Quasi-two-dimensional $S = 1/2$ magnetism of Cu\([\text{C}_6\text{H}_2(\text{COO})_4]\)[\text{C}_2\text{H}_5\text{NH}_3]_2

R. Nath,¹ M. Padmanabhan,² ³ S. Baby,³ A. Thirumurugan,⁴ and A. A. Tsirlin⁵

¹School of Physics, Indian Institute of Science Education and Research Thiruvananthapuram-695016, Kerala, India
²School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram-695016, Kerala, India
³School of Chemical Sciences, Mahatma Gandhi University Kottayam-686560, Kerala, India
⁴School of Chemistry, Indian Institute of Science Education and Research, Thiruvananthapuram-695016, India
⁵National Institute of Chemical Physics and Biophysics, 12618 Tallinn, Estonia

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We report structural and magnetic properties of the spin-\(\frac{1}{2}\) quantum magnet Cu\([\text{C}_6\text{H}_2(\text{COO})_4]\)[\text{C}_2\text{H}_5\text{NH}_3]_2 by means of single-crystal x-ray diffraction, magnetization and heat capacity measurements on polycrystalline samples, as well as band-structure calculations. The triclinic crystal structure of this compound features CuO\(~4\) plaquette units connected into a two-dimensional framework through anions of the pyromellitic acid \([\text{C}_6\text{H}_2(\text{COO})_4]\)^\text{2+}. The ethylamine cations \([\text{C}_2\text{H}_5\text{NH}_3]^+\) are located between the layers and act as spacers. Magnetic susceptibility and heat capacity measurements establish a quasi-two-dimensional, weakly anisotropic and non-frustrated spin-\(\frac{1}{2}\) square lattice with the ratio of the couplings \(J_a/J_c \simeq 0.7\) along the \(a\) and \(c\) directions, respectively. Long-range antiferromagnetic order sets in below \(T_N \simeq 2.6\) K in zero field and reveals a non-monotonic field dependence, as expected for a low-dimensional magnet. Leading magnetic couplings are mediated by the organic anion of the pyromellitic acid and exhibit a non-trivial dependence on the Cu–Cu distance, with the stronger coupling between those Cu atoms that are further apart.

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I. INTRODUCTION

\(\text{Cu}^{2+}\) compounds with organic cations and anions are in the focus of current research on quantum magnetism. Their advantages include facile crystal growth from the solution⁴ and large Cu–Cu separations leading to relatively weak exchange couplings that are on the scale of feasible magnetic fields and reveal remarkable sensitivity to the applied pressure. Therefore, both magnetic field and external pressure can be used to change the physical regime of the system and tune it toward a new phase or a quantum critical point. Remarkable examples include the operational low-temperature magnetoacoric effect in the Cu-oxalate-based compound⁴ magnetic-field-induced ferroelectricity in sulfolane copper chloride Sul-CuCl\(_4\)⁵ and pressure-induced incommensurate magnetism in piperazinium copper chloride PHCC⁶.

Despite numerous studies, microscopic aspects of Cu\(^{2+}\) magnets with organic components are relatively less developed⁷,⁸ Many of these systems are easy to understand empirically, because organic molecules provide only a few linkages between the spin-\(\frac{1}{2}\) Cu\(^{2+}\) ions, hence forming a clearly identifiable backbone of the low-dimensional magnetic unit.⁹ However, detailed understanding of the underlying exchange mechanisms is vitally important for the deliberate preparation of new compounds. Moreover, as we show below, the trends in magnetic exchange through organic molecules are far from being trivial and extend our knowledge of superexchange interactions in general.

Here, we consider Cu(PM)(EA)\(_2\), where EA stands for the ethylamine \([\text{C}_2\text{H}_5\text{NH}_3]^+\) cation, and PM is the \([\text{C}_6\text{H}_2(\text{COO})_4]\)^\text{2+} anion of pyromellitic acid. This newly synthesized compound features layered crystal structure, with organic anions connecting Cu\(^{2+}\) ions into a two-dimensional (2D) square-lattice-like network. Two EA\(^+\) cations then balance the negative charge of the resulting \textit{anionic} framework and reside between the layers. This type of structure is clearly reminiscent of quasi-2D magnets Cu(pz)\(_2\)X\(_2\), where Cu\(^{2+}\) ions are linked through pyrazine molecules (pz) and form a \textit{cationic} framework. Its charge is compensated by inorganic anions X, such as ClO\(_4\), F\(^-\), etc.⁷,⁹

An interesting feature of Cu(pz)\(_2\)X\(_2\) and related compounds is the weak frustration⁸ of their square-lattice magnetic network by second-neighbor interactions \(J_2\) yielding the well-known model of the frustrated square lattice (FSL) that enjoys close theoretical attention⁶ and possible connections to high-temperature superconductivity in doped Cu\(^{2+}\) oxides.¹⁰ We thus expected that Cu(PM)(EA)\(_2\) might also show the FSL physics and reveal a stronger frustration than in Cu(pz)\(_2\)X\(_2\). The latter compounds feature two nearest-neighbor couplings mediated by different pyrazine molecules, so that a direct superexchange pathway for \(J_2\) is missing. In contrast, both first- and second-neighbor couplings in Cu(PM)(EA)\(_2\) should be mediated by the same organic molecule of the pyromellitic acid, hence an increase in \(J_2\) is naturally expected.

Our experimental data and microscopic analysis confirm the quasi-2D nature of Cu(PM)(EA)\(_2\) with a weak spatial anisotropy of in-plane magnetic couplings and a very small interlayer coupling. We do not find any signatures of the frustration, though. Nevertheless, our data disclose a non-trivial mechanism of the remarkably long-
Single crystal x-ray diffraction (Bruker APEX-II machine with MoKα radiation of wave length \( \lambda = 0.71073 \text{Å} \)) was performed on a high-quality single crystal of Cu(PM)(EA)\(_2\) at room temperature. The data were reduced using SAINTPLUS\(^{10}\) and an empirical absorption correction was applied using the SADAB program\(^{12}\). The crystal structure was solved by direct methods using SHELXS97 and refined using SHELXL97 from the WinGx suite of programs (Version 1.63.04a)\(^{12}\). All the hydrogen atoms were placed geometrically and held in the riding mode for the final refinements. The final refinements included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The crystal data and structure refinement parameters are shown in Table I. Few single crystals were crushed into powder, and powder x-ray diffraction (PANalytical machine with CuK\(\alpha\) radiation of wave length \( \lambda = 1.54060 \text{Å} \)) was performed to confirm the purity of polycrystalline samples. Unfortunately, the size of individual single crystals of Cu(PM)(EA)\(_2\) was insufficient for thermodynamic measurements.

Magnetic susceptibility (\( \chi \)) was measured on the powder sample as a function of temperature (1.8 K \( \leq T \leq 300 \text{ K} \)) and at different applied magnetic fields (\( H \)) using a SQUID-VSM (Quantum Design). The magnetization isotherm (\( M \) vs. \( H \)) was measured at \( T = 2.5 \text{ K} \) in static fields up to 14 T with the VSM and in pulsed magnetic fields up to 30 T at the Dresden High Magnetic Field Laboratory (HLD). Heat capacity (\( C_p \)) was measured with Quantum Design PPMS as a function of \( T \) and \( H \) on three crystalline needles glued together on the heat capacity platform.

Individual exchange couplings in Cu(PM)(EA)\(_2\) were evaluated by density-functional (DFT) band-structure calculations in the FPLO code\(^{21}\). The Perdew-Burke-Ernzerhof (GGA) flavor of the exchange-correlation potential\(^{22}\) was supplied with the mean-field GGA+U correction for strong electronic correlations in the Cu 3d shell using the on-site Coulomb repulsion \( U_d = 9.5 \text{ eV} \) and Hund’s exchange \( J_d = 1 \text{ eV} \), as applied in previous studies\(^{21,22}\). All calculations were performed for the experimental crystal structure with the positions of hydrogen atoms fully relaxed within GGA\(^{23}\). Thermodynamic properties in zero field and in applied magnetic fields were calculated numerically using the loop\(^{24}\) and dirloop_sse\(^{24}\) quantum Monte-Carlo (QMC) algorithms of the ALPS simulations package\(^{5}\).  

FIG. 1. Top panel: an overall view of the Cu(PM)(EA)\(_2\) structure featuring negatively charged [Cu(PM)]\(^{2-}\) layers interleave by the EA\(^+\) cations. Bottom panel: the structure of the [Cu(PM)]\(^{2-}\) layers and relevant magnetic couplings forming a rectangular \( J_a = J_c \) lattice of spin-\( \frac{1}{2} \) Cu\(^{2+}\) ions with frustrating diagonal couplings \( J_2 \) and \( J_2' \). The estimates of individual exchange couplings are given in Table IV. The drawing was prepared using the VESTA software\(^{18}\).

II. METHODOLOGY

For the preparation of single crystals of Cu(PM)(EA)\(_2\), an aqueous solution of Cu(CH\(_3\)COO)\(_2\)-H\(_2\)O (5 mM, 1.0 g) was treated with 2 equivalents of ethylamine (0.9 ml, 10 mM, 70% solution in water) followed by the addition of pyromellitic (1,2,4,5-benzenetetracarboxylic) acid (5 mM, 1.27 g) solution in dimethylformamide. The initially formed greenish-blue precipitate was filtered out. The ensuing clear light-blue solution was kept at room temperature for slow evaporation. Blue needle-shaped crystals of the title compound were obtained after 8 days. They were repeatedly washed with water and finally with methanol. The sample dried in air was found to be phase-pure form of Cu(PM)(EA)\(_2\). Yield: 50% (based on Cu). Analysis (calculated for C\(_{13}\)H\(_{18}\)CuN\(_2\)O\(_8\)): C, 41.39; H, 4.43 ; N, 6.89. Found: C, 41.67; H, 4.42; N, 7.04%. Infra-red data (KBr pellet, in cm\(^{-1}\)): 3154 br, 3092 br, 3056 s, 2934 br, 2911 br, 2871 s, 2809 s, 1630 s, 1589 m, 1497 m, 1429 m, 1360 s, 1316 m, 1196 w, 1140 w, 1040 m, 992 s, 820 m, 712 s, 690 s, 536 s, 494 s.
TABLE I. Crystal structure data for Cu(PM)(EA)$_2$ at room temperature.

| Empirical formula   | $\text{C}_{14}\text{H}_{18}\text{CuN}_{2}\text{O}_{8}$ |
|---------------------|----------------------------------------------------------|
| Formula weight      | 405.84                                                   |
| Temperature         | 293 K                                                    |
| Wave length ($\lambda$) | 0.71073 Å                                          |
| Crystal system      | Triclinic                                                |
| Space group         | $\bar{P}\bar{1}$                                       |
| Lattice parameters  | $a = 5.8610(1)$ Å                                      |
|                     | $b = 8.3614(2)$ Å                                      |
|                     | $c = 9.1772(2)$ Å                                      |
|                     | $\alpha = 63.387(1)^{\circ}$                           |
|                     | $\beta = 89.913(1)^{\circ}$                            |
|                     | $\gamma = 76.531(1)^{\circ}$                           |
| Volume ($V$)        | 388.29(2) Å                                            |
| Calculated density  | $1.736 \text{ mg/mm}^3$                                |
| Absorption coefficient ($\mu$) | 1.455 mm$^{-1}$                          |
| $F(000)$            | 209.0                                                   |
| Crystal size        | $0.2 \times 0.15 \times 0.1 \text{ mm}^3$             |
| $2\Theta$ range for data collection | 5.556$^\circ$ to 56.646$^\circ$                         |
| Index ranges        | $-7 \leq h \leq 7$,                                     |
|                     | $-11 \leq k \leq 11$,                                  |
|                     | $-12 \leq l \leq 12$                                   |
| Reflections collected | 6870                                              |
| Independent reflections | 1919 [$R_{int} = 0.0186$]                           |
| Data/restraints/parameters | 1919/0/117                                        |
| Goodness-of-fit on $F^2$ | 1.278                                             |
| Final $R$ indexes [$I \geq 2\sigma(I)$] | $R_1 = 0.0195$, $wR_2 = 0.0634$                  |
| Final $R$ indexes [all data] | $R_1 = 0.0222$, $wR_2 = 0.0782$                |
| Largest diff. peak/hole | $+0.60/-0.63 \text{ e Å}^{-3}$                      |

III. RESULTS

A. Crystal Structure

Crystals of Cu(PM)(EA)$_2$ feature triclinic symmetry, space group $\bar{P}\bar{1}$. Their lattice parameters, atomic positions, and main interatomic distances and angles are given in Tables I, II and III respectively. The Cu$^{2+}$ ions are at the inversion center in the origin of the unit cell. They form nearly flat CuO$_4$ plaquette units that are linked by the PM$^{4-}$ anions and build layers in the $ac$ plane. The Ea$^+$ cations are located between these layers and connected to the anionic framework [Cu(PM)]$^{2-}$ through multiple hydrogen bonds.

A simple visual examination of the crystal structure suggests a pronounced spatial anisotropy. Given the large distance and the lack of direct connections between the CuO$_4$ plaquettes along the crystallographic $b$-direction, magnetic couplings along this direction should be very weak. The PM$^{4-}$ anion linking the Cu$^{2+}$ ions may introduce four different couplings in the $ac$ plane: the nearest-neighbor exchanges $J_a$ (along [100]) and $J_c$ ([001]) and second-neighbor diagonal exchanges $J_2$ ([101]) and $J'_2$ ([011]), all running through the benzene ring of the PM molecule. The resulting model is a spatially anisotropic frustrated square lattice akin to those considered in Refs. 13, 27–29. According to Cu-Cu distances in the experimental crystal structure (Table IV), we expect $J_a > J_c > J_2 \approx J'_2$, but experimentally and microscopically, the order of couplings turns out to be different: $J_c > J_a \gg J_2, J'_2$. In the following, we study the spin lattice of Cu(PM)(EA)$_2$ and the origin of magnetic superexchange in this compound.

B. Microscopic magnetic model

To determine the magnetic model of Cu(PM)(EA)$_2$, we evaluate individual exchange couplings. This procedure is two-fold. First, we analyze the band structure calculated within GGA. This band structure (Fig. 2 top) is

TABLE II. Fractional atomic coordinates ($\times 10^4$) for Cu(PM)(EA)$_2$. The isotropic atomic displacement parameters (ADP) $U_{eq}$ (in 10$^{-4}$ Å$^2$) are defined as one-third of the trace of the orthogonal $U_{ij}$ tensor. The error bars are from the least-squares structure refinement. The positions of hydrogen atoms were additionally relaxed in a DFT calculation, hence the error bars are not given, and the relevant atom connected to hydrogen is listed instead of the ADP.

| Atoms | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ |
|-------|-------|-------|-------|----------|
| Cu1   | 0     | 0     | 0     | 11.46(10) |
| O1    | 1999.0(19) | 786.7(16) | 1165.1(13) | 17.2(2) |
| O2    | 2850(2) | −2243.7(17) | 2823.6(15) | 24.5(3) |
| O3    | 6970(2) | 2913.1(17) | 1094.5(15) | 25.0(3) |
| O4    | 7557(2) | 27.5(17) | 1407.8(14) | 19.4(2) |
| N1    | 6718(3) | 6088(2) | 1595.4(19) | 26.1(3) |
| C1    | 2948(2) | −654(2) | 2502.5(18) | 14.5(3) |
| C2    | 4096(2) | −335.2(19) | 3782.4(17) | 12.5(3) |
| C3    | 5819(2) | 650.4(19) | 3456.3(17) | 12.4(3) |
| C4    | 6847(2) | 1292(2) | 1847.9(17) | 13.9(3) |
| C5    | 3301(2) | −981(2) | 5323.3(17) | 14.2(3) |
| C6    | 10885(4) | 4449(3) | 2683(3) | 39.3(5) |
| C7    | 8579(3) | 5448(2) | 2985(2) | 27.7(4) |
| H1    | 7123 | 7091 | 521 | N1 |
| H2    | 5099 | 6686 | 1851 | N1 |
| H3    | 6556 | 4975 | 1396 | N1 |
| H4    | 1928 | 8278 | 5562 | C1 |
| H5    | 7922 | 4559 | 4108 | C4 |
| H6    | 8742 | 6683 | 3075 | C4 |
| H7    | 1519 | 5378 | 1568 | C5 |
| H8    | 704 | 3249 | 2537 | C5 |
| H9    | 2238 | 3960 | 3720 | C5 |
TABLE III. Selected bond distances and angles for Cu(PM)(EA)$_2$.

| Bond distances (Å) | Cu1-O1 | Cu1-O1$^1$ | Cu1-O4$^2$ | Cu1-O4$^3$ | O1-C1 | O2-C1 | N1-C8 | C5-C2 | C5-C3$^4$ |
|-------------------|--------|------------|------------|------------|------|-------|-------|-------|-----------|
|                   | 1.9854(10) | 1.9853(10) | 1.9300(11) | 1.9300(11) | 1.2777(19) | 1.2414(19) | 1.490(2) | 1.3926(19) | 1.3937(19) |
| Bond angles (degree) | O1$^1$-Cu1-O1 | O4$^2$-Cu1-O1 | O$^4$-Cu1-O1$^1$ | O$^4$-Cu1-O1$^1$ | C1-O1-C2 | C2-O2-C4 | C3-O3-C4 | C4-O4-Cu1$^5$ | C4-O4-Cu1$^5$ |
|                   | 180.00(5) | 88.47(5) | 91.53(5) | 91.53(5) | 106.39(13) | 121.99(12) | 114.04(13) | 117.69(13) | 124.64(10) |

$^a$ Symmetry indices are defined as follows:
1. $-x, -y, z$
2. $-1-x, y, z$
3. $1-x, -y, z$
4. $1-x, -y, 1-z$
5. $1+x, y, z$

Our microscopic analysis concludes that $J_\perp$ along [010], but it is three orders of magnitude lower than $J_\parallel$ and $J_c$.

Alternatively, we estimate individual $J$'s from total energies of collinear spin configurations calculated within GGA+U. This approach verifies the results of our tight-binding analysis and provides ferromagnetic (FM) contributions to the superexchange, which were so far missing from the analysis. The GGA+U results confirm that $J_\perp > J_\parallel$, and both couplings are slightly below 10 K. Remarkably, $J_c$ systematically exceeds $J_\parallel$, even though it runs between those Cu$^{2+}$ ions that are further apart.

Our microscopic analysis concludes that Cu(PM)(EA)$_2$ features a rectangular lattice of Cu$^{2+}$ ions in the $ac$ plane. Both interlayer coupling and frustrating second-neighbor in-plane couplings are very weak. In the following, this microscopic scenario is confirmed experimentally.

FIG. 2. (Color online) Top: GGA density of states (DOS) for Cu(PM)(EA)$_2$. Bottom: the Cu $d_{x^2−y^2}$ band crossing the Fermi level (thin light line) and its tight-binding fit (thick dark line). Note the very weak dispersion along $\Gamma–Y$ and more pronounced dispersions along the two other directions rendering Cu(PM)(EA)$_2$ magnetically quasi-2D.

TABLE IV. Exchange couplings in Cu(PM)(EA)$_2$: metal distances $d_i$ (in Å), electron hoppings $t_i$ of the tight-binding model (in meV), AFM contributions to the exchange integrals calculated as $J_{\text{AFM}}^i = 4t_i^2/U_{\text{eff}}$ (in K), and total exchange integrals $J_i$ from GGA+U (in K). Weak exchange couplings $J_2, J_2'$, and $J_\perp$ were omitted in GGA+U calculations.

| $d_i$ | $t_i$ | $J_{\text{AFM}}^i$ | $J_i$ |
|-------|------|----------------|------|
| $J_\parallel$ | 5.86 | 37  | 14 | 7  |
| $J_c$ | 9.18 | 44  | 20 | 10  |
| $J_2$ | 10.88 | 7  | 0.5  |
| $J_2'$ | 10.90 | 10 | 1.0  |
| $J_\perp$ | 8.36 | -1 | 0.01  |

A qualitative inspection of the band in Fig. 2 reveals negligible dispersion along $\Gamma–Y$, hence the magnetic coupling along the $b$ direction is indeed very weak, in agreement with our crystallographic considerations in Sec. IIIA. On the other hand, comparable dispersions along $\Gamma–X$ and $\Gamma–Z$ imply only a weak spatial anisotropy in the $ac$ plane. The evaluation of individual $t_i$'s yields similar values of $t_\parallel$ and $t_c$, whereas second-neighbor couplings $t_2$ and $t_2'$ are very weak. The leading interlayer exchange is $J_\perp$ along [010], but it is three orders of magnitude lower than $J_\parallel$ and $J_c$. gapless, at odds with the blue crystal color, because essential correlation effects in the Cu 3d shell are missing in GGA. Nevertheless, the GGA band structure clearly identifies relevant magnetic states, which are Cu 3d$_{x^2−y^2}$ orbitals of $x^2−y^2$ symmetry contributing to the single band crossing the Fermi level, as shown in the bottom part of Fig. 2 (the $x$ and $y$ axes are directed to the corners of CuO$_4$ plaquettes; they are different from the crystallographic directions $a$ and $b$). The tight-binding description of this band yields hopping integrals $t_i$, which are introduced into a single-band Hubbard model and for the strongly localized case ($t_i \ll U_{\text{eff}}$) at half-filling provide antiferromagnetic (AFM) part of the exchange couplings as $J_{\text{AFM}}^i = 4t_i^2/U_{\text{eff}}$, where $U_{\text{eff}} = 4.5$ eV is an effective on-site Coulomb repulsion on the Cu site. 

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C. Magnetization

Magnetic susceptibility $\chi$ as a function of $T$ measured at different applied fields is shown in Fig. 3(a). With decreasing $T$, $\chi(T)$ at 1T increases in a Curie-Weiss manner and then shows a broad maximum ($T_N^{\text{max}}$) at about 6K indicative of the short-range magnetic order, which is a hallmark of low-dimensionality. With further decrease in $T$, the susceptibility reaches a plateau state at around 2.6K. As the field increases, a change in slope was observed at around $T_N \approx 2.6$K, which is a possible signature of the magnetic long-range order (LRO), as indeed confirmed by the heat-capacity measurements (see Sec. II D below).

To fit the bulk susceptibility data at high temperatures, we use the expression

$$\chi = \chi_0 + \frac{C}{T + \theta_{\text{CW}}} \quad (1)$$

where $\chi_0$ is the temperature-independent contribution and consists of diamagnetism of the core electron shells ($\chi_{\text{core}}$) and Van-Vleck paramagnetism ($\chi_{\text{VV}}$) of the open shells of the Cu$^{2+}$ ions present in the sample. The second term is the Curie-Weiss (CW) law with the Curie-Weiss temperature $\theta_{\text{CW}}$ and Curie constant $C = N_A \mu_{\text{eff}}^2 / 3k_B$, where $N_A$ is Avogadro’s number, $k_B$ is the Boltzmann constant, $\mu_B$ is the Bohr magneton, and the effective moment is $\mu_{\text{eff}} = g \sqrt{S(S+1)} \mu_B / \text{f.u.}$ and f.u. means formula unit.

Our fit in the temperature range between 210K and 300K (Fig. 3(b)) yields $\chi_0 \approx -1.0 \times 10^{-4}$ cm³/mol, $C \approx 0.389$ cm³ K/mol, and $\theta_{\text{CW}} \approx 3$ K. Positive value of $\theta_{\text{CW}}$ suggests that the dominant effective interactions are AFM in nature. The $C$ value yields an effective moment of 1.76 $\mu_B$, slightly higher than the spin-only $S = \frac{1}{2}$ value of 1.73 $\mu_B$ (assuming $g = 2$) and, thus, corresponding to the $g$-factor above 2.0, which is typical for Cu$^{2+}$ compounds.

Magnetization as a function of field is nearly linear in low magnetic fields and reaches saturation at $H_s \approx 20$T (Fig. 3). A slight mismatch between the data measured in static and pulsed fields may be related to dynamic effects. Nevertheless, when scaled against the static-field data, the magnetization in pulsed fields saturates at $M_s \approx 1.03 \mu_B / \text{f.u.}$ in excellent agreement with $M_s = g S \mu_B \approx 1.025 \mu_B / \text{f.u.}$ expected for $g \approx 2.05$.

Taking into account the results of the microscopic analysis in Sec. III B we discard frustrated scenarios and focus on the rectangular $J_a - J_c$ spin lattice with $J_a/J_c = 0.7$. For the sake of completeness, we also consider the limiting cases of purely 1D ($J_a$ or $J_c$ only) and purely 2D ($J_a = J_c$) spin lattices. First, we fit the susceptibility using $\chi(T)$ obtained from QMC simulations and scaled with the $g$-value, which is a fitting parameter together with the exchange coupling $J = J_c$ and the temperature-independent contribution $\chi_0$. The values of these fitting parameters are listed in Table V. All three models yield fits of comparable quality, although the purely 1D model fails to describe the data in the 3.5 – 5.0 K temperature range, where both 2D models still work reasonably well. As we go from 2D toward 1D,
the $J$ value systematically increases because the same overall coupling energy is distributed between only two bonds per site in 1D compared to four bonds per site in 2D.

The 1D and 2D spin models can be discriminated using high-field magnetization measurements and, in particular, the saturation field $H_s$. In Fig. 5 we show the experimental magnetization curve together with model curves simulated for the parameters from Table V. The purely 1D model yields $H_s^{1D} = 2J \times k_B/(g \mu_B) \approx 15.2$ T, which is far below the experimental value. In contrast, the purely 2D model reproduces the experimental curve quite well: $H_s^{2D} = 4J \times k_B/(g \mu_B) \approx 19.8$ T. The model of the rectangular lattice is likewise matching the experimental data: $H_s^{rect} = (2J_a + 2J_c) \times k_B/(g \mu_B) \approx 19.6$ T. Therefore, we conclude that Cu(PM)(EA)$_2$ is clearly a quasi-2D magnet, but the presence of spatial anisotropy in the ac plane (the difference between $J_a$ and $J_c$) can’t be assessed from the magnetization data.

D. Heat Capacity

A further insight into the nature of Cu(PM)(EA)$_2$ can be obtained from heat-capacity measurements. The heat capacity ($C_p$) in zero field is shown in the top panel of Fig. 6. While at high temperatures it is completely dominated by the contribution of phonon excitations, the magnetic contribution is clearly visible below 10 K. The maximum around $T^\text{max}_{C_p} \approx 4$ K is characteristic of the short-range order similar to the broad maximum in $\chi(T)$. No kinks associated with the magnetic LRO are seen down to 1.8 K.

For a quantitative estimation of $C_{\text{mag}}$, the phonon part $C_{\text{phon}}$ was subtracted from the total $C_p$. The phonon part was estimated following the procedure used in Refs. [10] and [24]. Above 15 K, the data were fitted by the following polynomial

$$C_p(T) = aT^3 + bT^5 + cT^7 + dT^9,$$

where $a$, $b$, $c$, and $d$ are arbitrary constants. The fit was then extrapolated down to 1.8 K [Fig. 6 top] and subtracted from the experimental $C_p(T)$ data.

The resulting $C_{\text{mag}}(T)$ is shown in the bottom panel of Fig. 6. Its broad maximum is at $T^\text{max}_{C_p} \approx 4.2$ K. The subtraction procedure has been verified by calculating the magnetic entropy

$$S_{\text{mag}}(T) = \int_0^T \frac{C_{\text{mag}}(T')}{T'} dT',$$

where the data below 1.8 K were extrapolated with a $T^3$ function. The estimated $S_{\text{mag}}$ at $T = 20$ K is 5.8 J mol$^{-1}$ K$^{-1}$ in excellent agreement with $R \ln [S(S+1)] \approx 5.76$ J mol$^{-1}$ K$^{-1}$ expected for $S = \frac{1}{2}$. Above 20 K, $C_{\text{mag}}$ is very small, and its contribution to the entropy is negligible, hence $S_{\text{mag}}$ is nearly constant.

Now, we compare the experimental $C_{\text{mag}}(T)$ with simulation results for different spin models (Fig. 7). Similar to the magnetization data, the purely 1D model utterly fails to reproduce the experiment. The rectangular ($J_a/J_c = 0.7$) and square ($J_a/J_c = 1$) lattices are again quite similar, although both the exact position and the height of the specific heat maximum clearly favor the rectangular-lattice model. Therefore, we confirm experimentally the weak spatial anisotropy in the ac plane and also demonstrate the remarkable sensitivity of the magnetic specific heat to fine details of the spin lattice.
we identify the low-temperature peak in $C_{\text{mag}}(T)$ as the transition anomaly. Its symmetric shape is most likely due to the magnetic anisotropy that results in a spread of Néel temperatures depending on the orientation of the applied field and broadens the transition anomaly in the data obtained on polycrystalline samples. Thermodynamic measurements on single crystals would be required to resolve this issue.

The field dependence of $T_N$ is plotted in the inset of Fig. 8 to produce the $T - H$ phase diagram. This field dependence is non-monotonic and quite typical for low-dimensional magnets.\(^{35,35}\) In low fields, the suppression of quantum fluctuations facilitates the LRO, thus increasing the $T_N$. Higher fields tend to induce the parallel spin alignment and compete with the AFM LRO, so that $T_N$ goes down and eventually vanishes at $H_s \simeq 20$ T. This effect is concomitant with the gradual shift of the magnetic entropy from the broad maximum around $T_N^{\text{max}} \simeq 4.2$ K to the transition anomaly at $T_N = 2 - 3$ K (Fig. 8).

### IV. DISCUSSION AND SUMMARY

By combining experimental data with the microscopic analysis, we have shown that Cu(PM)(EA)$_2$ is a non-frustrated quasi-2D antiferromagnet with the weak spatial anisotropy in the $ac$ plane. From thermodynamic properties only, we can’t decide which of the couplings in the $ac$ plane is stronger. However, the DFT results convincingly show that $J_c > J_a$, even though the Cu–Cu distance for $J_c$ is nearly twice longer than that for $J_a$ (Table IV). This points to the non-trivial nature of the superexchange through the PM anions. To understand the origin of this superexchange process, we explore the nature of ligand orbitals that mix with the half-filled $d_{x^2-y^2}$ orbital of Cu$^{2+}$ and, thus, mediate the superexchange.

The Cu $d_{x^2-y^2}$-based Wannier function (Fig. 9) features four leading contributions from the $2p$ orbitals of oxygen atoms surrounding the Cu$^{2+}$ ion (O1 and O4). These contributions are about 14% each. Additionally, we find minuscule 2.5% “tails” of the Wannier function on the C3 and C6 atoms belonging to the C$_6$ phenyl ring. The difference between $J_a$ and $J_c$ can be now traced back to the positions of relevant $2p$ orbitals on the carbon atoms. Their orientation is fixed by the C2–C3 (C7–C6) bonds, so that the effective bridging angles of the superexchange are $\varphi \simeq 59.9^\circ$ and $\psi \simeq 120.1^\circ$ for $J_a$ and $J_c$, respectively, and the $J_c$ superexchange is more favorable than that of $J_a$ according to Goodenough-Kanamori-Anderson rules. This explains why the order of magnetic couplings in Cu(PM)(EA)$_2$ does not follow the order of Cu–Cu distances and a counter-intuitive microscopic scenario emerges.

Cu(PM)(EA)$_2$ exhibits an interesting example of the superexchange through a very long Cu–O...C...C...O–Cu pathway. This case is by far more involved than that of Cu(pz)$_2$X$_2$ magnets, where two Cu atoms are directly linked through the pyrazine molecule C$_4$H$_4$N$_2$, with its
nitrogen atoms being first neighbors of Cu$^{2+}$ and, thus, featuring large 2$p$ contributions to the magnetic orbitals.

Then the tentative superexchange pathway is Cu–N...N–Cu akin to the Cu–O...O–Cu pathways that are abundant in Cu$^{2+}$ phosphates and related compounds.

The interactions of this type are quite sensitive to individual interatomic distances and require that the distance between the ligand atoms (N...N or O...O) stays below ~3.0 Å as to allow for the efficient overlap between the ligand 2$p$ orbitals. The case of Cu(PM)(EA)$_2$ is qualitatively different. The stronger coupling $J_c$ pertains to the longer C...C distance, hence the spatial arrangement of interacting 2$p$ orbitals plays crucial role in this material.

Cu(PM)(EA)$_2$ is a quasi-2D antiferromagnet. Its pronounced 2D nature is supported by the fact that the magnetic ordering transition is not even seen in the specific heat at zero field, because the amount of entropy available at $T_N$ is too low to form a discernible A-type anomaly.

Magnetic field suppresses the short-range order and shifts the entropy from the broad maximum toward the transition anomaly, which then becomes clearly visible experimentally. The non-monotonic field dependence of $T_N$ is also quite typical for low-dimensional magnets.

In Table VI we compare Cu$^{2+}$-based square-lattice antiferromagnets, both purely inorganic compounds and those containing organic moieties. The interlayer couplings $J_{\perp}$ are determined from the $T_N/J$ ratio using the empirical relation:

$$T_N/J = 2.30/[2.43 - \ln(J_{\perp}/J)]$$

from Ref. where non-frustrated interlayer couplings are assumed. These systems fall into two different groups. CuF$_2$ and R$_2$CuBr$_4$ (R = 5MAP or 5CAP) feature $T_N/J > 0.5$ and a sizable $J_{\perp}$, which is only few times smaller than $J$. Other materials reveal $T_N/J < 0.5$ and a very small $J_{\perp}$, which is at least one order of magnitude below $J$. This difference stems from different separations between the magnetic layers. For example, two water molecules in CuF$_2$ · 2H$_2$O enhance the 2D nature of copper fluoride and decrease $J_{\perp}/J$ by one order of magnitude. Bigger organic molecules tend to be even more efficient spacers, but this is not always the case. In R$_2$CuBr$_4$, organic moieties do not separate magnetic planes, and in Cu(pz)$_2$(ClO$_4$)$_2$ the organic cations form magnetic planes, whereas the inorganic ClO$_4^-$ anions act as spacers. In Cu(PM)(EA)$_2$, magnetic planes are separated by ethylamine cations that lead to a pronounced quasi-2D nature of the system, although its $J_{\perp}/J$ is 0.025 is not as low as in other materials.

Turning now to the in-plane physics, we note that its trends are somewhat counter-intuitive. Within the family of Cu$^{2+}$ square-lattice antiferromagnets, the signatures of magnetic frustration by second-neighbor couplings $J_2$ have been so far observed in Cu(pz)$_2$(ClO$_4$)$_2$ only.

In this compound, two nearest-neighbor couplings are mediated by different pyrazine molecules, hence an efficient superexchange pathway for $J_2$ is missing, because each pyrazine molecule connects nearest-neighbor Cu$^{2+}$ ions only, and any obvious linkage between the second-neighbor Cu$^{2+}$ ions is missing. Our Cu(PM)(EA)$_2$ compound was supposed to remedy this problem by pinning both nearest-neighbor and second-neighbor couplings on the same PM anion. However, it turns out that the superexchange is not mediated by the benzene ring as a whole but by the 2$p$ orbitals of individual carbon atoms. The couplings $J_a$ and $J_c$ rely on the orbital overlap between those carbon atoms that are, respectively, first and second neighbors within the hexagonal benzene ring (Fig. 9). Diagonal couplings $J_2$ and $J_{\perp}$

\[
\begin{array}{cccccc}
\text{Compounds} & J & T_N & T_N/J & J_{\perp}/J & \text{Refs.} \\
\hline
\text{CuF}_2 & 106 & 69 & 0.65 & 3.3 \times 10^{-1} & \text{12 and 13} \\
(5\text{CAP})_2\text{CuBr}_4 & 8.5 & 5.1 & 0.60 & 2.4 \times 10^{-1} & \text{14} \\
(5\text{MAP})_2\text{CuBr}_4 & 6.5 & 3.8 & 0.58 & 2.2 \times 10^{-1} & \text{14} \\
\text{CuF}_2 \cdot 2\text{H}_2\text{O} & 26 & 10.9 & 0.42 & 4.7 \times 10^{-2} & \text{44} \\
\text{Pb}_2\text{Cu(OH)}_2\text{Cl}_2 & 35 & 11 & 0.31 & 7.5 \times 10^{-3} & \text{31} \\
\text{Cu(pyNO)}_6(\text{BF}_4)_2 & 2.2 & 0.62 & 0.28 & 3.2 \times 10^{-3} & \text{46} \\
\text{Cu(pz)}_2(\text{HF}_2)\text{BF}_4 & 5.7 & 1.54 & 0.27 & 2.3 \times 10^{-3} & \text{47} \\
\text{Cu(pz)}_2(\text{ClO}_4)_2 & 17.7 & 4.21 & 0.24 & 6.8 \times 10^{-4} & \text{10} \\
\text{Cu(COO)}_2 \cdot 4\text{H}_2\text{O} & 70 & 16.5 & 0.24 & 6.6 \times 10^{-4} & \text{48} \\
\text{Cu(PM)(EA)}_2 & 6.93 & 2.5 & 0.36 & 2.48 \times 10^{-2} & \text{this work} \\
\end{array}
\]

$^a$ Note that we do not list systems like La$_2$CuO$_4$ where interlayer couplings are geometrically frustrated.
will, in contrast, require the overlap between third neighbors, which is by far less efficient.

We speculate that the frustrating coupling $J_2$ can be enhanced by fine-tuning the organic anion. The straightforward approach of removing two “idle” carbon atoms C1 seems to be not viable from chemistry viewpoint. However, five-member rings with a heteroatom, such as the furantetracarboxylic acid $C_4(O\text{COOH})_4$, may be suitable molecular bridges for frustrated-square-lattice magnets with comparable first- and second-neighbor couplings. The realm of organic chemistry offers many other acids with cyclic carbon units and four carboxyl-groups ($\text{COOH}$) that are amenable to bond formation with the $\text{Cu}^{2+}$ ion. Our work is a natural first step toward the preparation of such quantum magnets and understanding superexchange in these compounds.

In summary, we reported synthesis, crystal structure, magnetic properties, and microscopic magnetic model of a spin-$\frac{1}{2}$ magnet $\text{Cu}(\text{PM})(\text{EA})_2$. Its quasi-two-dimensional magnetic unit features two leading exchange couplings, $J_c \approx 10$ K and $J_a \approx 7$ K forming a non-frustrated rectangular spin lattice. Superexchange couplings are mediated by carbon atoms of the phenyl ring and conform to the conventional Goodenough-Kanamori-Anderson rules, so that the stronger coupling is $J_c$, even though the relevant Cu–Cu distance is nearly twice larger than that of $J_a$. The larger spacing between the magnetic layers gives rise to only a weak coupling along the interlayer direction, with $J_\perp/J \approx 0.025$ and $T_N/J \approx 0.36$.

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* rnanth@iisertvm.ac.in
† altsirlin@gmail.com

1. Yankova, D. Hüvonen, S. Mühlbauer, D. Schmidiger, E. Wulf, S. Zhao, A. Zheludev, T. Hong, V. O. Garlea, R. Custelcean, and G. Ehlers, Phil. Mag. 92, 2629 (2012).
2. B. Wolf, Y. Tsui, D. Jaiswal-Nagar, U. Tutsch, A. Honecke, K. Remović-Langer, G. Hofmann, A. Prokofiev, W. Assmus, G. Donath, and M. Lang, Proc. Nat. Acad. Sci. 108, 6862 (2011).
3. F. Schrettle, S. Krohns, P. Lunkemeiner, A. Loidl, E. Wulf, T. Yankova, and A. Zheludev, Phys. Rev. B 87, 121105(R) (2013).
4. M. Thede, A. Mannig, M. M. ansson, D. Hüvonen, R. Khasanov, E. Morenzoni, and A. Zheludev, Phys. Rev. Lett. 112, 087204 (2014).
5. Note, however, several recent studies: J. Jornet-Somoza, M. Deumal, C. P. Landee, M. M. Turnbull, and J. J. Novoa, Inorg. Chem. 49, 8017 (2010); J. Jornet-Somoza, M. Deumal, M. A. Robb, C. P. Landee, M. M. Turnbull, R. Feyherm, and J. J. Novoa, ibid. 49, 1750 (2010).
6. S. Vela, J. Jornet-Somoza, M. M. Turnbull, R. Feyherm, J. J. Novoa, and M. Deumal, Inorg. Chem. 52, 12923 (2013).
7. 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. Southeron, and J. A. Schlueter, New. J. Phys. 10, 083025 (2008).
8. J. L. Manson, M. L. Warter, J. A. Schlueter, T. Lancaster, A. J. Steele, S. J. Blundell, F. L. Pratt, J. Singleton, R. D. McDonald, C. Lee, M.-H. Whangbo, and A. Plonczak, Angew. Chem. Int. Ed. 50, 1573 (2011).
9. 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. Southeron, P. Sengupta, and J. A. Schlueter, Phys. Rev. Lett. 108, 077208 (2012).
10. 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. Papa-georgiou, A. D. Bianchi, T. Herrmannsdörfer, J. Wosnitza, and J. A. Schlueter, Phys. Rev. B 75, 094421 (2007).
11. N. Tsyrulin, 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); N. Tsyrulin, F. Xiao, A. Schneidewind, P. Link, H. M. Rennow, J. Gavilano, C. P. Landee, M. M. Turnbull, and M. Kenzelmann, Phys. Rev. B 81, 134409 (2010).
12. M. Siahañgar, B. Schmidt, and P. Thalmeier, Phys. Rev. B 84, 064431 (2011).
13. G. Misguich and C. Lhuillier, in *Frustrated spin systems*, edited by H. T. Diep (World Scientific, Singapore, 2004) and references therein, and references therein.A. A. Tsirlin and H. Rosner, Phys. Rev. B 79, 214417 (2009).
14. P. A. Lee, Rep. Prog. Phys. 71, 012501 (2008).
15. K. Momma and F. Izumi, J. Appl. Crystallogr. 44, 1272 (2011).
16. SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL; Bruker AXS Inc.: Madison, WI, 2004.
17. G. M. Sheldrick, (1994), Siemens Area Correction Absorption Correction Program; University of Göttingen: Göttingen, Germany.
18. G. M. Sheldrick, (1997), SHELXL-7 Program for Crystal structure solution and Refinement; University of Göttingen: Göttingen, Germany; J. L. Farruiga, J. Appl. Cryst. 32 (1999).
19. K. Koepernik and H. Eschrig, Phys. Rev. B 59, 1743 (1999).
20. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
21. O. Janson, I. Rousochatzakis, A. A. Tsirlin, J. Richter,
Y. Skourski, and H. Rosner, Phys. Rev. B 85, 064404 (2012).

R. Nath, A. A. Tsirlin, P. Khuntia, O. Janson, T. Förster, M. Padmanabhan, J. Li, Y. Skourski, M. Baenitz, H. Rosner, and I. Rousochatzakis, Phys. Rev. B 87, 214417 (2013).

Note that the relaxation within GGA is sufficient for this purpose, as shown in: S. Lebernegg, A. A. Tsirlin, O. Janson, and H. Rosner, Phys. Rev. B 88, 224406 (2013).

22 R. Nath, A. A. Tsirlin, P. Khuntia, O. Janson, T. Förster, M. Padmanabhan, J. Li, Y. Skourski, M. Baenitz, H. Rosner, and I. Rousochatzakis, Phys. Rev. B 87, 214417 (2013).

23 Note that the relaxation within GGA is sufficient for this purpose, as shown in: S. Lebernegg, A. A. Tsirlin, O. Janson, and H. Rosner, Phys. Rev. B 88, 224406 (2013).

24 S. Todo and K. Kato, Phys. Rev. Lett. 87, 047203 (2001).

25 F. Alet, S. Wessel, and M. Troyer, Phys. Rev. E 71, 036706 (2005), and references therein.

26 A. Albuquerque, F. Alet, P. Corboz, P. Dayal, A. Feiguin, S. Fuchs, L. Gamper, E. Gull, S. Gürtler, A. Honecker, R. Noack, G. Pawlowski, L. Pollet, T. Pruschke, U. Schollwöck, S. Todo, S. Trebst, M. Troyer, P. Werner, and S. Wessel, J. Magn. Magn. Mater. 310, 1187 (2007).

27 B. Schmidt, M. Siahatgar, and P. Thalmeier, Phys. Rev. B 81, 165101 (2010); 83, 075123 (2011).

28 R. F. Bishop, P. H. Y. Li, R. Darradi, and J. Richter, J. Phys.: Cond. Matter 20, 255251 (2008).

29 K. Majumdar, Phys. Rev. B 82, 144407 (2010).

30 O. Janson, A. A. Tsirlin, J. Sichelschmidt, Y. Skourski, F. Weickert, and H. Rosner, Phys. Rev. B 83, 094435 (2011).

31 A. A. Tsirlin, O. Janson, S. Lebernegg, and H. Rosner, Phys. Rev. B 87, 064404 (2013).

32 R. Nath, K. M. Ranjith, J. Sichelschmidt, M. Baenitz, Y. Skourski, F. Alet, I. Rousochatzakis, and A. A. Tsirlin, Phys. Rev. B 89, 014407 (2014).

33 S. Lebernegg, A. A. Tsirlin, O. Janson, R. Nath, J. Sichelschmidt, Y. Skourski, G. Amthauer, and H. Rosner, Phys. Rev. B 84, 174436 (2011).

34 T. Matsumoto, Y. Miyazaki, A. S. Albrecht, C. P. Landee, M. M. Turnbull, and M. Sorai, J. Phys. Chem. B 104, 9993 (2000).

35 The fitting results in $a \approx 0.00474 \text{J mol}^{-1} \text{K}^{-4}$, $b \approx -5.95 \times 10^{-6} \text{J mol}^{-1} \text{K}^{-6}$, $c \approx 4.0 \times 10^{-9} \text{J mol}^{-1} \text{K}^{-8}$, and $d \approx -1.06 \times 10^{-12} \text{J mol}^{-1} \text{K}^{-10}$.

36 The $C_{\text{mag}} \sim T^3$ behavior is expected for a 3D antiferromagnet at low temperatures. In the purely 2D case, $C_{\text{mag}}$ should be proportional to $T^2$. Both extrapolations yield similar values of $S_{\text{mag}}$ with less than 1% difference.

37 P. Sengupta, A. W. Sandvik, and R. R. P. Singh, Phys. Rev. B 68, 094423 (2003).

38 R. Nath, A. A. Tsirlin, H. Rosner, and C. Geibel, Phys. Rev. B 78, 064422 (2008).

39 P. Sengupta, C. D. Batista, R. D. McDonald, S. Cox, J. Singleton, L. Huang, T. P. Papageorgiou, O. Ignatchik, T. Herrmannsdörfer, J. L. Manson, J. A. Schluter, K. A. Funk, and J. Wosnitza, Phys. Rev. B 79, 060409(R) (2009).

40 A. A. Tsirlin, R. Nath, A. M. Abakumov, Y. Furukawa, D. C. Johnston, M. Hemmida, H.-A. Krug von Nidda, A. Loidl, C. Geibel, and H. Rosner, Phys. Rev. B 84, 014429 (2011).

41 C. Yasuda, S. Todo, K. Hukushima, F. Alet, M. Keller, M. Troyer, and H. Takayama, Phys. Rev. Lett. 94, 217201 (2005).

42 R. J. Joenk and R. M. Bozorth, J. Appl. Phys. 36, 1167 (1965).

43 A. A. Tsirlin, Unpublished susceptibility data for CuF$_2$ showing the maximum in $\chi$ around 95 K, hence $J \approx 106$ K.

44 F. M. Woodward, A. S. Albrecht, C. M. Wynn, C. P. Landee, and M. M. Turnbull, Phys. Rev. B 65, 144412 (2002).

45 R. M. Bozorth and J. W. Nielsen, Phys. Rev. 110, 879 (1958); S. C. Abrahams, J. Chem. Phys. 36, 56 (1962).

46 H. A. Algra, L. J. de Jongh, and R. L. Carlin, Physica B 93, 24 (1978).

47 J. L. Manson, M. M. Conner, J. A. Schluter, T. Lancaster, S. J. Blundell, M. L. Brooks, F. L. Pratt, T. Papageorgiou, A. D. Bianchi, J. Wosnitza, and M.-H. Whangbo, Chem. Comm., 4894 (2006).

48 H. M. Rønnow, D. F. McMorrow, R. Coldea, A. Harrison, I. D. Youngson, T. G. Perring, G. Aeppli, O. Sylijäsen, K. Lefmann, and C. Rischel, Phys. Rev. Lett. 87, 037202 (2001).