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Magnetic properties of a quantum spin ladder in proximity to the isotropic limit

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We report on the synthesis, crystal structure, magnetic, thermodynamic, and electron-spin-resonance (ESR) properties of the coordination complex $[\text{Cu}_2(\text{pz})_3(4\text{-HOpy})_4](\text{ClO}_4)_4$ [pz = pyrazine; 4-HOpy = 4-hydroxypyridine]. This material is identified as a spin-1/2 Heisenberg ladder system with exchange-coupling parameters $J_{\text{rung}}/k_B = 12.1(1)$ K and $J_{\text{leg}}/k_B = 10.5(3)$ K [$J_{\text{rung}}/J_{\text{leg}} = 1.15(4)$]. For single crystals our measurements revealed two critical fields, $\mu_0 H_{c1} = 4.63(5)$ T and $\mu_0 H_{c2} = 22.78(5)$ T (for $H \parallel a^*$), separating the gapped spin-liquid, gapless Tomonaga-Luttinger-liquid, and fully spin-polarized phase. No signature of a field-induced transition into a magnetically ordered phase was found at temperatures down to 0.5 K. The material bridges an important gap by providing an excellent physical realization of an almost isotropic spin-1/2 strong-rung Heisenberg ladder system with modest exchange-coupling energy and critical-field scales.

I. INTRODUCTION

Spin-1/2 Heisenberg antiferromagnetic (AF) ladders continue to attract considerable attention, providing an excellent ground for testing various concepts of materials science and quantum physics [1, 2]. Apart from their possible relevance to high-temperature superconductivity [3–5], the interest in these systems is motivated by their unusual ground-state properties and spin dynamics. In zero magnetic field, the ground state of a two-leg spin-1/2 AF ladder is a nonmagnetic singlet, separated from the first excited triplet by an energy gap. At a first critical field, H_{c1} , the gap closes and the ladder undergoes a transition into a gapless phase with a magnetic ground state. In this phase, the system can be mapped onto a network of interacting bosons with the density of states controllable by the applied magnetic field. At low-enough temperatures, when three-dimensional (3D) correlations are relevant, the system undergoes a transition into a 3D ordered state (a process, that often is referred to as magnon Bose-Einstein condensation [6, 7]). Above the ordering temperature, short-range correlations are still relevant; the field-induced phase can be regarded as a Tomonaga-Luttinger liquid (TLL). At a second critical field, H_{c2} , the system undergoes a transition into a classical spin-polarized magnetically saturated phase.

The Hamiltonian for a two-leg spin-1/2 Heisenberg AF

ladder can be written as

$$\mathcal{H} = J_{\text{leg}} \sum_{\langle l,j \rangle} \mathbf{S}_{l,j} \cdot \mathbf{S}_{l+1,j} + J_{\text{rung}} \sum_{\langle l \rangle} \mathbf{S}_{l,1} \cdot \mathbf{S}_{l,2} - g\mu_B H \sum_{l,j} S_{l,j}^z + \mathcal{H}_\delta, \quad (1)$$

where J_{leg} and J_{rung} are exchange-coupling constants along the legs and rungs, respectively, $\mathbf{S}_{l,j}$ are the spin operators on site l of the ladder leg ($j = 1, 2$), and $g\mu_B H$ is the Zeeman term (g is the g factor, μ_B is the Bohr magneton, H is the applied magnetic field). The fourth term represents various possible, usually small, anisotropic contributions.

In the limit $\gamma = J_{\text{rung}}/J_{\text{leg}} \rightarrow \infty$, a two-leg ladder can be regarded as a network of isolated spin dimers. For $\gamma = 0$ the gap vanishes and the system is equivalent to a spin-1/2 Heisenberg AF chain. It would be interesting to experimentally study the evolution between the strong-rung ($\gamma > 1$) and strong-leg ($\gamma < 1$) phases, in particular in the vicinity of the critical ($\gamma \sim 1$) regime [8–11].

Recent progress in coordination chemistry made it possible to synthesize new materials with variable γ and accessible critical fields (for a review see, e.g., [12]), allowing one to systematically study magnetic properties of quantum spin ladders across different regions of their phase diagrams. Among others, the strong-leg ladder compound DIMPY (chemical formula $(\text{C}_7\text{H}_{10}\text{N})_2\text{CuBr}_4$; $\gamma = 0.58$) [13–22] and strong-rung ladder material BPCB (chemical formula $(\text{C}_5\text{H}_{12}\text{N})_2\text{CuBr}_4$; $\gamma \approx 3.6$) [23–30] are the most intensively studied. The exchange-coupling ratio of another strong-rung ladder compound, $\text{Cu}(\text{quinoxoline})\text{Cl}_2$,

$\gamma = 1.58$ is much closer to unity [31]. The case of an isotropic ladder ($\gamma \sim 1$) has been less studied, presented currently only by the compound $(5\text{-NAP})_2\text{CuBr}_4 \cdot \text{H}_2\text{O}$ with $\gamma = 1.04$ [32, 33].

Here, we report on the synthesis, crystal structure, magnetic, thermodynamic, and electron-spin-resonance properties of another coordination complex compound, copper pyrazine pyridone perchlorate (hereafter CPPP), with the chemical formula $[\text{Cu}_2(\text{pz})_3(4\text{-HOpy})_4](\text{ClO}_4)_4$ [pz = pyrazine; 4-HOpy = 4-hydroxypyridine]. This material is characterized by $\gamma = 1.15$, bridging an important gap between $\text{Cu}(\text{quinox})\text{Cl}$ and $(5\text{-NAP})_2\text{CuBr}_4 \cdot \text{H}_2\text{O}$ and providing an excellent realization of a two-leg spin-1/2 strong-rung ladder in close proximity to the isotropic limit with modest exchange-coupling parameters and critical fields.

II. EXPERIMENTAL DETAILS

X-ray data collection for CPPP was carried out on an Oxford Gemini diffractometer employing graphite-monochromated $\text{Mo-K}\alpha$ radiation, using ω scans. Data collection and reduction were done using CrysAlisPro [34], while absorption corrections were made analytically employing the method of Clark and Reid within the CrysAlisPro software. Structure solution was carried out using SHELXS-97 [35], while refinements were performed using SHELXL-2018 [36]. All non-hydrogen atoms were refined using anisotropic thermal parameters. All hydrogen atoms were refined with fixed isotropic thermal parameters. Those bonded to carbon atoms were inserted geometrically and refined with a riding model, while those bonded to N atoms were located in the lattice and their positions refined.

Infrared (IR) spectra were obtained with a Perkin Elmer Spectrum 100 FT-IR spectrometer. Elemental analyses were performed at the Marine Science Institute, University of California-Santa Barbara, CA, USA. Magnetic susceptibility (M/B , where M is the magnetic moment) was measured in Clark University using an MPMS-XL SQUID magnetometer (Quantum Design, Inc.) at temperatures down to 1.8 K in a magnetic field of 1 kOe.

Torque magnetometry was performed at the LNCMI-Grenoble, France, in magnetic fields up to 32 T, using a capacitive beam cantilever mounted on a rotator and placed in a top-loading $^3\text{He}/^4\text{He}$ dilution refrigerator. High-field magnetization was measured at the HLD, Dresden, Germany, using a pulsed magnet with a rise time of 7 ms and a total pulse duration of 25 ms. The magnetization was obtained by integrating the voltage induced in a compensated coil system surrounding the sample [37].

The specific heat was measured at temperatures down to ca. 0.5 K in magnetic fields up to 15 T using a superconducting magnet with a HelioxVL ^3He insert (Oxford

Instruments). The heat capacity was determined from the time dependence of the temperature relaxation as described in Ref. [38].

Electron spin resonance (ESR) measurements were performed using a Bruker ELEXSYS E500 spectrometer at a frequency of 9.4 GHz at temperatures down to 2 K. The spectrometer is equipped with a continuous flow cryostat (Oxford Instruments).

III. SYNTHESIS.

To grow crystals, $\text{Cu}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ (1.824 g, 4.9 mmol), pyrazine (802 mg, 10.0 mmol) and 4-hydroxypyridine (957 mg, 10.1 mmol) were each dissolved in 2 ml of MeOH. The pz solution was then rinsed into the stirred pyridone solution with an additional 2 ml MeOH. This combined solution was added slowly to the stirred copper solution. The initial medium-blue solution rapidly darkened and a precipitate appeared before a third of the organic solution was added. Once the solutions were totally combined, 2 ml of MeOH was added and stirred for another 45 minutes. The mixture was filtered through a fine frit, rinsed with 2 ml MeOH, then dried under vacuum for 90 minutes. The light-blue product was dried to constant weight of 1.866 mg. The light-blue filtrate was transferred to a 50 ml beaker, partially covered, and set aside. Within 2 weeks, small flat blue-green crystals appeared on the sides and bottom of the beaker. They were collected, rinsed with MeOH and dried under vacuum to constant weight of 253 mg. Yield (based on copper) = 8.8%. IR (cm^{-1}): 3318 (w), 1637 (m), 1581 (m), 1540 (m), 1518 (s), 1429 (m), 1383 (m), 1192 (m), 1155 (m), 1117 (w, sh), 1076 (w, sh), 1065 (s), 1040 (w, sh), 997 (m), 928 (w), 862 (w), 827 (m), 754 (m), 620 (s), 572 (w) [here the intensities are indicated as s = strong, m = medium, w = weak, and sh = shoulder]. Combustion Analysis: Found (%), duplicate trials): C; 33.6, 33.5, H; 2.83, 2.61, N; 12.2, 12.2. Calculated (%): C; 33.6, H; 2.80, N; 12.2. The immediate light-blue precipitate corresponds to the pyrazine-bridged hydrated copper chain with the formula $[\text{Cu}(\text{pz})(\text{H}_2\text{O})_2(4\text{-OHpy})_2](\text{ClO}_4)_2$ [39].

IV. STRUCTURE ANALYSIS.

The crystal data and structure refinement of CPPP, as obtained by our x-ray structural studies, are summarized in Table I. The asymmetric unit (shown in Fig. 1) comprises one Cu(II) ion, 1.5 pyrazine molecules, two 4(1H)-pyridone molecules, and two perchlorate anions. Each copper ion exists in a significantly distorted octahedral geometry (perhaps better described as 4+1+1) with four short bonds to three N atoms from pyrazine ligands and the O atom from one pyridone (which constitute the equatorial plane), one slightly longer bond to the O atom

TABLE I. Crystal data and structure refinement.

Empirical formula	C ₁₆ H ₁₆ Cl ₂ CuN ₅ O ₁₀
Formula weight	572.78 g/mol
Data collection temperature	123(2) K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit-cell dimensions	<i>a</i> = 18.9263(13) Å <i>b</i> = 6.9072(2) Å <i>c</i> = 16.8169(6) Å α = 90° β = 105.031(5)° γ = 90°
Volume	2123.22(18) Å ³
Z	4
Density (calculated)	1.792 Mg/m ³
Absorption coefficient	1.348 mm ⁻¹
<i>F</i> (000)	1160
Crystal size	0.66 × 0.43 × 0.16 mm ³
Theta range	3.153 to 41.046°
Index ranges	-34 ≤ <i>h</i> ≤ 34 -12 ≤ <i>k</i> ≤ 12 -23 ≤ <i>l</i> ≤ 3
Reflections collected	14392
Independent reflections	14392 [<i>R</i> (<i>int</i>) = 0.0000]
Data / restraints / parameters	14392 / 0 / 314
Goodness-of-fit on <i>F</i> ²	1.024
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0521, <i>wR</i> 2 = 0.1281
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0903, <i>wR</i> 2 = 0.1386
Largest diff. peak and hole	1.331 and -1.374 e Å ⁻³

of the second pyridone ligand, and a very long (~ 3 Å) contact to an oxygen (O3) of one of the perchlorate anions. The greatest deviation from octahedral geometry is the N7-Cu1-O14 bond angle [162.28(8)°]. Table II contains selected bond lengths and angles around the Cu(II) ion.

There are two crystallographically independent pyrazine ligands. One, the ring containing N1 and N4, forms bridges parallel to the *b* axis, linking Cu(II) ions in successive unit cells into chains with a 6.907 Å separation (the *b*-axis repeat unit). The second pyrazine ring (containing N7) sits athwart a crystallographic inversion center, hence only one-half of the ring is seen in the asymmetric unit (Fig. 1). This pyrazine ring links pairs of Cu(II) ions with a Cu...Cu distance of 6.841 Å, slightly shorter than that through the N1 pyrazine ring. The combination of pyrazine bridges links the asymmetric units covalently into a ladder structure parallel to the *b* axis (Fig. 2).

The ladders are well isolated in the lattice. The pack-

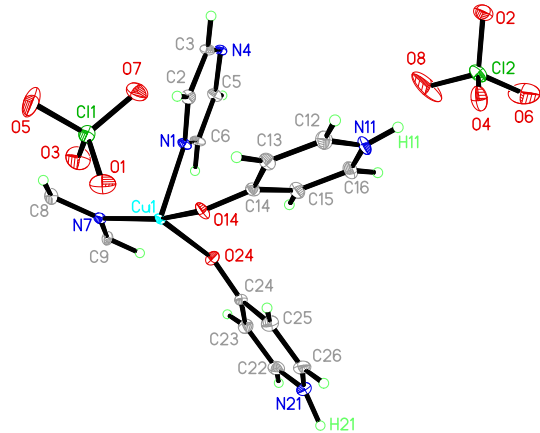


FIG. 1. A thermal ellipsoid plot of the asymmetric unit of CPPP. Hydrogen atoms are shown as spheres of arbitrary size. Only those hydrogen atoms whose positions were refined are labeled.

TABLE II. Selected bond lengths [Å] and angles [°]. Symmetry transformations used to generate equivalent atoms: #1 *x*, *y*-1, *z*.

Cu1-O14	1.9163(17)	Cu1-N7	2.0309(19)
Cu1-N4#1	2.0603(18)	Cu1-N1	2.0631(18)
Cu1-O24	2.1548(18)	Cu1...O3	2.990(3)
O14-Cu1-N7	162.28(8)	O14-Cu1-N4#1	88.03(7)
N7-Cu1-N4#1	88.61(8)	O14-Cu1-N1	92.33(7)
N7-Cu1-N1	89.24(8)	N4#1-Cu1-N1	173.98(8)
O14-Cu1-O24	106.55(7)	N7-Cu1-O24	91.06(7)
N4#1-Cu1-O24	94.55(7)	N1-Cu1-O24	91.10(7)

ing structure of CPPP viewed parallel to the *b* axis is shown in Fig. 3. Successive ladders parallel to the *a* axis are offset by one-half unit cell (parallel to *b*) and separated by the interdigitated pyridone ligands with a minimum Cu...Cu distance of 13.10 Å, while the closest Cu...Cu distance between successive ladders in the *c* direction is 9.08 Å.

The lattice is stabilized by bifurcated hydrogen bonds between the pyridone N-H hydrogen atoms and oxygen atoms from the Cl2-perchlorate ion (Fig. 4). The hydrogen bonds (see Table III for details) result in unusually short O2...O2 and O4...O4 distances (2.90 Å and 2.83 Å, respectively).

TABLE III. Hydrogen bond lengths [d in Å] and angles [\angle in degrees] for CPPP (here, D is a donor and A is an acceptor). Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$ #2 $-x+1, y-3/2, -z+1/2$ #3 $x, -y+1/2, z-1/2$.

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
N11-H11...O4	0.86(3)	2.14(3)	2.946(3)	155(3)
N11-H11...O4#1	0.86(3)	2.49(3)	3.111(3)	129(3)
N21-H21...O2#2	1.03(3)	2.12(3)	2.975(3)	139(2)
N21-H21...O2#3	1.03(3)	2.24(3)	3.055(3)	135(2)

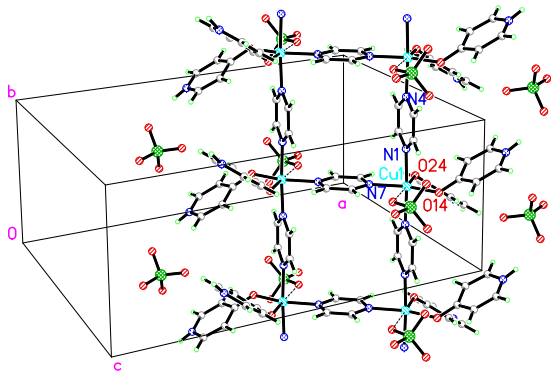


FIG. 2. The ladder structure of CPPP [light blue (Cu), black (C), red (O), green (Cl), turquoise (H)]. The ladder extends along the b axis.

IV. MAGNETIC PROPERTIES

The magnetic susceptibility of a powder sample at a temperature of 1.5 K is shown in Fig. 5. The data display a rounded maximum near 9 K, characteristic of short-range correlations. The rapid descent towards zero at the lowest temperature (1.8 K) is indicative of a spin-singlet ground state. The solid red line through the data points in Fig. 5 corresponds to results of calculations [40], revealing $J_{\text{leg}}/k_B = 10.5(3)$ K and $J_{\text{rung}}/k_B = 12.1(1)$ K [$\gamma = 1.15(4)$]. Figure 6 shows pulsed-field magnetization data of a powder sample at a temperature of 1.5 K, indicating change of the magnetization behavior at about 4.5 and 23 T, which corresponds to transitions to the gapless TTL and magnetically saturated phase, respectively.

In order to accurately determine the critical fields we performed high-field low-temperature torque-magnetometry measurements of single-crystal samples. The data obtained for $H \parallel a^*$ are summarized in Fig. 7, revealing $\mu_0 H_{c1} = 4.63(5)$ T and $\mu_0 H_{c2} = 22.78(5)$ T (measured at 20 mK). With increasing temperature (starting approximately at 400 mK) the phase transi-

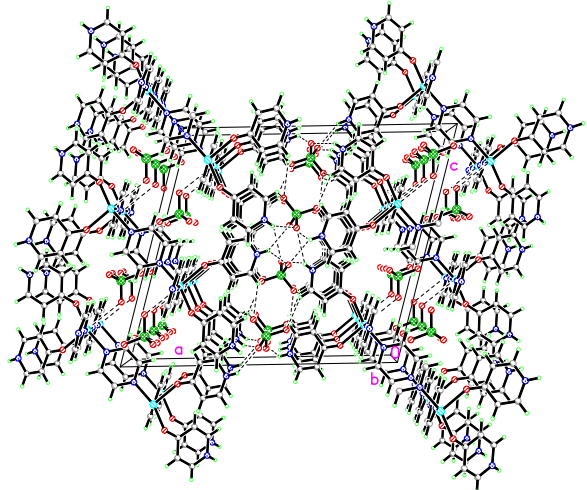


FIG. 3. The packing structure of CPPP viewed parallel to the b axis [a is horizontal; light blue (Cu), black (C), red (O), green (Cl), turquoise (H)]. Dashed lines represent hydrogen bonds.

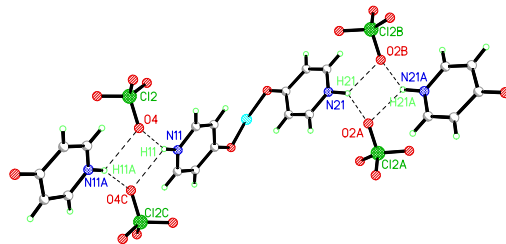


FIG. 4. The bifurcated hydrogen bonds (dashed lines) observed between pyridone ligands and perchlorate ions of CPPP viewed parallel to the body diagonal.

tions become less sharp, washed out by thermal fluctuations. Results of the density matrix renormalization group (DMRG) calculation for zero-temperature magnetization (in the calculations we used $J_{\text{rung}}/k_B = 12.1$ K, $J_{\text{leg}}/k_B = 10.5$ K, and $g_{a^*} = 2.147$) are shown in Fig. 7 by dotted line, leading to $\mu_0 H_{c1} = 4.42$ T and $\mu_0 H_{c2} = 22.95$ T. These values are in excellent agreement with the experimentally observed critical fields. Both critical fields shift to higher values, when the applied magnetic field is tilted to the c direction (Fig. 8), so that for $H \parallel c$ we obtained $\mu_0 H_{c1} = 4.80(5)$ T and $\mu_0 H_{c2} = 23.88(5)$ T. Interestingly, recent infrared spectroscopy studies of CPPP [41] showed pronounced changes in the pyrazine-related vibrational phonon spec-

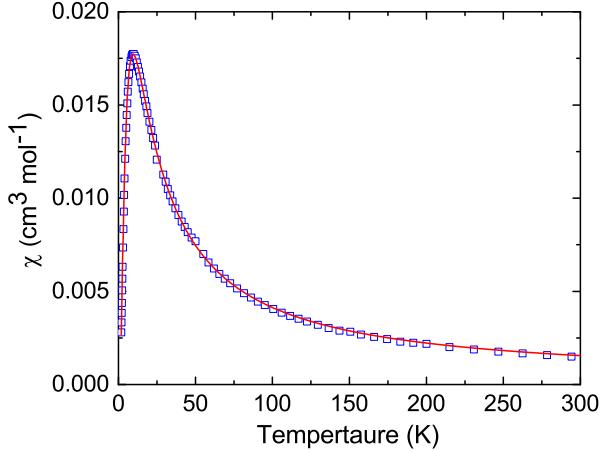


FIG. 5. Magnetic susceptibility of a powder CPPP sample as collected in a 1 kOe field (symbols). Results of calculations are shown by the red line (see text for details)

tra across different regions of the phase diagram, revealing a significant role of spin-lattice coupling in this compound.

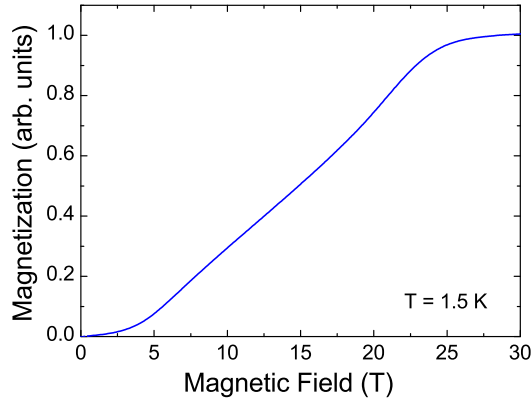


FIG. 6. Pulsed-field magnetization of a powder CPPP sample at a temperature of 1.5 K.

As mentioned, at H_{c1} the system undergoes a transition into the low-temperature TTL phase. Typically, upon decreasing temperature, 3D interactions become relevant, resulting in a field-induced magnetically ordered ground state. Usually, such a transition can be observed by means of specific-heat measurements (see, e.g., [17, 42–44]). Our thorough search using heat-capacity technique did not reveal any signature of the field-induced 3D ordering at least down to ~ 450 mK (Fig. 9), suggesting a very small interladder coupling J' .

Finally, we would like to comment on some ESR prop-

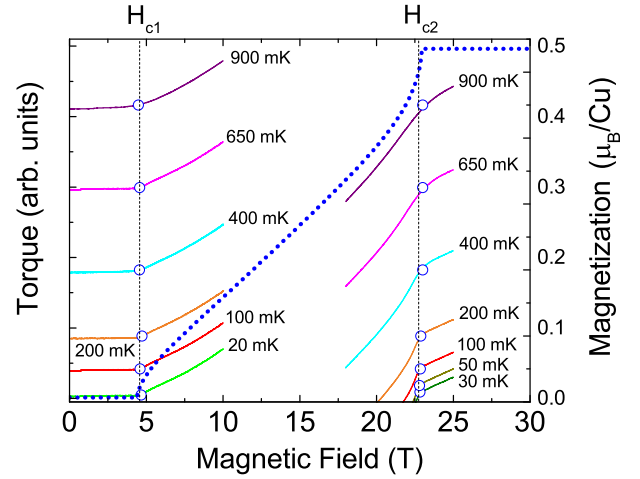


FIG. 7. Temperature dependences of the first and second critical fields, as determined by torque magnetometry (symbols) for $H \parallel a^*$. Examples of torque signals at different temperatures in the vicinity of critical fields are shown by solid lines (the data are offset for clarity, in accordance with the measurement temperature). The calculated zero-temperature magnetization is shown by blue dotted line (see text for details).

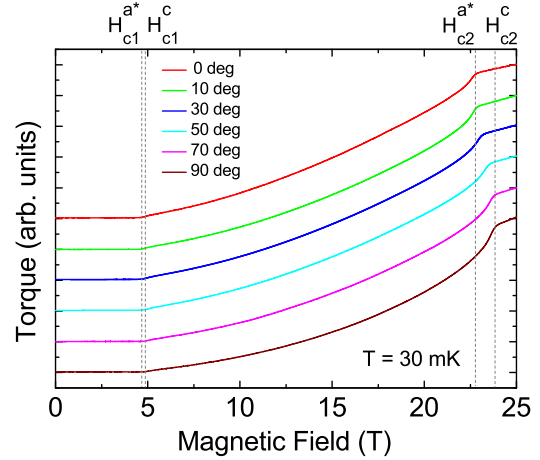


FIG. 8. Angular dependence of the torque signal at a temperature of 30 mK. The angle 0 deg corresponds to $H \parallel a^*$, while 90 deg corresponds to $H \parallel c$. The data are rescaled and offset for clarity.

erties of CPPP. Room-temperature ESR on a single crystal revealed $g_{a^*} = 2.147(3)$, $g_b = 2.183(6)$, and $g_c = 2.077(4)$; $g_{a^*} = 2.147(3)$ was used to calculate the single crystal magnetization for $H \parallel a^*$ (Fig. 7). The resonance measured at room temperature at a frequency of 9.4 GHz exhibits a relatively narrow line with peak-to-peak linewidths $\Delta H_{pp} = 26, 36, \text{ and } 15$ G for

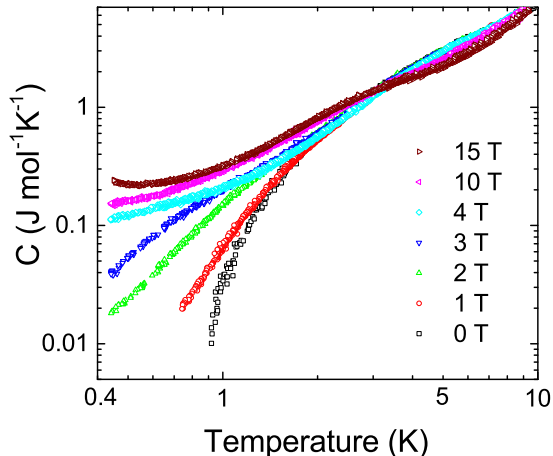


FIG. 9. Specific heat of CPPP measured in magnetic fields up to 15 T ($H \parallel a^*$).

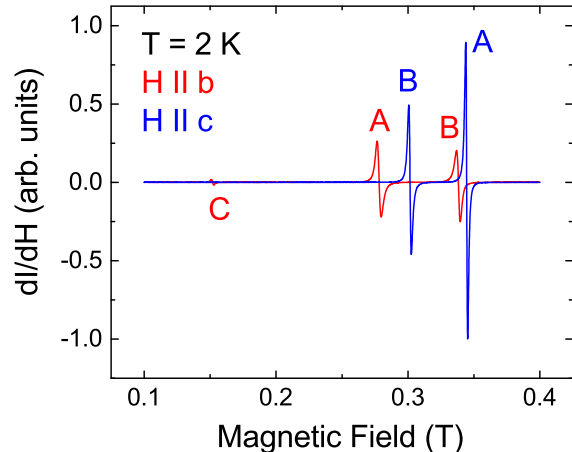


FIG. 11. ESR spectra at 2 K for $H \parallel b$ (red) and $H \parallel c$ (blue). I is the microwave intensity and H is the applied magnetic field; the spectra are collected at a frequency of 9.4 GHz.

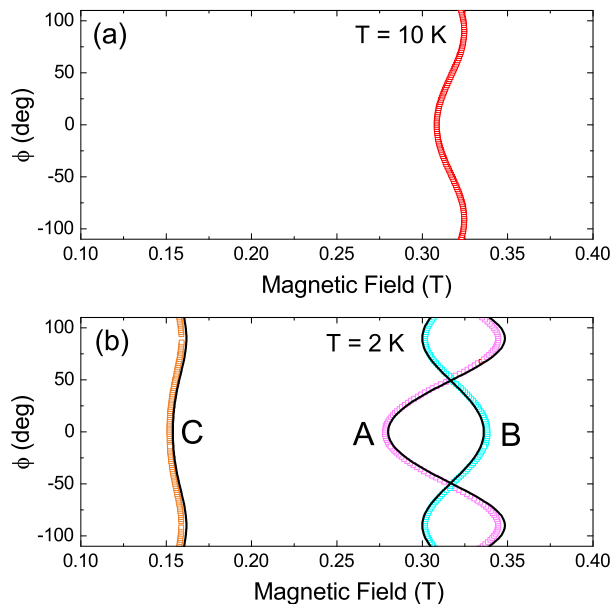


FIG. 10. Angular dependences of the ESR magnetic fields in the bc -plane measured at a frequency of 9.4 GHz at 10 K (a) and 2 K (b). ϕ is the angle between the direction of the applied magnetic field and the b -axis. Fit results are shown by black solid lines.

magnetic field applied along the a^* , b , and c axis, respectively. Upon decreasing temperature below approximately 30 K, the ESR line developed pronounced broadening, followed by a splitting of the ESR spectrum in two $\Delta M_s = 1$ components (lines A and B in Figs. 10 and 11). Such a behavior is a clear indication of the excited spin triplet; the splitting within the triplet is de-

termined by the anisotropic magnetic dipole-dipole coupling [45]. Results of the low-temperature ESR simulations with $D = 34$ mK and $E = 16$ mK (for the uniaxial and in-plane anisotropy, respectively) are shown in Fig. 10(b) by black lines, revealing a tiny crystal-field anisotropy ($\sim 0.4\%$ of J_{rung}). The low-field resonance C corresponds to a $\Delta M_s = 2$ transition, which is nominally forbidden, but becomes allowed if wave functions from neighboring spin levels are mixed.

V. CONCLUSIONS

We reported on the synthesis and extensive magnetic, thermodynamic, and electron-spin-resonance studies of the coordination complex $[\text{Cu}_2(\text{pz})_3(\text{HOpy})_4](\text{ClO}_4)_4$, which is identified as a quantum spin-1/2 ladder system with the exchange-coupling parameters $J_{\text{rung}}/k_B = 12.1(1)$ K and $J_{\text{leg}}/k_B = 10.5(3)$ K, and modest critical fields. The coupling parameters, obtained from the analysis of the temperature dependence of magnetic susceptibility, are found in excellent agreement with results of numerical calculations, performed for the high-field magnetization. The absence of a resolvable field-induced long-range ordering in specific heat down to 0.45 K (indicative of the very good ladder isolation) makes $[\text{Cu}_2(\text{pz})_3(\text{HOpy})_4](\text{ClO}_4)_4$ a very attractive model system to study physical properties of a quantum spin-1/2 Heisenberg AF ladder close to the isotropic limit.

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