the $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]X$ family of polymers. To fully determine how this difference arises, as well as to ascertain in more general terms the means by which exchange is mediated through pyrazine and other molecular ligands, considerable further work (e.g., density functional theory, neutron scattering, spin density mapping) will be required.

Our results imply that characterising the mechanism of the in-plane symmetry breaking in real examples of highly two-dimensional $S = 1/2$ antiferromagnets is necessary to achieve a complete understanding of their phase diagram and particularly the precise nature of the ordered phases observed at very low temperatures (e.g., Néel, Berezinsky-Kosterlitz-Thouless, or 3D XY). It is becoming increasingly clear that similar considerations regarding in-plane symmetry are probably vital for explaining the high-temperature superconductivity observed in underdoped cuprates (see Ref. [75] and references therein), whose parent phase is also a quasi-two-dimensional $S = 1/2$ square-lattice antiferromagnet. In addition, our data provide guidelines for future attempts to create extremely two-dimensional quantum magnets with highly suppressed ordering temperatures, thereby engineering a magnetic system in close proximity to a quantum critical point in the temperature-coupling phase diagram. Clearly, it is not sufficient to curb the interlayer coupling alone; even in $S = 1/2$ systems efforts must be taken to suppress any intralayer magnetic anisotropy. We point out that for the related material $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{SbF}_6$ it was not possible to detect any spin-exchange anisotropy using either magnetometry or neutron diffraction down to the lowest temperature measured [76], suggesting that the observed transition to long-range order is driven predominantly by interlayer coupling. That material, unlike the systems considered here, has tetragonal structural symmetry in the ordered phase, and it is probable that the magnetic anisotropy we observe in our materials is linked to their reduced structural symmetry. Whether it is possible to produce a molecule-based material with tetragonal symmetry at low temperatures and a large interlayer spacing is the subject of continuing research.

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- [1] M. Lines, *J. Phys. Chem. Solids* **31**, 101 (1970).
- [2] S. Chakravarty, B. I. Halperin, and D. R. Nelson, *Phys. Rev. Lett.* **60**, 1057 (1988).
- [3] S. Chakravarty, B. I. Halperin, and D. R. Nelson, *Phys. Rev. B* **39**, 2344 (1989).
- [4] S. Tyc, B. I. Halperin, and S. Chakravarty, *Phys. Rev. Lett.* **62**, 835 (1989).
- [5] E. Manousakis, *Rev. Mod. Phys.* **63**, 1 (1991).
- [6] N. D. Mermin and H. Wagner, *Phys. Rev. Lett.* **17**, 1133 (1966).
- [7] O. F. Syljuasen and P. A. Lee, *Phys. Rev. Lett.* **88**, 207207 (2002).
- [8] A. Cuccoli, T. Roscilde, V. Tognetti, R. Vaia, and P. Verrucchi, *Phys. Rev. B* **67**, 104414 (2003).
- [9] P. Chandra and B. Doucot, *Phys. Rev. B* **38**, 9335 (1988).
- [10] O. P. Sushkov, J. Oitmaa, and Z. Weihong, *Phys. Rev. B* **63**, 104420 (2001).
- [11] P. A. Goddard, J. Singleton, P. Sengupta, R. D. McDonald, T. Lancaster, S. J. Blundell, F. L. Pratt, S. Cox, N. Harrison, J. L. Manson, H. I. Southerland, and J. A. Schlueter, *New J. Phys.* **10**, 083025 (2008).
- [12] T. Lancaster, S. J. Blundell, M. L. Brooks, P. J. Baker, F. L. Pratt, J. L. Manson, M. M. Conner, F. Xiao, C. P. Landee, F. A. Chaves, S. Soriano, M. A. Novak, T. P. Papageorgiou, A. D. Bianchi, T. Herrmannsdörfer, J. Wosnitzer, and J. A. Schlueter, *Phys. Rev. B* **75**, 094421 (2007).
- [13] J. L. Manson, K. H. Stone, H. I. Southerland, T. Lancaster, A. J. Steele, S. J. Blundell, F. L. Pratt, P. J. Baker, R. D. McDonald, P. Sengupta, J. Singleton, P. A. Goddard, C. Lee, M.-H. Whangbo, M. M. Warter, C. H. Mielke, and P. W. Stephens, *J. Am. Chem. Soc.* **131**, 4590 (2009).
- [14] A. J. Steele, T. Lancaster, S. J. Blundell, P. J. Baker, F. L. Pratt, C. Baines, M. M. Conner, H. I. Southerland, J. L. Manson, and J. A. Schlueter, *Phys. Rev. B* **84**, 064412 (2011).
- [15] V. Selmani, C. P. Landee, M. M. Turnbull, J. L. Wikaira, and F. Xiao, *Inorg. Chem. Commun.* **13**, 1399 (2010).
- [16] Y. Kohama, M. Jaime, O. E. Ayala-Valenzuela, R. D. McDonald, E. D. Mun, J. F. Corbey, and J. L. Manson, *Phys. Rev. B* **84**, 184402 (2011).
- [17] N. A. Fortune, S. T. Hannahs, C. P. Landee, M. M. Turnbull, and F. Xiao, *J. Phys. Conf. Ser.* **568**, 042004 (2014).
- [18] P. A. Goddard, J. Singleton, C. Maitland, S. J. Blundell, T. Lancaster, P. J. Baker, R. D. McDonald, S. Cox, P. Sengupta, J. L. Manson, K. A. Funk, and J. A. Schlueter, *Phys. Rev. B* **78**, 052408 (2008).
- [19] F. M. Woodward, P. J. Gibson, G. B. Jameson, C. P. Landee, M. M. Turnbull, and R. D. Willett, *Inorg. Chem.* **46**, 4256 (2007).
- [20] R. T. Butcher, C. P. Landee, M. M. Turnbull, and F. Xiao, *Inorganica Chimica Acta* **361**, 3654 (2008).
- [21] S. H. Lapidus, J. L. Manson, J. Liu, M. J. Smith, P. Goddard, J. Bendix, C. V. Topping, J. Singleton, C. Dunmars, J. F. Mitchell, and J. A. Schlueter, *Chem. Commun.* **49**, 3558 (2013).
- [22] G. J. Halder, K. W. Chapman, J. A. Schlueter, and J. L. Manson, *Angewandte Chemie International Edition* **50**, 419 (2011).
- [23] S. Ghannadzadeh, J. S. Moller, P. A. Goddard, T. Lancaster, F. Xiao, S. J. Blundell, A. Maisuradze, R. Khasanov, J. L. Manson, S. W. Tozer, D. Graf, and J. A. Schlueter, *Phys. Rev. B* **87**, 241102 (2013).
- [24] J. Darriet, M. S. Haddad, E. N. Duesler, and D. N. Hendrickson, *Inorg. Chem.* **18**, 2679 (1979).
- [25] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, 2002.
- [26] SAINTPLUS: v. 6.45a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, 2001.
- [27] SADABS: v.1.05, an empirical absorption correction program, Sheldrick, G. M., Bruker AXS Inc., Madison, WI, 2002.
- [28] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G. M., Bruker AXS Inc., Madison, WI, 2003.
- [29] J. M. Schrama, J. Singleton, R. S. Edwards, A. Ardavan, E. Rzepniewski, R. Harris, P. Goy, M. Gross, J. Schlueter, M. Kurmoo, and P. Day, *J. Phys.: Condens. Matter* **13**, 2235 (2001).
- [30] L. J. Noodleman, *J. Chem. Phys.* **74**, 5737 (1981).
- [31] F. Neese, ORCA Version 2.8, revision 2131 (2010) <https://orcaforum.cec.mpg.de/>.
- [32] F. Neese, *Coord. Chem. Rev.* **253**, 526 (2009).
- [33] S. Sinnecker, F. Neese, and W. Lubitz, *J. Biol. Inorg. Chem.* **10**, 231 (2005).
- [34] K. Yamaguchi, Y. Takahara, and T. Fueno, *Applied Quantum Chemistry*, edited by V. H. Smith, F. Schafer III, and K. Morokuma (D. Reidel: Boston, MA, 1986), p. 155.
- [35] T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka, and K. Yamaguchi, *Chem. Phys. Lett.* **319**, 223 (2000).
- [36] J. L. Manson, S. H. Lapidus, P. W. Stephens, P. K. Peterson, K. E. Carreiro, H. I. Southerland, T. Lancaster, S. J. Blundell, A. J. Steele, P. A. Goddard, F. L. Pratt, J. Singleton, Y. Kohama, R. D. McDonald, R. E. Del Sesto, N. A. Smith, J. Bendix, S. A. Zvyagin, J. H. Kang, C. Lee, M. H. Whangbo, V. S. Zapf, and A. Plonczak, *Inorg. Chem.* **50**, 5990 (2011).
- [37] A. Schaefer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.* **97**, 2571 (1992).
- [38] The Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk); CCDC reference codes: 683413, 1456465-1456470.
- [39] Jean-Pierre Launay and Michel Verdaguer, *Electrons in Molecules* (Oxford University Press, Oxford, 2014)

- [40] T. Lancaster, P. A. Goddard, S. J. Blundell, F. R. Foronda, S. Ghannadzadeh, J. S. Möller, P. J. Baker, F. L. Pratt, C. Baines, L. Huang, J. Wosnitzer, R. D. McDonald, K. A. Modic, J. Singleton, C. V. Topping, T. A. W. Beale, F. Xiao, J. A. Schlueter, A. M. Barton, R. D. Cabrera, K. E. Carreiro, H. E. Tran, and J. L. Manson, *Phys. Rev. Lett.* **112**, 207201 (2014)
- [41] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, Oxford, 2013).
- [42] E. A. Turov, *Physical Properties of Magnetically Ordered Crystals* (Academic Press, 1965).
- [43] T. Knafflic, M. Klanjsek, A. Sans, P. Adler, M. Jansen, C. Felser, and D. Arcon, *Phys. Rev. B* **91**, 174419 (2015).
- [44] *Novel NMR and EPR Techniques*, edited by J. Dolinsek, M. Vilfan, and S. Zumer, Lecture Notes in Physics Vol. 684 (Springer, Berlin, 2006).
- [45] Note that previous reports of the g factors for some of these materials have often been derived from measurements at only one frequency, and/or at temperatures very close to T_c , resulting in slight discrepancies with the values given in the present work (cf. Refs. [11,24]).
- [46] M. M. Turnbull, A. S. Albrecht, G. B. Jameson, and C. P. Landee, *Mol. Cryst. and Liq. Cryst.* **335**, 245 (1999).
- [47] P. A. Goddard, J. L. Manson, J. Singleton, I. Franke, T. Lancaster, A. J. Steele, S. J. Blundell, C. Baines, F. L. Pratt, R. D. McDonald, O. E. Ayala-Valenzuela, J. F. Corbey, H. I. Southerland, P. Sengupta, and J. A. Schlueter, *Phys. Rev. Lett.* **108**, 077208 (2012).
- [48] C. Yasuda, S. Todo, K. Hukushima, F. Alet, M. Keller, M. Troyer, and H. Takayama, *Phys. Rev. Lett.* **94**, 217201 (2005).
- [49] F. Mohri, K. Yoshizawa, T. Yambe, T. Ishida, and T. Nogami, *Mol. Eng.* **8**, 357 (1999).
- [50] H. W. Richardson, J. R. Wasson, and W. E. Hatfield, *Inorg. Chem.* **16**, 484 (1977).
- [51] S. Vela, J. Jornet-Somoza, M. M. Turnbull, R. Feyerherm, J. J. Novoa, and M. Deumal, *Inorg. Chem.* **52**, 12923 (2013).
- [52] Note the definition of J used in Ref. [51] differs by a factor of 2 from the one employed in this paper.
- [53] N. Tsyrlin, T. Pardini, R. R. P. Singh, F. Xiao, P. Link, A. Schneidewind, A. Hiess, C. P. Landee, M. M. Turnbull, and M. Kenzelmann, *Phys. Rev. Lett.* **102**, 197201 (2009).
- [54] J. R. Viana and J. R. de Sousa, *Phys. Rev. B* **75**, 052403 (2007).
- [55] N. Tsyrlin, F. Xiao, A. Schneidewind, P. Link, H. M. Ronnow, J. Gavilano, C. P. Landee, M. M. Turnbull, and M. Kenzelmann, *Phys. Rev. B* **81**, 134409 (2010).
- [56] P. Sengupta, A. W. Sandvik, and R. R. P. Singh, *Phys. Rev. B* **68**, 094423 (2003).
- [57] S. J. Blundell, *Contemp. Phys.* **40**, 175 (1999).
- [58] L. P. Le, A. Keren, G. M. Luke, B. J. Sternlieb, W. D. Wu, Y. J. Uemura, J. H. Brewer, T. M. Riseman, R. V. Upasani, L. Y. Chiang, W. Kang, P. M. Chaikin, T. Csiba, and G. Grüner, *Phys. Rev. B* **48**, 7284 (1993).
- [59] M. B. Hastings and C. Mudry, *Phys. Rev. Lett.* **96**, 027215 (2006).
- [60] A. Praz, C. Mudry, and M. B. Hastings, *Phys. Rev. B* **74**, 184407 (2006).
- [61] D. Bloch, *J. Phys. Chem. Solids* **27**, 881 (1966).
- [62] M. T. Hutchings, R. J. Birgeneau, and W. P. Wolf, *Phys. Rev.* **168**, 1026 (1968).
- [63] R. N. Rogers, L. Finegol, and B. Morosin, *Phys. Rev. B* **6**, 1058 (1972).
- [64] K. C. Johnson and A. J. Sievers, *Phys. Rev. B* **10**, 1027 (1974).
- [65] J. M. Luttinger and L. Tisza, *Phys. Rev.* **70**, 954 (1946).
- [66] C. Kraemer, N. Nikseresht, J. O. Piatek, N. Tsyrlin, B. D. Piazza, K. Kiefer, B. Klemke, T. F. Rosenbaum, G. Aeppli, C. Gannarelli, K. Prokes, A. Podlesnyak, T. Stresle, L. Keller, O. Zaharko, K. W. Kramer, and H. M. Ronnow, *Science* **336**, 1416 (2012).
- [67] S. Kotler, N. Akerman, N. Navon, Y. Glickmann, and R. Ozeri, *Nature (London)* **510**, 376 (2014).
- [68] Kurmoo [69] has shown that dipole interactions are responsible for the ordering in the family of quasi-2D materials based on cobalt hydroxide layers, which have interlayer separations as large as 22.8 Å. In those materials, the intralayer exchange interactions are ferrimagnetic in nature and so the onset of short-range order causes a significant moment to develop within the layers, thus enhancing the effectiveness of the dipolar coupling.
- [69] M. Kurmoo, *Chem. Mater.* **11**, 3370 (1999).
- [70] F. Xiao, F. M. Woodward, C. P. Landee, M. M. Turnbull, C. Mielke, N. Harrison, T. Lancaster, S. J. Blundell, P. J. Baker, P. Babkevich, and F. L. Pratt, *Phys. Rev. B* **79**, 134412 (2009).
- [71] H.-Q. Ding, *Phys. Rev. Lett.* **68**, 1927 (1992).
- [72] A later ESR study provided evidence for a further, smaller anisotropy within the xy plane in compound No. 4 [73].
- [73] K. Yu. Povarov, A. I. Smirnov and C. P. Landee, *Phys. Rev. B* **87**, 214402 (2013).
- [74] E. Cizmar, S. A. Zvyagin, R. Beyer, M. Uhlarz, M. Ozerov, Y. Skourski, J. L. Manson, J. A. Schlueter, and J. Wosnitzer, *Phys. Rev. B* **81**, 064422 (2010).
- [75] B. J. Ramshaw, S. E. Sebastian, R. D. McDonald, James Day, B. S. Tan, Z. Zhu, J. B. Betts, Ruixing Liang, D. A. Bonn, W. N. Hardy, and N. Harrison, *Science* **348**, 317 (2015).
- [76] J. Brambleby, P. A. Goddard, R. D. Johnson, J. Liu, D. Kaminski, A. Ardavan, A. J. Steele, S. J. Blundell, T. Lancaster, P. Manuel, P. J. Baker, J. Singleton, S. G. Schwalbe, P. M. Spurgeon, H. E. Tran, P. K. Peterson, J. F. Corbey, and J. L. Manson, *Phys. Rev. B* **92**, 134406 (2015).