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Magnetization and spin dynamics of the spin $S = \frac{1}{2}$ hourglass nanomagnet Cu$_5$(OH)$_2$(NIPA)$_4$·10H$_2$O

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We report a combined experimental and theoretical study of the spin $S = \frac{1}{2}$ nanomagnet Cu$_5$(OH)$_2$(NIPA)$_4$·10H$_2$O (Cu$_5$-NIPA). Using thermodynamic, electron spin resonance and $^1$H nuclear magnetic resonance measurements on one hand, and $ab$ initio density-functional band-structure calculations, exact diagonalizations and a strong coupling theory on the other, we derive a microscopic magnetic model of Cu$_5$-NIPA and characterize the spin dynamics of this system. The elementary five-fold Cu$^{2+}$ unit features an hourglass structure of two corner-sharing scalene triangles related by inversion symmetry. Our microscopic Heisenberg model comprises one ferromagnetic and two antiferromagnetic exchange couplings in each triangle, stabilizing a single spin $S = \frac{1}{2}$ doublet ground state (GS), with an exactly vanishing zero-field splitting (by Kramer’s theorem), and a very large excitation gap of $\Delta \approx 68$ K. Thus, Cu$_5$-NIPA is a good candidate for achieving long electronic spin relaxation ($T_1$) and coherence ($T_2$) times at low temperatures, in analogy to other nanomagnets with low-spin GS’s. Of particular interest is the strongly inhomogeneous distribution of the GS magnetic moment over the five Cu$^{2+}$ spins. This is a purely quantum-mechanical effect since, despite the non-frustrated nature of the magnetic couplings, the GS is far from the classical collinear ferrimagnetic configuration. Finally, Cu$_5$-NIPA is a rare example of a $S = \frac{1}{2}$ nanomagnet showing an enhancement in the nuclear spin-lattice relaxation rate $1/T_1$ at intermediate temperatures.

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I. INTRODUCTION

The field of molecular nanomagnets has enjoyed an enormous experimental and theoretical activity over the last few decades. 1 Owing to the nanoscopic size of their elementary magnetic units, these compounds provide experimental access to a plethora of quantum mechanical (QM) effects, including quantum tunneling of the magnetization2,3 or the Néel vector,4 quantum phase interference,5 level-crossings and magnetization plateaus.6 They also allow to probe on the macroscopic scale the crossover from quantum to classical physics.7 Finally, molecular magnets are promising materials for spintronic applications8 and quantum computing.9

Here we report on the magnetic behavior, microscopic magnetic model, and spin dynamics of Cu$_5$(OH)$_2$(NIPA)$_4$·10H$_2$O, hereinafter referred to as Cu$_5$-NIPA, where the acronym NIPA stands for the 5-nitro-isophthalic acid ligand. It is a hourglass-shaped molecular magnet comprising five Cu$^{2+}$ spin-1/2 ions. The ground state (GS) of this magnet has a low spin value $S = \frac{1}{2}$ with a very large spin gap of $\Delta \approx 68$ K. Therefore, Cu$_5$-NIPA behaves as a rigid spin $S = \frac{1}{2}$ entity in a wide temperature range, and resembles other spin-1/2 molecular magnets, such as V$_6$.10,11 Given that both compounds comprise $s = \frac{1}{2}$ spins, we expect similarly long electron spin-phonon relaxation times $T_1$, which allow for the observation of rich hysteresis effects in pulsed fields.10,12 However, in contrast to V$_6$, here we do not expect abrupt steps in the magnetization curve,10 because the present compound features an odd number of half-integer spins, thus the zero-field splitting vanishes exactly by Kramer’s theorem.

In analogy with other molecular magnets with low-spin GS’s, such as iron-sulfur clusters,13–15 heterometallic rings,16 iron trimers,17 V$_{15}$,18 and single-molecule magnets (SMM),19 we expect that Cu$_5$-NIPA manifests also long coherence times $T_2$, which is a crucial step towards implementations in quantum computing.20

Another attractive feature of Cu$_5$-NIPA is the presence of two corner-sharing scalene triangles, related by inversion symmetry.21,22 The spin triangle is the most elementary unit for highly frustrated magnetism,23 while its chirality may induce a finite magnetoelectric coupling24,25 and may also be used as a qubit.26 In molecular magnetism, the spin triangle is common in many compounds,1 as well as the giant icosidodecahedral kagome clusters,28 the chiral Dy$_3$ cluster,29 the cuboctahedron Cu$_{12}$La$_8$,30 as well as the giant icosidodecahedral kagome clusters Mo$_7$Fe$_{30}$,31 W$_7$Fe$_{30}$,32 Mo$_7$Cr$_{30}$,33 Mo$_7$V$_{30}$34 and W$_7$V$_{30},35$ which host highly frustrating kagome-like physics.36

The distinct feature of the present compound is the strong distortion of its regular spin triangles, featuring
A powder sample of Cu$_{35}$-NIPA was prepared according to the procedure described in Ref. 21. Sample purity was checked by powder x-ray diffraction (Huber G670 Guinier Camera, CuK$_{\alpha1}$ radiation, $2\theta = 3 - 100^\circ$ angular range).

The magnetic susceptibility ($\chi$) was measured in the temperature range $1.8 \, K \leq T \leq 400 \, K$ in an applied field of $\mu_0 H = 1 \, T$ using the commercial Quantum Design MPMS SQUID. The magnetization isotherm $M$ vs. $H$ was measured at $T = 2 \, K$ in fields up to 14 T using the vibrating sample magnetometer (VSM) option of Quantum Design PPMS. Additionally, pulsed-field measurements in fields up to 60 T were performed at 1.4 K in the Dresden High Magnetic Field Laboratory. Details of the measurement procedure are described in Ref. 43.

The heat capacity $C_p(T)$ was measured on a small piece of pellet over the temperature range $2 \, K \leq T \leq 300 \, K$ in zero field using the Quantum Design PPMS.

The electron spin resonance (ESR) measurements were performed at Q-band frequencies ($f = 34 \, GHz$) using a standard spectrometer together with a He-flow cryostat that allows us to vary the temperature from 1.6 to 300 K. ESR probes the absorbed power $P$ of a transversal magnetic microwave field as a function of a static and external magnetic field $B$. To improve the signal-to-noise ratio, we used a lock-in technique by modulating the static field, which yields the derivative of the resonance signal $dP/dB$.

The nuclear magnetic resonance (NMR) measurements were carried out using pulsed NMR technique on $^1$H nuclei (nuclear spin $I = \frac{1}{2}$ and gyromagnetic ratio $\gamma_n/2\pi = 42.576 \, MHz/T$) in the $2 - 230 \, K$ temperature range. The NMR measurements were performed at two different radio frequencies of 70 MHz and 38.5 MHz, which correspond to an applied field of about 1.6608 T and 0.9135 T.
FIG. 2. (Color online) Left panel: Inverse magnetic susceptibility of Cu$_5$-NIPA measured upon heating from 2 K (circles, hydrated form) and upon cooling from 400 K (triangles, dehydrated form). Lines show Curie-Weiss fits to Eq. (1), as described in the text. Right panel: $\chi^*T$ plot showing the formation of the $|\frac{1}{2}\rangle$ state in the pristine sample ($\chi^*T = \frac{1}{2}$) and the high-temperature paramagnetic regime of the dehydrated sample ($\chi^*T = \frac{3}{2}$). Here, $\chi^* = \chi \left(\frac{N g^2 \mu_B^2}{k_B T}\right)^{-1}$, $N = N_A/5$, and $g = 2.2$ according to ESR (Sec. III B). For the $\chi(T)$ plot, see Fig. 13.

respectively. Spectra were obtained by Fourier transform of the NMR echo signal. The $^1$H spin-lattice relaxation rate, $1/T_1$, was measured by using the conventional saturation pulse sequence.

The electronic structure of Cu$_5$-NIPA was calculated in the framework of density functional theory (DFT) using the VASP code$^{44}$ for crystal structure optimization and FPLO$^{45}$ for the evaluation of magnetic parameters. The generalized gradient approximation (GGA)$^{46}$ exchange-correlation potential was augmented with the mean-field DFT+$U$ correction for Coulomb correlations in the Cu $3d$ shell. The DFT+$U$ parameters were chosen as $U_d = 9.5$ eV (on-site Coulomb repulsion), $J_d = 1$ eV (on-site Hund’s exchange), and fully-localized-limit (FLL) flavor of the double-counting correction, following earlier studies of Cu$^{2+}$-based magnets.$^{47}$ Reference calculations with other exchange-correlation potentials and double-counting corrections arrived at qualitatively similar results. The reciprocal space was sampled by a $k$ mesh with 64 points in the first Brillouin zone. The convergence with respect to the $k$ mesh was carefully checked. Details of the computational procedure are reported in Sec. IV A.

Thermodynamic and GS properties of the Cu$_5$ molecule were evaluated by full numerical diagonalizations.

III. EXPERIMENTAL RESULTS

A. Thermodynamic properties

1. Magnetization

The magnetic susceptibility of Cu$_5$-NIPA was measured for the as-prepared sample under field-cooling (FC) condition upon heating from 1.8 K to 400 K. At 400 K, the sample was kept inside the SQUID magnetometer for about 20 minutes, and $\chi(T)$ was measured again upon cooling from 400 K to 1.8 K. The drastic difference between the heating and cooling curves (Fig. 2) indicates the decomposition of Cu$_5$-NIPA shortly above room temperature. Indeed, the sample color changed from blue to green, and the weight loss of 13 % was detected. This weight loss is in good agreement with the preceding thermogravimetric data of Ref. 22 that reported the weight loss of 13.15 %$^{22}$, no detailed information on the decomposed sample is available in the literature.

The pristine sample shows a sharp decrease in the magnetic susceptibility (increase in $1/\chi$) upon heating and a bend around 30 K followed by the nearly linear regime of $1/\chi$ above 200 – 250 K. In contrast, the decomposed sample remains paramagnetic down to at least 10 K. Below 320 K, where the decomposition process is finished, the inverse susceptibility of dehydrated Cu$_5$-NIPA follows a straight line that can be fitted with the Curie-Weiss law in the 20 – 320 K temperature range,$^{48}$

$$\chi = \frac{C}{T + \theta}. \quad (1)$$

The resulting Curie constant $C \approx 0.383$ emu K/(mol Cu) leads to an effective moment $\mu_{\text{eff}} \approx 1.75 \mu_B$, which is close to 1.73 $\mu_B$ expected for spin-$\frac{1}{2}$. The Weiss temperature is $\theta \approx 9$ K.

The inverse susceptibility of the pristine Cu$_5$-NIPA sample does not have a well-defined paramagnetic region, because the data above 320 – 350 K are affected by the decomposition. A tentative Curie-Weiss fit in the 220 – 320 K range yields an effective moment of $\mu_{\text{eff}} \approx 1.75 \mu_B$ ($C = 0.383$ emu K/(mol Cu)), which is same as in the dehydrated sample. However, the Weiss
temperature of \( \theta \simeq 34 \) K in the pristine sample is notably larger than \( \theta \simeq 9 \) K observed in the dehydrated sample.

The conspicuous difference between the hydrated and dehydrated samples suggests a huge effect of dehydration on the magnetism of the Cu\(_5\) molecule. The dehydration proceeds in a single step and results in the loss of all 10 water molecules per formula unit. As 4 out of these 10 molecules enter the first coordination sphere of Cu (Fig. 1, left), a large effect on the local environment of Cu sites and, thus, on the magnetism should be expected. Unfortunately, no structural data for the dehydrated version of Cu\(_5\)NIPA are presently available. Therefore, we restrict ourselves to a detailed study of the hydrated compound.

At low temperatures, the inverse susceptibility of Cu\(_5\)NIPA approaches another linear regime, with the Curie constant \( C = 0.101 \) emu K/(mol Cu) (\( \mu_{\text{eff}} \simeq 0.90 \mu_B \)) and vanishingly small \( \theta \simeq 0.5 \) K. This low-temperature paramagnetic state can be also seen in the \( \chi^*T \) plot (\( \chi^* = \chi(Ng^2\mu_B^2/k_B)^{-1} \)) is the reduced susceptibility), where \( \chi^*T \) approaches the value of \( 1/2 \) expected for the total spin \( S = 1/2 \) per molecule (Fig. 2, right). Likewise, the magnetization curve of Cu\(_5\)NIPA (Fig. 3) saturates at \( M_s = 1.19 \mu_B / \text{molecule} \), which is, however, higher than the free-electron value of \( 1 \mu_B / \text{f.u.} \). This difference can be well accounted for by the large \( g \)-value of 2.38 according to \( M_s = gS\mu_B \). The same \( g \)-value explains the low-temperature effective moment: \( C = Ng^2\mu_B^2/3k_B = 0.106 \) emu K/(mol Cu), where we use \( N = N_A/5 \) for the magnetic moment of \( 1/2 \) per Cu\(_5\) molecule. As we explain later, this change in the \( g \)-value (Sec. IV B) can be traced back to the presence of three non-equivalent Cu positions with different \( g \)-tensor anisotropies. At room temperature, the Cu spins are nearly independent, and their \( g \)-values average with same weights for all Cu positions. At low temperatures, the powder averaging of the \( g \)-values is determined by the distribution of the magnetization in the \( S = 1/2 \) GS.

Our results suggest that at low temperatures Cu\(_5\)NIPA is in the paramagnetic state with the total moment of \( S = 1/2 \) per Cu\(_5\) molecule. This state is further denoted as \( (1/2)^* \). The experimental magnetization curve follows the Brillouin function

\[
B(H) = g\mu_B S \times \text{th} \left( \frac{g\mu_B S H}{k_B T} \right)
\]

with \( S = 1/2 \), \( g = 2.38 \), and \( T = 1.8 \) K (Fig. 3). A marginal departure of the experimental curve toward higher fields may be due to anisotropies and/or intermolecular couplings. The maximum deviation of about 0.3 T puts an upper limit of about 0.5 K on the total energy of such couplings. This low energy scale is in agreement with the large spatial separation between the molecules (Fig. 1, right).

Below 4 K, the susceptibility of Cu\(_5\)NIPA departs from \( \chi^*T = 1/4 \) (Fig. 2, right). This decrease in \( \chi^*T \) may indicate an evolution of the system toward a long-range magnetic order between the Cu\(_5\) molecules. However, we were unable to see any clear signatures of a magnetic transition in the susceptibility data measured down to 2 K.

2. Specific heat

The specific heat \( (C_p) \) of Cu\(_5\)NIPA is smooth down to 2 K (Fig. 4). It steeply increases up to 60 – 70 K and shows a slower increase at higher temperatures, as shown by a broad maximum in the temperature dependence of \( C_p/T \). The signal is dominated by the phonon contribution, whereas the magnetic part is quite small. The total magnetic entropy of Cu\(_5\)NIPA is \( 5R\ln 2 \approx 28.8 \) J mol\(^{-1}\) K\(^{-1}\), which is only 2 % of the total entropy of about 1100 J mol\(^{-1}\) K\(^{-1}\) released up to 200 K (the latter is obtained by integrating the temperature dependence of \( C_p/T \)).

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**FIG. 3.** (Color online) Magnetization curve of Cu\(_5\)-NIPA measured at 1.8 K up to 14 T. The dashed line denotes the saturation of the \( 1/2 \) state at \( M_s = 1.19 \mu_B / \text{f.u.} \). The solid line is the Brillouin function calculated at 1.8 K with \( g = 2.38 \).

**FIG. 4.** (Color online) Specific heat of Cu\(_5\)-NIPA divided by temperature \((C_p/T)\). The inset in the upper left corner magnifies the data at low temperatures. The inset in the bottom right corner shows the specific heat \((C_p)\).
At 200 K, the heat capacity of Cu$_5$-NIPA is still very far from its maximal Dulong-Petit value of $C_p = 3R_N \simeq 2767 \text{ J mol}^{-1} \text{ K}^{-1}$, because Cu$_5$-NIPA features a large number of high-energy phonon modes related to the O–H, C–C, C–N, and C–O vibrations. The entropy associated with these modes can be released at very high temperatures, only. The complexity of the Cu$_5$-NIPA structure and the presence of multiple phonon modes of different nature hinder a quantitative analysis of the specific heat data. A non-magnetic reference compound would be ideal to extract the magnetic contribution and analyze it in more detail. Unfortunately, such a reference compound is presently not available.

At low temperatures, the heat capacity of Cu$_5$-NIPA does not fall smoothly to zero. The temperature dependence of $C_p/T$ shows an increase below 3 K (see the upper left inset of Fig. 2). The origin of this behavior is presently unclear. The increase in $C_p/T$ could signify a Schottky anomaly or a proximity to the magnetic ordering transition. However, our susceptibility data, as well as NMR (Sec. III C), rule out any magnetic transition down to 2 K. The heat capacity data are consistent with these observations.

### B. ESR

The ESR spectrum of Cu$_5$-NIPA could be detected from the lowest measured temperature (5 K) up to 135 K. Above 135 K, the ESR line broadens and eventually becomes invisible. Between 70 K and 135 K, the spectra contain only one line that can be fitted with a single Lorentzian function (1L-Fit) providing the ESR parameters, the linewidth $\Delta B$ and g-factor, $g = \frac{h\nu}{\mu_B B_{res}}$, where $B_{res}$ is the resonance field. Below 70 K, the single ESR line splits, so that at 40 – 60 K the fit is only possible with two Lorentzian lines (2L-Fit), whereas at even lower temperatures a plethora of narrow lines appear (Fig. 5). At 5 K, more than 20 lines are visible in the spectrum. This complex structure is typical in low-temperature ESR spectra of molecular magnets and is related to the hyperfine coupling. The complexity of the signal and the presence of multiple Cu sites and anisotropy parameters prevent us from a detailed analysis of the low-temperature powder spectra. One would need much higher frequencies and, preferably, single crystals of Cu$_5$-NIPA, in order to discriminate the multiple resonances that are visible below 40 K. So we restrict ourselves to the analysis of the data above 40 K.

Fig. 6 shows the temperature evolution of the ESR g-factor, linewidth, and line intensities. Above 70 K, the observed powder-averaged values of $g \simeq 2.2$ are typical for Cu$^{2+}$ in the planar oxygen environment. Our microscopic insight into the energy spectrum of the Cu$_5$ molecule (Sec. IV B) suggests that the formation of two lines below 70 K is related to two lowest $S = \frac{1}{2}$ energy levels, which are separated by $\Delta \simeq 68$ K. Indeed, lines 1 and 2 show different temperature evolution. While the intensity of line 2 is reduced upon cooling, the intensity of line 1 is growing. In Sec. IV B below, we provide the explicit dependence of the effective g-tensors for the GS and the first excited doublet (in terms of the individual g-tensors of the three inequivalent Cu sites) in order to
we can write FWHM as:

$$\text{FWHM} \propto \sqrt{\langle \Delta \nu^2 \rangle_d + \langle \Delta \nu^2 \rangle_m}, \quad (3)$$

where the broadening due to the nuclear-nuclear dipolar interactions ($\langle \Delta \nu^2 \rangle_d$) is temperature-independent, while the broadening due to the hyperfine couplings ($\langle \Delta \nu^2 \rangle_m$) scales with the local susceptibilities. For each given proton site $p$,

$$\frac{\sqrt{\langle \Delta \nu^2 \rangle_p}}{H} \simeq \sum_j A_j \chi_j, \quad (4)$$

where $A_j$ is the dipolar coupling constant between the proton and the Cu$^{2+}$ ions at site $j$, and $\chi_j$ is the local susceptibility. We should note here that, in general, the temperature dependence of $\chi_j$ is different from that of the bulk susceptibility $\chi$ (Fig. 2), especially at higher temperatures, and they are also different from each other (see Fig. 15). The sharp increase in FWHM at low temperatures can be ascribed to the corresponding low-temperature increase in $\chi_j$.

The shallow minimum in FWHM observed around 70 K is paralleled by the peculiar evolution of the spectral line (Fig. 7, top). On cooling down, the right side of the line shifts weakly but monotonously to the right, following the central position of the line. The left side, on the other hand, shows a non-monotonic behavior, shifting backwards for the data at 20 K and below. The origin of this feature (and the minimum in FWHM) can in principle be traced back to the temperature dependence of the local Cu$^{2+}$ moments, and indeed such a non-monotonic behavior is shown by the moments on the Cu2 sites. As we discuss in detail below (Sec. IV B and Fig. 15), at $T \ll \Delta \simeq 68$ K, the moments of the two Cu2 sites are antiparallel to the field, owing to the large negative exchange field exerted by the neighboring Cu1 and Cu3 sites. These exchange fields are balanced by entropy at some characteristic temperature $T^*$, at which the Cu2 moments turn positive. Our calculations based on the actual exchange couplings give $T^* \simeq 38$ K (see Fig. 15 below). At even higher temperatures, the Cu2 moments attain their paramagnetic Curie-like behavior of isolated spins. The contribution to the second moment from the Cu2 sites is then expected to decrease down to zero and then increase again as we cool down, starting from the high-temperature paramagnetic to the low-temperature “ferrimagnetic” $S = \frac{1}{2}$ state of Cu$_5$-NIPA.

2. Wipe-out effect

The wipe-out effect is common in molecular nanomagnets, and refers to the gradual loss in the NMR signal intensity below a characteristic temperature. Here, we have measured the temperature dependence of $M_{xy}(0)T$, where $M_{xy}(0)$ is the transverse

![Graph](image)

FIG. 7. (Color online) Top panel: Fourier-transform $^1$H NMR spectra measured at different temperatures. Arrows show the shifts of the left and right shoulders upon cooling. Note that while the right shoulder is moving toward higher frequencies, the left shoulder shows a non-monotonic behavior. Bottom panel: Full width at half-maximum (FWHM) of $^1$H NMR spectra plotted as a function of temperature ($T$) measured in an external field $\mu_0 H = 1.6608$ T.

demonstrate the origin of their difference.

C. $^1$H NMR

1. Linewidth

Considering the nuclear spin $I = \frac{1}{2}$ of the $^1$H nucleus, one expects a single spectral line for each of the 17 nonequivalent proton sites (see Table III of App. B). However, these lines merge into a single broad line with a nearly Gaussian line shape over the whole measured temperature range (Fig. 7, top). The linewidth at 215 K is 95 kHz and almost comparable with the linewidth reported for other molecular magnets (see, e.g., Ref. 52). The line position shifts weakly with temperature. The bottom panel of Fig. 7 shows the temperature evolution of the full width at half-maximum (FWHM) of the $^1$H NMR line measured in an applied field of $\mu_0 H = 1.6608$ T. It is almost temperature-independent at high temperatures and increases progressively upon cooling below about 30 K.

The shape and width of the $^1$H NMR spectra are governed by two main interactions: the nuclear-nuclear dipolar interactions and the hyperfine couplings between the proton and unpaired electrons at the Cu sites. Therefore,
magnetization at time $t = 0$, obtained by the extrapolation of the $M_z(t)$ recovery curve to $t=0$. The integrated intensity $M_{xy}(0)/T$ is proportional to the total number of protons resonating at the irradiated frequency. The normalized integrated intensity of the NMR signal in Cu$_5$-NIPA as a function of temperature is shown in Fig. 8. We find that the loss of the NMR signal begins below 150 K and becomes more pronounced at low temperatures. The onset of the NMR signal loss around 150 K coincides with the regime where $1/T_1$ starts increasing towards the maximum (see Fig. 9 below).

The loss in the NMR signal is related to the slowing down of the electron spin dynamics which, as we explain below, is also responsible for the enhancement in $1/T_1$. On decreasing $T$, a progressively larger fraction of protons close to the magnetic Cu$^{2+}$ ions attain spin-spin relaxation times ($T_2$) shorter than the dead time ($\tau_d$) of the spectrometer, hence the signal from these protons cannot be detected. At low temperatures, only the protons that are very far from the magnetic ions contribute to the signal intensity. For further details, see Refs. 56 and 57.

3. Nuclear spin-lattice relaxation rate $1/T_1$

The spin-lattice relaxation rate $1/T_1$ for Cu$_5$-NIPA was measured at two different applied fields. The recovery of the longitudinal nuclear magnetization after a saturation pulse was fitted well by the stretched exponential function (top panel of Fig. 9, inset)

$$1 - \frac{M(t)}{M_0} \simeq A' e^{-(t/T_1)^\beta},$$

where $M(t)$ is the nuclear magnetization at a time $t$ after the saturation pulse, and $M_0$ is the equilibrium magnetization. The value of the exponent $\beta$ for both fields was found to decrease slowly from 0.95 to 0.7 upon cooling. The deviation of $\beta$ from unity reflects the distribution of relaxation rates according to different hyperfine couplings between the $^1$H nuclei and Cu$^{2+}$ ions. Accordingly, the spin-lattice relaxation rate $1/T_1$ obtained by fitting the recovery with Eq. (5) provides a value averaged over the whole distribution.

The $T$ dependence of $1/T_1$ is presented in the top panel of Fig. 9 for two values of the external field. At high temperatures ($T > 150$ K), $1/T_1$ is almost $T$-independent. This behavior is typical for uncorrelated paramagnetic moments fluctuating fast and at random. At lower temperatures, $1/T_1$ increases and passes through a maximum at $T \approx 40$ K. Such a characteristic enhancement has been found in numerous AFM homometallic rings with predominantly AFM couplings and low-spin GS. Systems with predominantly AFM couplings and low-spin GS (e.g., $V_{12}$ having an $S = 0$ GS, Ref. 65) do not show such a feature in $1/T_1$.

In homometallic rings, the maximum in $1/T_1$ essentially signals the slowing down of phonon-driven spin fluctuations. The equivalence between the spins (by virtue of the nearly perfect rotation symmetry of the ring) allows to express $1/T_1$ in terms of the spectral density of the total magnetic moment $S_1$ of the molecule. As shown numerically and by a microscopic theory, the...
the phonon-driven decay of $S_z$ proceeds independently from the remaining observables of the problem, which in turn leads to a single Lorentzian form for $1/T_1$:

$$\frac{1}{T_1} \simeq A \chi T \frac{\omega_c(T)}{\omega^2_c(T) + \omega^2_L},$$  

(6)

where $A$ is the average square of the transverse hyperfine field, $\omega_c$ is the nuclear Larmor frequency, and $\omega_L = \frac{\gamma \chi}{\omega_c}$ is the decay rate of the total moment $S_z$. The enhancement in the spin-lattice relaxation rate $1/T_1$ takes place when $\omega_c$ approaches the order of magnitude of $\omega_L$.

There are two qualitative differences between Cu$_5$-NIPA and homometallic rings that should be emphasized, though. First, Cu$_5$-NIPA features a very sparse excitation spectrum (Sec. IV B), which means that there are very few spin-phonon channels available for relaxation. According to Ref. 42, this also means that here $\omega_c$ is not expected to show the strong power-law $\sim T^3$ or $T^4$ behavior. Instead, one expects a much weaker $T$ dependence, with longer relaxational times in a wide temperature range.

The second difference is the fact that the Cu$_5$ molecule comprises three inequivalent Cu sites with different local magnetizations, and so the above single-Lorentzian formula for $1/T_1$ is not valid any longer, but instead a multi-Lorentzian form should be expected on general grounds, as in the case of the heterometallic Cr$_7$Ni ring.

Given the large spin gap, $\Delta \simeq 68$ K, one could still argue in favor of the single-Lorentzian formula of Eq. (6) over a wide low-$T$ range, since the Wigner-Eckart theorem allows to replace individual spin operators with the total spin operators times a constant. However, such a treatment would only capture the resonant spin-phonon interactions present in this system. Note that we neglect the Zeeman splitting contribution to the resonance energy, because it is negligible compared to $\Delta$. By fitting the $\omega_c$ data with Eq. (7), we obtain $\lambda/k_B \simeq 3.9(v/c)^3$ K.

A more complete quantitative understanding of $1/T_1$ (e.g. the high-temperature behavior and field dependence) must take into account the multi-exponential behavior of the relaxation, discussed above, but also the presence of the wipe-out effect discussed above, see e.g. Ref. 66.

IV. THEORY

A. Microscopic magnetic model

To determine individual exchange parameters in the Cu$_5$ molecule, we calculate the electronic structure of the Cu$_5$-NIPA compound. This procedure requires reliable crystallographic information, including precise positions of all atoms in the unit cell. However, the available structural data are obtained from x-ray diffraction that has only limited sensitivity to the positions of hydrogen atoms. Therefore, we used the literature data as a starting model and optimized the hydrogen positions, whereas all other atoms were kept fixed. The equilibrium positions of hydrogen are listed in Table III of App. B. The relaxed structure is 18.6 eV/f.u. lower in energy.
the starting model taken from the literature. This energy reduction should be ascribed to the elongation of O–H distances that are unrealistically short (about 0.8 Å) in the experimental structural data.

The LDA energy spectrum of Cu5-NIPA (Fig. 10) comprises narrow lines that represent molecular orbitals of the NIPA molecules and the Cu5(OH)2 unit. The states at the Fermi level belong to the narrow Cu 3d bands with a sizable admixture of O 2p. The local environment of Cu atoms resembles the conventional CuO4 plaquette units (four-fold coordination, see Fig. 1, left). Therefore, the highest-lying Cu 3d bands have predominantly $x^2 - y^2$ origin, following the crystal-field levels of Cu$^{2+}$ with $x$ and $y$ axes lying in the plane of the CuO4 plaquette. The five Cu atoms of the Cu5 molecule (one molecule per unit cell) give rise to five bands, with the middle band crossing the Fermi level (Figs. 10 and 11). This spurious metallicity is due to the strong underestimate of electronic correlations in LDA. DFT+U calculations reveal the robust insulating behavior with a band gap of about 2.2 eV in reasonable agreement with the light-blue color of the sample.

![Graphical representation of Cu5-NIPA](image1)

**FIG. 11.** (Color online) LDA band structure of Cu5-NIPA (thin light lines) and the fit with the tight-binding model (thick dark lines). The Fermi level is at zero energy (white dashed line). The notation of $k$ points is as follows: $\Gamma(0,0,0)$, $X(\frac{1}{2},0,0)$, $M(\frac{1}{2},\frac{1}{2},0)$, $Y(0,\frac{1}{2},0)$, $Z(0,0,\frac{1}{2})$, $T(\frac{1}{2},0,\frac{1}{2})$, $R(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and $A(0,\frac{1}{2},\frac{1}{2})$, where the coordinates are given in units of the reciprocal lattice parameters.

**TABLE I.** Interatomic distances $d$ (in Å), Cu–O–Cu bridging angles $\varphi$ (in deg), hopping parameters $t_i$ (in meV), and exchange integrals $J_i$ (in K) in Cu5-NIPA. The $J_i$ values are obtained from DFT+U calculations. The AFM contributions $J_i^{\text{AFM}}$ are evaluated as $4t_i^2/U_{\text{eff}}$, where $U_{\text{eff}}$ is the effective on-site Coulomb repulsion. The FM contributions are $J_i^{\text{FM}} = J_i - J_i^{\text{AFM}}$.

<table>
<thead>
<tr>
<th>$d_{\text{Cu-Cu}}$</th>
<th>$\varphi_{\text{Cu-O-Cu}}$</th>
<th>$t_i$</th>
<th>$J_i^{\text{AFM}}$</th>
<th>$J_i^{\text{FM}}$</th>
<th>$J_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{13}$</td>
<td>3.20</td>
<td>107.9</td>
<td>-0.054</td>
<td>34</td>
<td>-89</td>
</tr>
<tr>
<td>$J_{12}$</td>
<td>3.33</td>
<td>114.5</td>
<td>-0.128</td>
<td>191</td>
<td>-134</td>
</tr>
<tr>
<td>$J_{23}$</td>
<td>3.51</td>
<td>125.7</td>
<td>-0.161</td>
<td>302</td>
<td>-34</td>
</tr>
</tbody>
</table>

To evaluate the magnetic couplings, we fit the five Cu bands with a tight-binding model (Fig. 11) and extract the relevant hopping parameters $t_i$ using Wannier functions (WFs) based on the Cu $d_{x^2-y^2}$ orbital character. The $t_i$'s are further introduced into an effective Hubbard model with the on-site Coulomb repulsion $U_{\text{eff}}$. As the conditions of the half-filling and strong correlations ($t_i \ll U_{\text{eff}}$) are fulfilled, the lowest-lying excitations can be described by a Heisenberg model with the AFM exchange $J_i^{\text{AFM}} = 4t_i^2/U_{\text{eff}}$. The values of $t_i$ and $J_i^{\text{AFM}}$ obtained from the LDA band structure are listed in Table I and provide an overview of the magnetic couplings in Cu5-NIPA. Considering only nearest-neighbor interactions, we find a strong coupling between Cu2 and Cu3, a somewhat weaker coupling between Cu1 and Cu2, and a relatively weak coupling between Cu1 and Cu3. Long-range couplings are several times smaller than $J_i^{\text{AFM}}$.

The long-range exchanges in the Cu5 molecule are within 10 K, whereas the interactions between the molecules are below 3 K (note the experimental estimate of 0.5 K in Sec. III A). As the long-range couplings are much weaker than $J_{12}$, $J_{13}$, and $J_{23}$, we further restrict ourselves to the minimum microscopic model that comprises three nearest-neighbor interactions, only.

Possible FM contributions to the short-range couplings require that the evaluation of $J_i^{\text{AFM}}$ is supplied by an independent estimate of total exchange couplings $J_i$. In a so-called supercell approach, total energies of collinear spin configurations are mapped onto the Heisenberg model to yield the $J_i$ values, as listed in Table I. All nearest-neighbor interactions have sizable FM components $J_i^{\text{FM}} = J_i - J_i^{\text{AFM}}$ that reduce $J_{12}$ and $J_{23}$, whereas $J_{13}$ eventually becomes ferromagnetic. This way, the triangular units in the Cu5 molecule feature a combination of FM interaction $J_{13}$ and AFM interactions $J_{12}$ and $J_{23}$ (Fig. 1, left).

The microscopic origin of the magnetic couplings can be understood from the analysis of Cu-based Wannier functions (Fig. 12). Each WF features the Cu $d_{x^2-y^2}$
orbits together with the 2p orbitals of the surrounding oxygen atoms. These oxygen atoms have different chemical environment and belong to one of the ligands: $\mu_3$-OH$^-$, COO$^-$, and H$_2$O. While the ligands affect the positions of oxygen atoms (note the slight downward displacement of the O atoms in COO$^-$ groups) and modify the “shape” of the p orbitals (note the oxygen atom belonging to the H$_2$O molecule), they do not provide any sizable long-range contributions to the WFs. The short-range nature of the WFs underlies the diminutively small long-range exchange in Cu$_5$-NIPA. Further microscopic aspects of the magnetic interactions in Cu$_5$-NIPA are discussed in Sec. V.

Our microscopic model can be directly compared to the experimental data. Using full diagonalization for the Cu$_5$ molecule, we calculate thermodynamic properties and refine the $J_i$ parameters as to match the experiment. This way, we fit the experimental magnetic susceptibility curve with $J_{12} = -J_{13} = 62$ K and $J_{23} = 217$ K (so that $J_{12}/J_{23} \approx \frac{1}{2}$), as well as $g = 2.22$ and the temperature-independent contribution $\chi_0 = -1.7 \times 10^{-4}$ emu/mol Cu (Fig. 13). The experimental estimates of $J_i$ are in excellent agreement with the DFT results (Table I), whereas the $g$-value matches the high-temperature $g \approx 2.2$ from ESR (Sec. IIIIB). Regarding the sizable $\chi_0$, it may originate from the diamagnetic gelatin capsule that was used in the susceptibility measurement.

The combination of the FM coupling $J_{13}$ and AFM couplings $J_{12}$ and $J_{23}$ implies that the spin triangles in Cu$_5$ are non-frustrated. In a classical picture, all three couplings are satisfied in a configuration with Cu3 and Cu1 spins pointing up and Cu2 spins pointing down, thus leading to the total moment of $\frac{1}{2}$ per molecule. Indeed, at low temperatures Cu$_5$-NIPA shows paramagnetic behavior with the magnetic moment of $\frac{1}{2}$ per molecule ($\frac{1}{2}$) state). In high magnetic fields, the $\frac{1}{2}$ and, eventually, $\frac{3}{2}$ states will be stabilized. The formation of states with the higher magnetic moment can be seen from the simulated magnetization curve of Cu$_5$-NIPA. The $\frac{1}{2}$ state persists up to about 50 T, where the magnetization increases abruptly until the $\frac{3}{2}$ state is reached.

We endeavored to verify this prediction with magnetization measurements in pulsed fields. Unfortunately, the results are strongly affected by dynamic effects. The typical duration of the pulse (about 20 $\mu$s) is insufficient to change the magnetic moment of the molecule. Therefore, all features are blurred and, moreover, the curve shows a non-zero slope above 5 T (Fig. 14, top), in contrast to the flat plateau that is observed in static field (Fig. 14, bottom). The apparent mismatch between the pulsed-field and static-field data also prevents us from scaling the high-field curve. Nevertheless, the bound observed at 50 – 55 T is likely the signature of the $\frac{1}{2} \rightarrow \frac{3}{2}$ transition and confirms our expectations.

**B. Exact Diagonalization**

We are now ready to evaluate the magnetic energy spectrum of each Cu$_5$ molecule and deduce its basic properties, according to the DFT values of the exchange couplings $J_i$. Using a site labeling convention in accord with the site symmetries, the spin Hamiltonian (disregarding anisotropies) reads:

$$\mathcal{H} = J_{12} S_1 S_2 + J_{13} (S_1 \cdot S_2 + S_1 \cdot S_3 - S_3 S_{11'}) + J_{23} (S_2 \cdot S_3 + S_2 \cdot S_{11'}) + J_{34} (S_3 \cdot S_4 + S_3 \cdot S_{11'}) + J_{34} (S_4 \cdot S_{11'} + S_4 \cdot S_{11'B}),$$

where $S_{11'}$ and $S_{11'B}$ are the central site $S_3$, which maps $S_3 \leftrightarrow S_3$, and $S_1 \leftrightarrow S_{11'}$, and

![FIG. 13. (Color online) Fit of the magnetic susceptibility ($\chi$) and inverse magnetic susceptibility ($\chi^{-1}$, inset) with the exact-diagonalization result for the Cu$_5$ pentamer ($J_{12} = -J_{13} = 65$ K and $J_{23}/J_{12} = 3.5$).](image1)

![FIG. 14. (Color online) Upper panel: magnetization of Cu$_5$-NIPA measured in pulsed magnetic field (in arb. units). Bottom panel: magnetization measured in static field up to 14 T and the simulated curve for $J_{12} = -J_{13} = 65$ K and $J_{23}/J_{12} = 3.5$ (both in units of $\mu_B$/f.u.). The arrow denotes the bend in the pulsed-field curve that matches the transition between the $\frac{1}{2}$ and $\frac{3}{2}$ states of the Cu$_5$ molecule.](image2)
$S_i \leftrightarrow S_{j'}$. So all eigenstates can be characterized by the total spin $S$, its projection $M$ along some quantization axis $z$, and the parity $p$ (even or odd) under inversion.

**Global spectral structure.** A straightforward numerical diagonalization of $\mathcal{H}$ yields the energy spectrum given in Table II. For each level we also provide the good quantum numbers $S$ and $p$, as well as the expectation values of the square of the composite spins $S_{22y}^2$, $S_{32y}^2$, and $S_{11'}^2$. The essential finding is that the GS is a total spin $S = \frac{1}{2}$ doublet and the lowest excitation (also a $S = \frac{1}{2}$ doublet) has a very high energy gap $\Delta = 0.313 \pm 0.024$ K. Thus the Cu$_5$ molecule behaves as a rigid $S = \frac{1}{2}$ entity for $T \ll \Delta$, confirming the previous experimental picture from magnetization measurements (Sec. III A 1).

Looking at Table II, we also find that the spectrum is organized in three compact groups of states, which are separated by horizontal lines. All states belonging to a given group show a very similar value of $\langle S_{ij}^z \rangle$, suggesting that the trimer of $S_3$, $S_2$, and $S_1$ plays a special role in the physics of Cu$_5$-NIPA. Moreover, the expectation values of $S_{22y}^2$, $S_{32y}^2$, and $S_{11'}^2$ are for all states very close to the formula $S(S + 1)$ for some integer or half-integer $S$, suggesting that these composite spins are almost conserved quantities. Below, we shall demonstrate that all these spectral features as well as the GS properties can be physically understood quite naturally on the basis of a strong coupling expansion around the limit of $J_{12} = J_{13} = 0$.

From the spectrum, we can also obtain the level-crossing fields at which the GS of the molecule changes from $S = \frac{1}{2}$ to $S = \frac{3}{2}$ and from $S = \frac{3}{2}$ to $S = \frac{5}{2}$. We find:

$$g \mu_B H_{c1}/k_B \approx 0.40 J_{23}, \quad g \mu_B H_{c2}/k_B \approx 1.43 J_{23}. \quad (9)$$

With $J_{23} = 217$ K and the average $g \approx 2.38$ (see previously), these numbers yield $H_{c1} \approx 54$ T (compare to Fig. 14) and $H_{c2} \approx 194$ T.

**GS properties.** To probe the nature of the GS, we calculate several experimentally relevant GS expectation values. We first consider how the total spin $S$ of the molecule changes (at low $T$, this moment can be attained by a small applied field) is distributed among the five Cu sites. At $T \ll \Delta$, we find

$$\langle S_i^z \rangle = \langle S_i^z \rangle_0 \times \tanh \left( \frac{g \mu_B H}{2k_BT} \right), \quad (10)$$

where $\langle S_i^z \rangle_0$ are the GS expectation values (in an infinitesimal field):

$$\langle S_3^z \rangle_0 = 0.1416, \quad \langle S_2^z \rangle_0 = \langle S_1^z \rangle_0 = -0.1415, \quad \langle S_1^z \rangle_0 = \langle S_1' \rangle_0 = 0.3207. \quad (11)$$

The signs of the above numbers are in agreement with the classical ferrimagnetic GS discussed above (Fig. 1, right), whereby the spins $S_3$, $S_1$, and $S_1'$ are aligned parallel to each other, but antiparallel to $S_2$ and $S_2'$. However, the strong deviation (especially for $S_3$, $S_2$, and $S_2'$) from their maximum (classical) value of $\frac{1}{2}$ indicates that this state has strong QM corrections, as can be directly seen from the explicit form of the wavefunction (not shown). This feature will be explained on the basis of the strong coupling description developed below.

The deviation of the local moments from Eq. (10) at high temperatures is shown in Fig. 15 at a field of 1.6608 T. We note in particular the non-monotonic temperature dependence of the magnitude of the Cu2 moments, which was discussed in Sec. III C 1 above in relation to the NMR lineshape.

To further probe the nature of the GS, we consider the strength of various spin-spin correlations $e_{ij} = \langle S_i \cdot S_j \rangle_0$.
We find $e_3 = e_3' \simeq 0.2122$, $e_2 = e_2' \simeq -0.4810$, $e_1 = e_1' \simeq -0.4299$, $e_1' = e_{112} \simeq -0.2858$, and $e_{111} = e_{112} \simeq 0.2345$. These values corroborate the above QM ferrimagnetic picture for the GS, and in addition highlight that the bonds with the largest exchange coupling $J_{23}$ (i.e., the bonds 3-2 and 3-2') exhibit also the strongest correlations. Moreover, using the above correlations and the values of the exchange couplings, one finds that the $J_{23}$ bonds contribute about 72% of the total GS energy $E_0 \simeq -1.3289 J_{23}$.

We should remark here that the above result $e_{111} = e_{112}$ does not arise from the symmetry of the Hamiltonian, but it is an exact property of the particular GS (see explanation below).

**Effective g-tensors.** To make contact with our ESR findings in Sec. III B we calculate the effective g-tensors of the GS and the first excited state in terms of the individual g-tensors of the three inequivalent Cu sites. To this end, one needs the equivalent spin operators within each multiplet in order to rewrite the Zeeman Hamiltonian as

$$\sum_i B \cdot g_i \cdot S_i \rightarrow B \cdot g_{\text{eff}} \cdot S.$$  \hspace{1cm} (12)

For the GS, the equivalent operators can be extracted from Eq. 11 above, which yields

$$g_{\text{eff}, \text{GS}} = +0.0708 g_3 - 0.1415 g_2 + 0.3207 g_1.$$  \hspace{1cm} (13)

So the deviation from the isotropic $g = 2$ value is coming mainly from that of $g_1$.

For the first excited state, our exact wavefunctions give the equivalent operators

$$S_3^x \rightarrow -\frac{1}{3} S, \quad S_2^x, S_2^z \rightarrow +0.1647 S, \quad S_1^x, S_1^z \rightarrow +0.002 S,$$  \hspace{1cm} (14)

leading to

$$g_{\text{eff}, \text{1st exc.}} = -\frac{1}{3} g_3 + 0.3294 g_2 + 0.004 g_1.$$  \hspace{1cm} (15)

So here the deviation from the isotropic $g = 2$ value is mainly governed by that of $g_2$ and $g_3$. The contribution from $g_1$ is extremely small because in the first excited doublet the pair of $S_1$ and $S_1'$ forms almost a singlet (see Table II and Sec. IV C below).

These expressions demonstrate why the effective g-tensors of the two ESR lines appearing below 70 K are different.

**C. Strong coupling description**

We are now going to show that almost all properties of the model at $y \equiv J_{12} = -J_{13} = \frac{1}{2}$ can be adiabatically traced back – even on a quantitative level – to the strong coupling limit $y = 0$.

**Global spectral structure.** At $y = 0$, the spins $S_1$ and $S_1'$ are isolated and are, thus, free to point up or down. On the other hand, the spins $S_3, S_2$, and $S_2'$ form an AFM spin trimer with the Hamiltonian

$$\mathcal{H}_0/J_{23} = S_3 \cdot (S_2 + S_2') = \frac{1}{2} (S_{322'} - S_{22'} - S_3^2).$$  \hspace{1cm} (16)

Hence the spectrum of $\mathcal{H}_0$ can be derived analytically in terms of the good quantum numbers $S_{22'}, S_{322'}$:

$$\begin{array}{cccc}
S_{22'}, S_{322'}, \text{parity}, \text{deg}, & E^{(0)} \\
1 \quad \frac{1}{2} & \text{even} & 8 & -J_{23} \\
0 \quad \frac{1}{2} & \text{odd} & 8 & 0 \\
1 \quad \frac{1}{2} & \text{even} & 16 & +J_{23}/2 \\
\end{array}$$  \hspace{1cm} (17)

where we have also indicated the parity and the degeneracy (deg) of each unperturbed level. The latter takes into account the four possible states of the space of $S_1$ and $S_1'$, and the Zeeman degeneracy. So we find three well separated unperturbed manifolds. The remaining couplings $\mathcal{V} \equiv \mathcal{H} - \mathcal{H}_0$ split these manifolds but, as we show below, most of these splittings are fairly weak, thus explaining the overall spectral structure at $y = \frac{1}{2}$ (Table II).

Since each unperturbed manifold has a well-defined $S_{322'}$, we can find the first-order splitting with the use of the “equivalent operators”:

$$S_3 \rightarrow \lambda_3 S_{322'}, \quad S_2 \rightarrow \lambda_2 S_{322'}, \quad S_2' \rightarrow \lambda_2' S_{322'},$$  \hspace{1cm} (18)

where the values of $\lambda_{1,2,2'}$ can be derived from the coupling (Clebsh-Gordan) coefficients of the respective angular momenta of each manifold (see below). Using $\lambda_2 = \lambda_2'$, which holds in all manifolds, and replacing (18) in $\mathcal{V}$, we obtain

$$\mathcal{V} \rightarrow J_{\text{eff}} S_{322'} \cdot S_1' = \frac{1}{2} J_{\text{eff}} (S_2 - S_{322'}^2 - S_1')^2,$$  \hspace{1cm} (19)

where $J_{\text{eff}} = (\lambda_2 - \lambda_3) y$. Thus, to lowest order, the perturbation gives rise to an effective exchange coupling between $S_{11'}$ and $S_{322'}$.

For the lowest eight-dimensional manifold, we couple the spin $S_3 = \frac{1}{2}$ to the spin $S_{22'} = 1$ to get an $S_{322'} = \frac{1}{2}$ object, which gives (see Appendix A): $\lambda_3 = -\frac{1}{2}$, $\lambda_2 = \lambda_2' = +\frac{1}{2}$, and thus $J_{\text{eff}} = y$. The resulting correction to the lowest unperturbed manifold reads:

$$\begin{array}{cccc}
S_{22'}, S_{322'}, S_{11'}, S, \text{parity}, \text{deg}, & \Delta E^{(1)} \\
1 \quad \frac{1}{2} & 1 \quad \frac{1}{2} & \text{even} & 2 & -y \\
1 \quad \frac{1}{2} & 0 \quad \frac{1}{2} & \text{odd} & 2 & 0 \\
1 \quad \frac{1}{2} & 1 \quad \frac{1}{2} & \text{even} & 4 & +y/2 \\
\end{array}$$  \hspace{1cm} (20)

Similarly, the second unperturbed manifold has $S_{22'} = 0$ and thus $\lambda_2 = \lambda_2' = 0$ and $\lambda_3 = 1$, giving $J_{\text{eff}} = -y$, which is now FM. So the first-order splitting of this manifold has the opposite structure from that of the lowest manifold,
remain good quantum numbers in higher orders of the maximum polarized perturbation theory, as can be easily checked, e.g., for its $J = 0$ up to $y = \frac{4}{7}$. The energies are given in units of $J_{23}$.

\[ \Delta E^{(1)} = \frac{1}{2} y \]

The third manifold has $S^{22'} = \frac{3}{2}$ and thus $\lambda_3 = \lambda_2 = \lambda_2' = \frac{1}{3}$, which in turn gives $J_{45} = 0$. Thus, the third unperturbed manifold remains intact in lowest order, i.e., all 16 states have $\Delta E^{(1)} = 0$:

\[ S^{22'}, S^{322'}, S^{11'}, S, \text{ parity } p, \text{ deg. } \Delta E^{(1)} \]

1. $\frac{3}{2}$ 1 $\frac{1}{2}$ even 2 0
2. $\frac{3}{2}$ 0 $\frac{1}{2}$ odd 2 $+y$
3. $\frac{3}{2}$ 1 $\frac{1}{2}$ even 2 0
4. $\frac{1}{2}$ 0 $\frac{1}{2}$ odd 2 0

In particular, the energy of the state with the maximum spin ($S = \frac{3}{2}$) remains equal to $J_{23}/2$ in all orders of perturbation theory, as can be easily checked, e.g., for its maximum polarized $M = \frac{3}{2}$ portion, which is a trivial eigenstate of $\mathcal{H}$.

Up to this lowest order, the level-crossing fields $H_{c1}$ and $H_{c2}$ are given by

\[ g\mu_B H_{c1}/k_B \approx \frac{3}{2} y / 2, \quad g\mu_B H_{c2}/k_B \approx (3J_{23} - y)/2. \]  

With $J_{23} = 217$ K, $y = 2J_{23}/7$, and the average $g \approx 2.2$, these numbers give: $H_{c1} \approx 54$ T, and $H_{c2} \approx 170$ T, which are close to the exact numbers at $y = \frac{4}{7}$ given above.

Figure 16 shows the evolution of the spectrum from $y = 0$ up to $y = \frac{4}{7}$, and demonstrates that the above first-order spectral structure reproduces quantitatively the spectrum at $y = \frac{4}{7}$.

We should add here that $S^{22'}, S^{322'},$ and $S^{11'}$ do not remain good quantum numbers in higher orders of the perturbative expansion, which is expected, since the corresponding angular momenta are not conserved quantities under the full Hamiltonian. Still, their expectation values reported in Table II are very close to the above strong-coupling values.

As a final remark, we note that one may use the above basis provided by the lowest-order theory and the good quantum numbers $S$, $M$, and $p$ to find the invariant subspaces of $\mathcal{H}$. Most of the subspaces turn out to be two-dimensional, except for the space with $S = M = \frac{1}{2}$ and $p = \text{even}$ (in which the GS belongs), which is three-dimensional. Here, it may be readily checked that each of the three states has $S^{11'} = S^{22'}$, thus explaining the equality $e^{11'} = e^{22'}$ discussed above. The excited states do not share this property, so at higher temperatures the two correlations deviate from each other.

**GS properties.** Let us now return to the nature of the GS. According to the above lowest order result, the GS is a total $S = \frac{1}{2}$ doublet with even parity and total energy $E^{(1)} = -J_{23} - J_{12}$. To understand the nature of this state, we note that it arises from the coupling of a spin $s = \frac{1}{2}$ (here $S^{322'}$) and a spin $s = 1$ (here $S^{11'}$) to a total $S = \frac{1}{2}$ state. So we may again use the “equivalent operators”

\[ S^{322'} \rightarrow -\frac{1}{2} S, \quad S^{11'}, S \rightarrow +\frac{2}{3} S. \]

which in conjunction with the ones relating $S_1$, $S_3$, and $S_5$ to $S^{322'}$ (see Eq. (18) above) gives the central relations:

\[ S_3 \rightarrow +\frac{1}{2} S, \quad S_2, S_4 \rightarrow -\frac{2}{3} S, \quad S_1, S_1' \rightarrow +\frac{2}{3} S. \]

This equation provides a very clear explanation for the peculiar local moment distribution discussed above, since, when the total $S = \frac{1}{2}$ moment is saturated (by
applying a small field), this equation gives:
\[
\langle S_{ij}^z \rangle = + \frac{1\hbar}{2}, \\
\langle S_{ij}^x \rangle = \langle S_{ij}^y \rangle = - \frac{1\hbar}{2}, \\
\langle S_{ij}^y \rangle = \langle S_{ij}^x \rangle = + \frac{1\hbar}{2}.
\] (26)

The same numbers can be extracted directly from the explicit form of the GS wavefunction, which for the \( M = + \frac{1}{2} \) portion reads:
\[
\langle \hat{\sigma} \rangle = - \frac{2}{3} \langle \uparrow \rangle_3 |t_1|_{11} \langle \downarrow \rangle_{-1} |t_2|_{22} + \frac{1}{3} \langle \uparrow \rangle_3 |t_0|_{11} |t_0|_{22} \\
+ \sqrt{\frac{2}{3}} \langle \downarrow \rangle_3 (|t_1|_{11} |t_0|_{22} |t_0|_{11} |t_1|_{22}),
\] (27)

where \( |t_i|_{jj} | = | \uparrow \rangle_j \), \( |t_{-1}|_{jj} = | \downarrow \rangle_j \), and \( |t_0|_{jj} = (| \uparrow \rangle_j + | \downarrow \rangle_j) / \sqrt{2} \). The leading term of Eq. (27) is the classical ferrimagnetic configuration. However, the overall form of the wavefunction demonstrates explicitly the presence of strong QM corrections to the GS.

The strong coupling limit reproduces the ferrimagnetic arrangement of the local moments and even their strengths, except for \( S_3 \) which has almost tripled its moment at \( y = \frac{1}{2} \). This is further demonstrated in Fig. 16(b), which shows the evolution of the local moments from \( y = 0 \) up to \( y = \frac{1}{2} \). All moments, except \( \langle S_{ij}^y \rangle \), exhibit a small slope, i.e., higher-order corrections are weak.

In a similar fashion, the strong coupling prediction for the spin-spin correlations are: \( e_{11} = e_{31'} = \frac{1}{2} \), \( e_{32} = e_{32'} = - \frac{1}{2} \), \( e_{12} = e_{12'} = e_{13'} = e_{13} = - \frac{1}{2} \), and \( e_{11'} = e_{22'} = + \frac{1}{2} \), which are in close agreement with the exact values for \( y = \frac{1}{2} \) given earlier. This is again demonstrated in Fig. 16(c) that shows the evolution of the spin-spin correlation strengths from \( y = 0 \) up to \( y = \frac{1}{2} \). All correlations exhibit weak corrections, except \( e_{12} \) which shows a somewhat larger slope in \( y \).

V. DISCUSSION AND SUMMARY

The Cu$_5$-NIPA molecule comprises two non-frustrated spin triangles with two AFM couplings and one FM coupling each (Fig. 1, left). This coupling regime is rather unusual and deserves a further analysis with respect to the underlying crystal structure and interacting orbitals. Three leading couplings – \( J_{12}, J_{13}, \) and \( J_{23} \) – represent the Cu–O–Cu superexchange running via the $\mu_3$-O atom in the middle of the Cu$_5$ triangle. According to Goodenough-Kanamori rules, high values of the bridging angle should lead to an AFM interaction, whereas low bridging angles should lead to a zero interaction, whereas low bridging angles close to 90° favor AFM couplings. Our results for Cu$_5$-NIPA (Table I) follow this general trend. However, a closer examination pinpoints two peculiarities of this compound.

First, the coupling remains FM for the bridging angle of 107.9°, although the standard and commonly accepted threshold value of the FM-AFM crossover is slightly below 100°.\(^{70}\) Second, \( J_{12}^{FM} \) is much larger than \( J_{13}^{FM} \), even though the respective bridging angle is also larger and should lead to a smaller FM contribution. Both peculiarities should be traced back to the twisted configuration of the interacting CuO$_4$ plaquettes (Fig. 1, left). The systematic work on the angular dependence of the exchange coupling is usually restricted to systems with two plaquettes lying in the same plane or only weakly twisted (the dihedral angle between the planes is close to 180°). The Cu$_5$ molecule represents an opposite limit of strongly twisted CuO$_4$ plaquettes, with the dihedral angles of 91.8 deg (\( J_{12} \)), 125.2 deg (\( J_{13} \)), and 99.9 deg (\( J_{23} \)) between the CuO$_4$ planes.\(^{71}\)

The large FM contribution to \( J_{12} \) (\( J_{12}^{FM} = -134 \) K) can be ascribed to the nearly orthogonal configuration of the interacting CuO$_4$ plaquettes. However, the mechanism of this FM interaction is yet to be determined. The large FM coupling for the bridging angle of 90 deg is generally understood as the Hund’s coupling on the oxygen site\(^{72}\) or the direct FM exchange between Cu and O.\(^{73}\) Both mechanisms depend solely on the Cu–O–Cu angle and should be rather insensitive to the mutual orientation of the CuO$_4$ plaquettes. Therefore, other effects, such as the direct Cu–Cu exchange and the Cu–O–Cu interaction involving fully filled Cu 3d orbitals, may be operative. Experimental information on the magnetic exchange between the strongly twisted CuO$_4$ plaquettes remains scarce and somewhat unsystematic. The Cu–O–Cu angle of 104.5 deg combined with the sizable twisting give rise to a FM nearest-neighbor interaction in the kagome material kapellasite Cu$_2$Zn(OH)$_6$Cl$_2,\(^{74}\) whereas a similar geometry with the Cu–O–Cu angle of 107.6 deg results in an overall AFM coupling in dioptase, Cu$_6$Si$_6$O$_{18}$·6H$_2$O.\(^{75}\)

We also note that Cu$_5$-NIPA brings a fresh perspective on magnetostructural correlations in Cu$_5$ triangular molecules, where the Cu–X–Cu bridging angle was previously considered the key geometrical parameter. As long as the ligand atom X lies in the Cu$_5$ plane, the bridging angles remain close to 120 deg and should generally lead to the AFM exchange. The FM exchange would only be possible when the ligand atoms are shifted out of the plane, as in the Cl- and Br-containing Cu$_5$ molecules where the Cu–X–Cu angles are below 90 deg.\(^{76}\) The twisting of the CuX$_3$ plaquettes provides another opportunity for creating the FM exchange and, moreover, for introducing it selectively. Surprisingly, organic ligands have only a weak effect on the magnetic interactions. Although carboxyl groups (COO$^-$) provide an additional superexchange pathway between Cu1 and Cu3 (Fig. 1, left), their molecular orbitals do not influence the Cu d$_{xy}$ Wannier functions (Fig. 12). For example, the FM contribution to \( J_{12} \) exceeds that to \( J_{13} \). This demonstrates that the FM exchange is basically unrelated to the organic ligands. It should be understood as a joint effect of the the low Cu–O–Cu angle and twisting.

The combination of FM and AFM couplings also has an important effect on the magnetic GS of Cu$_5$-NIPA. A regular spin triangle entails the four-fold degenerate
GS that further splits into two close-lying doublets by virtue of anisotropy, 27 residual interactions between the triangles, 10 or a marginal distortion of the triangle. 29 In Cu5-NIPA, there is only one doublet state, which is separated by about 68 K from the first excited state (see Table I). According to Kramer’s theorem, in zero field the degeneracy of this state can not be lifted, hence the tunnel splitting is exactly zero, and no magnetization steps (Landau-Zener-Stückelberg transitions) should occur, in contrast to, e.g., the V6 molecule. 10 Therefore, broad butterfly hysteresis effects but without tunneling are expected in the magnetization process of Cu5-NIPA.

Of particular interest is our experimental finding of the enhanced 1H nuclear spin-lattice relaxation rate 1/T1 at a characteristic temperature slightly below the spin gap (T ≃ 40 K). While such an enhancement has been repeatedly found in numerous AFM homometallic 38 and heterometallic 39 rings of spins S > 1/2, it is very rare for S = 1/2 and has been observed only in molecules with a high-spin GS. 63,64 The origin of the peak is likely the same in both cases, namely, the slowing down of the phonon-driven magnetization fluctuations. 38,40–42 However, the sparse excitation spectrum and the presence of nonequivalent Cu sites with different local magnetizations render Cu5-NIPA dissimilar to typical homometallic rings. We argue that in Cu5-NIPA inter-multiplet Orbach processes make the dominant contribution to the spin-lattice relaxation process, as in the heterometallic ring Cr3Ni at very low temperatures. 56

The use of molecular magnets in quantum computing is severely restricted by their short coherence time. Coherence times on the order of 100 μs could be achieved in, e.g., V15 by arranging magnetic molecules in a self-assembled layer formed by an organic surfactant. 18 This method is fundamentally similar to the formation of the metal-organic framework in Cu5-NIPA. Therefore, it may be interesting to study the decoherence process in this molecular magnet and, more generally, explore the role of organic bridges in the decoherence process.

Finally, we would like to note that only a few examples of magnetic pentamers based on spin-1/2 ions have been reported so far. The [Cu(μ-L)3]2Cu3(μ3-OH)(PF6)3·5H2O (L− = 3,5-bis(2-pyridyl)pyrazolate) shows a somewhat similar phenomenology with the spin S = 1/2 GS and the respective magnetization plateau ranging up to 30 T. 77 However, the geometrical structure of this compound is a trigonal bipyramid that is notably different from the hourglass shape of the magnetic cluster in Cu5-NIPA.

The magnetic pentamer based on Cu5(OH)4(H2O)2(α-SiW6O34)2] is more similar to our case and also reveals the spin S = 1/2 GS. 51,78 Nevertheless, the equivalence of J23 and J34, as well as sizable long-range couplings, distinguishes its spectrum and magnetic properties from that of Cu5-NIPA.

In summary, we have studied thermodynamic properties, spin dynamics, microscopic magnetic model, and energy spectrum of the spin-1/2 Cu5 pentamer in Cu5-NIPA. This magnetic molecule has an hourglass shape with two AFM couplings and one FM coupling on each of the two triangles that form the non-frustrated pentamer. In zero field, the ground state of Cu5-NIPA is a doublet with the total spin of S = 1/2. This ground state is separated from the first excited state by an energy gap of Δ ≃ 68 K. Our results evidence a highly inhomogeneous distribution of magnetization over the nonequivalent Cu sites according to the quantum nature of the magnetic ground state. The maximum in the spin-lattice relaxation rate 1/T1 is very rare among molecular magnets with spin-1/2 ions and a low-spin ground state.

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Appendix A: Coupling of a spin 1 to a spin 1/2 object and “equivalent operators”

Here we work out the coupling of two spins, one with spin Sα = 1/2 and the other one with Sβ = 1. For the latter, we shall imagine that there are two spins Sβ = Sβ = 1/2 forming a triplet, namely |t1⟩ = |↑⟩, |t−1⟩ = |↓⟩, and |t0⟩ = 1/√2 (|↑⟩ + |↓⟩). The states of the system can be labeled by S, M, where S is the total spin (here S = 1/2 or 3/2) and M is the projection along some axis z.

The states with S = 3/2 are given by:

| 3/2, 3/2⟩ = |↑⟩a ⊗ |t1⟩bc,  
| 3/2, 1/2⟩ = 1/√3 (|↓⟩a ⊗ |t1⟩bc + √2 |↑⟩a ⊗ |t0⟩bc),  
| 3/2, −1/2⟩ = 1/√3 (|↑⟩a ⊗ |t−1⟩bc + √2 |↓⟩a ⊗ |t0⟩bc),  
| 3/2, −3/2⟩ = |↓⟩a ⊗ |t−1⟩bc.

On the other hand, the two states of the S = 1/2 doublet read:

| 1/2, 1/2⟩ = 1/√3 (|↑⟩a ⊗ |t0⟩bc − √2 |↓⟩a ⊗ |t1⟩bc),  
| 1/2, −1/2⟩ = 1/√3 (−|↓⟩a ⊗ |t0⟩bc + √2 |↑⟩a ⊗ |t−1⟩bc).

Using the above explicit relations, it is straightforward to find out the equivalent operators within the 2×2 manifold.
of the $S = \frac{1}{2}$ doublet. We find:

$$S_a \rightarrow -\frac{1}{3} S, \quad S_b \rightarrow +\frac{2}{3} S, \quad S_c \rightarrow +\frac{2}{3} S. \quad (A1)$$

### Appendix B: Structural data

Table III shows the equilibrium positions of the 17 hydrogen nuclei in the structure.

**TABLE III.** Relaxed hydrogen positions in Cu$_5$-NIPA. Last column lists atoms bonded to the given hydrogen atom. The notation of atoms follows Ref. 22, $a = 10.8303$ Å, $b = 11.4692$ Å, and $c = 11.5697$ Å.

<table>
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<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>Bonded to</th>
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</tr>
<tr>
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<td>0.3482</td>
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</tr>
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</tr>
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</tr>
<tr>
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<tr>
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<tr>
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<tr>
<td>H18B</td>
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<td>0.1190</td>
<td>0.6921</td>
</tr>
</tbody>
</table>

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15 B. Guigliarelli, C. More, A. Fournel, M. Asso, E. C. Hatchikian, R. Williams, R. Cammack, and P. Bertrand,


Note that we do not use the temperature-independent term \( \chi_0 \), because fits for the pristine sample are done in a narrow temperature range that does not support the evaluation of three variable parameters. The lack of \( \chi_0 \) results in subtle deviations of the high-temperature effective moment from the \( g \)-value obtained in the model fit (Fig. 13).


Here, we averaged four Cu–O vectors of each plaquette, because Cu and O atoms do not form a single plane owing to the low crystallographic symmetry of the compound.