Magnetic and entanglement properties of molecular $\text{Cr}_{2n}\text{Cu}_2$ heterometallic spin rings

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We investigate the low-temperature magnetic and entanglement properties of a series of molecular $\text{Cr}_{2n}\text{Cu}_2$ heterometallic spin rings (with $n = 4, 5, 6$). These are cyclic spin systems, consisting of two Cu^{2+} ($s = 1/2$) ions, coupled by two antiferromagnetic segments of n Cr^{3+} ($s = 3/2$) ions. Thermodynamic measurements (magnetization, susceptibility, and specific heat) allow us to determine the total spin of the ground state and to estimate the spin-Hamiltonian parameters related to magnetic anisotropy. X-ray spectroscopies (XAS and XMCD) are used to probe the local magnetization of the Cr and Cu ions, and provide results that are consistent with the bulk magnetization data. We finally investigate the relation between heterometallicity and entanglement in these prototypical spin systems. In particular, we focus on the spatial modulation of entanglement induced by the Cu defect spins and on the long-distance entanglement between them induced by the two Cr chains.

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I. INTRODUCTION

Molecular nanomagnets represent a rich playground to test new concepts and theoretical models. The interest of both chemists and physicists was aroused by the discovery of quantum phenomena in high-spin Mn_{12} and Fe_8 molecules¹ that first revealed the potentialities of these systems. These are mostly related to the possibility of tuning the relevant physical parameters in molecular nanomagnets, such as the spin values and their mutual interactions, as well as the size, dimensionality, and topology.

More recently, a great deal of interest has been directed to the possible exploitation of molecular nanomagnets for quantum-information processing.² In this perspective, one of the fundamental requirements is the control of quantum entanglement,³ which represents a key resource in quantum computation and communication.⁴ The controlled introduction of magnetic defects can be regarded as a suitable means for engineering entanglement in molecular spin clusters. In particular, the replacement of a given magnetic ion with a different chemical element can introduce a different spin and different exchange couplings in an otherwise homogeneous system. Both these features are present in the class of systems considered hereafter. These are a family of hourglass-shaped molecular nanomagnets, namely $\text{Cr}_{2n}\text{Cu}_2$, where two identical antiferromagnetic chains of Cr^{3+} ($s = 3/2$)—with variable length n —connect two Cu ions ($s = 1/2$). The synthesis and some magnetic properties of a part of these derivatives have already been reported in the literature.^{5–7} Here we use susceptibility, magnetization, and heat capacity experiments to determine the essential microscopic parameters that characterize these spin systems. More specifically, the fine structure in the low-energy spectra is investigated by means of low-temperature specific-heat measurements that allow us to determine the anisotropy parameters within the lowest spin multiplet. The inhomogeneities introduced within the molecules by heterometallicity are captured by experimental techniques which are chemically selective, such as x-ray magnetic dichroism. So, experiments of x-ray absorption spectra

(XAS) and circularly polarized magnetic dichroism (XMCD) are also performed, in order to probe local magnetization.

The heterometallic nature of these molecules also has interesting implications from the point of view of quantum entanglement, which we investigate here by theoretical means. In this perspective, the $\text{Cr}_{2n}\text{Cu}_2$ heterometallic spin rings offer the possibility of investigating two peculiar features with respect to, e.g., the molecules of the Cr_7M series.⁸ The first one is the interplay between the entanglement modulation induced by the two magnetic defects and by the additional inhomogeneity introduced by the Cu ions (besides the spin value), which is represented by the exchange couplings. The second issue is long-range entanglement, and can be related to specific protocols in quantum communication. In fact, while quantum correlations typically take place between neighboring spins that are directly coupled by an exchange interaction, one might ask under which conditions (i.e., in which parameter range) entanglement can arise between distant spins.⁹ In this perspective, the $s = 1/2$ spins of the Cu ions can be regarded here as the carriers of quantum information, and the two chains of n Cr spins as two parallel quantum channels that induce an effective coupling between them.

The paper is organized as follows: In Sec. II we present the synthesis and the structure for different derivatives; in the successive Sec. III we report on the thermodynamic properties and use them to derive the essential parameters that enter the spin Hamiltonian; in Sec. IV we report results of x-ray spectroscopies and their analysis; in Sec. V we theoretically investigate the effect on entanglement of heterometallicity. Finally, in Sec. VI, we summarize the results and provide a brief outlook.

II. STRUCTURES AND SYNTHESIS DETAILS

The investigated family, namely $\text{Cr}_{2n}\text{Cu}_2$, is formed by three molecular rings, each one constituted by two twin chromium Cr^{3+} ($s = 3/2$) chains of length n , linked by two copper Cu^{2+} ions (with $s = 1/2$). Their chemical formulas are as follows:

$[\text{HBz}]_2[\text{Cr}_8\text{Cu}_2\text{F}_{14}(\text{O}_2\text{CCMe}_3)_{16}(\text{Bz})_2]$ (Cr_8Cu_2 in short), ($\text{Bz} = \text{C}_7\text{H}_6\text{N}_2$)

$[(\text{C}_8\text{H}_{17})_2\text{NH}_2]_2[\text{Cr}_{10}\text{Cu}_2\text{F}_{14}(\text{O}_2\text{CCMe}_3)_{22}]$ ($\text{Cr}_{10}\text{Cu}_2$ in short),

$[(\text{Me}_2\text{CH})_2\text{NH}(\text{C}_2\text{H}_5)]_2[\text{Cr}_{12}\text{Cu}_2\text{F}_{16}(\text{O}_2\text{CCMe}_3)_{26}]$ ($\text{Cr}_{12}\text{Cu}_2$ in short).

The synthesis of Cr_8Cu_2 is described in Ref. 5 (compound 5). $\text{Cr}_{10}\text{Cu}_2$ was obtained similarly to compound 1c in Ref. 5, by using the dioctylamine instead of the diethylamine. X-ray quality crystals were obtained by crystallization of the compound from an Et_2O /acetone mixture. The yield is 27%, the elemental analysis calculated (%) for $\text{C}_{142}\text{H}_{270}\text{Cr}_{10}\text{Cu}_2\text{F}_{14}\text{N}_2\text{O}_{44}$ is Cr 14.35, Cu 3.51, C 47.08, H 7.51, N 0.77; while was found Cr 14.69, Cu 3.50, C 46.81, H 7.72, N 0.74.

The $\text{Cr}_{12}\text{Cu}_2$ molecule was obtained similarly to compound 2 in Ref. 5, by using the N,N-diisopropylethylamine instead of the diisopropylamine, and the heating was at 140 °C for 8 h. X-ray quality crystals were obtained by crystallization of the compound from toluene. In this case, the yield is 30%, the elemental analysis calculated (%) for $\text{C}_{146}\text{H}_{274}\text{Cr}_{12}\text{Cu}_2\text{F}_{16}\text{N}_2\text{O}_{52}$ reads Cr 15.82, Cu 3.22, C 44.45, H 7.00, N 0.71; while was measured Cr 15.72, Cu 3.23, C 44.55, H 7.07, N 0.69.

Figure 1 shows the crystallographic structures of the $\text{Cr}_{2n}\text{Cu}_2$ systems. In Cr_8Cu_2 each Cu-Cr edge is bridged by one fluoride and one pivalate; moreover, each Cr adjacent to the copper sites has terminal fluorides attached to it. In all the other cases, the copper centers are bridged to the two adjacent chromium ions in different ways: on one side through one fluoride and two pivalates, and on the other side through only one fluoride and one pivalate. The Cr-Cr edges are bridged by one fluoride and two carboxylates in Cr_8Cu_2 , and by one fluoride and two pivalates in all the other derivatives. As a result, in all the systems antiferromagnetic exchange coupling between neighboring Cr spin centers is achieved, while the Cu ions have a ferromagnetic coupling with one of the neighboring chromiums, and an antiferromagnetic coupling with the other one.

FIG. 1. (Color online) Crystallographic structure of (a) Cr_8Cu_2 , (b) $\text{Cr}_{10}\text{Cu}_2$, and (c) $\text{Cr}_{12}\text{Cu}_2$ from Ref. 5. Colors: Cr, green; Cu, orange; F, yellow; O, red; C, black; N, blue. Hydrogen atoms and terminal carbons in the pivalates groups are omitted for clarity.

III. THERMODYNAMIC PROPERTIES

In order to magnetically characterize the molecules and to estimate the parameters that enter their spin Hamiltonian, we measure different thermodynamic quantities. In particular, ac susceptibility and dc magnetization allow us to estimate the dominant exchange couplings, whereas low-temperature specific-heat measurements allow us to derive anisotropy parameters. All these measurements were performed with a Quantum Design PPM system. Heat capacities were measured by the relaxation method on samples of pressed powders with a typical mass of 2 mg.

A. Magnetic properties

In Fig. 2, we report the temperature dependence of the ac susceptibility χ for all the $\text{Cr}_{2n}\text{Cu}_2$ derivatives. The χT curves rise with the temperature. At high temperatures, the χT values are progressively higher with increasing dimension of the ring (e.g., the χT curve of $\text{Cr}_{10}\text{Cu}_2$ is above that of Cr_8Cu_2), as expected for increasing number of paramagnetic noninteracting spins. At low temperature the susceptibilities of Cr_8Cu_2 and $\text{Cr}_{12}\text{Cu}_2$ merge and point to the same value of 1 emu K mol^{-1} (dashed line), as expected for an $S = 1$ ground state. In the case of $\text{Cr}_{10}\text{Cu}_2$, the susceptibility at low T goes to zero, consistently with the expected $S = 0$ ground state.⁶

These guesses are supported by isothermal ($T = 2.2 \text{ K}$) dc magnetization, plotted in Fig. 3 for all the derivatives. In the case of Cr_8Cu_2 , $M(H)$ has a first plateau at $2 \mu_B$ (dashed line), suggesting an $S = 1$ ground state.⁵ This magnetization curve also indicates that the gap between excited and ground states becomes comparable to the experimental temperature for fields above $\sim 6 \text{ T}$, and that consequently excited states are contributing to the magnetization. This behavior is more accentuated in $\text{Cr}_{12}\text{Cu}_2$, where a clear change of $M(H)$ is

FIG. 2. Temperature dependence of the ac susceptibility (χT), measured for Cr_8Cu_2 (Ref. 5), $\text{Cr}_{10}\text{Cu}_2$, and $\text{Cr}_{12}\text{Cu}_2$. At low temperature, Cr_8Cu_2 and $\text{Cr}_{12}\text{Cu}_2$ tend to saturate to the value 1 emu K mol^{-1} (dashed line), as expected for an $S = 1$ ground state. The solid line is the result of spin-Hamiltonian calculations for Cr_8Cu_2 , as described in the text.

FIG. 3. Magnetization measured at $T = 2.2$ K for Cr_8Cu_2 (Ref. 5), $\text{Cr}_{10}\text{Cu}_2$, and $\text{Cr}_{12}\text{Cu}_2$. The solid curves are guidelines for the eyes.

visible, with a flex at about 5 T. We deduce that in this case the ground and excited states are closer in energy with respect to Cr_8Cu_2 . For $\text{Cr}_{10}\text{Cu}_2$ finally, isothermal magnetization curves continuously increase with the field, confirming that low-lying excited levels are well populated at 2.2 K.

B. Specific heat

Low-temperature specific heat $C(T, H)$ allows evidence of the zero-field splitting of the lowest energy levels. The $C(T, H)$ curves are shown in Fig. 4 for different compounds of the $\text{Cr}_{2n}\text{Cu}_2$ family at different applied magnetic fields H between 0 and 7 T; the specific heat is normalized to the gas constant $R = 8.314 \text{ J/mol K}$. As a common characteristic, data obtained at different magnetic fields overlap at temperatures $T > 5$ K. This is due to the fact that above such temperature, the lattice contribution overwhelms the magnetic term. At lower temperatures magnetic features become visible. Consis-

tently with susceptibility and magnetization measurements, the low-temperature specific heat behaviors evidence a difference between the Cr_8Cu_2 and $\text{Cr}_{12}\text{Cu}_2$ systems (both with an even number n of Cr ions in each chain) from one side, and $\text{Cr}_{10}\text{Cu}_2$ (with odd n) from the other side. For the former compounds, the specific heat at $H = 0$ shows two well-defined Schottky anomalies that can be attributed to the zero-field splitting of the ground-state multiplet (energy gap $\Delta_{zfs} < 1$ K) and to the energy gap between the ground and the excited states ($\Delta \simeq 10$ K). For $\text{Cr}_{10}\text{Cu}_2$, the ground state is a singlet, but we may consider a finite zero-field splitting ($\Delta_{zfs} = 1.2$ K) within the first excited $S = 1$ triplet, which lies $\Delta = 3.6$ K above the ground state.⁶

C. Analysis of the thermodynamic properties

Thanks to these pronounced Schottky anomalies, the low-temperature specific heat allows us to estimate the zero-field splitting of the ground-state multiplet. In fact, C is given by the sum of a lattice and a magnetic contribution: $C = C_{\text{mag}} + C_{\text{latt}}$.¹⁰ Below 20 K, the lattice term C_{latt} is mainly due to the acoustic phonon branches, and it can be fitted by the phenomenological (Debye-like) expression:

$$\frac{C_{\text{latt}}}{R} = \frac{234rT^3}{(\Theta_D + \delta T^2)^3}, \quad (1)$$

as discussed in Ref. 10. The lattice parameters Θ_D and δ are obtained by least-squares fitting of the specific heat in the temperature range 5–15 K, while r is the number of atoms per unit cell, known by the structure formula. The magnetic contribution C_{mag} can be written as a function of the energy levels ϵ_j :¹⁰

$$\frac{C_{\text{mag}}}{R\beta^2} = \frac{\sum_j \epsilon_j^2 e^{-\beta\epsilon_j} \sum_j e^{-\beta\epsilon_j} - (\sum_j \epsilon_j e^{-\beta\epsilon_j})^2}{(\sum_j e^{-\beta\epsilon_j})^2}, \quad (2)$$

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ being the gas constant and $\beta = 1/k_B T$. The term C_{mag} , as well as the magnetization and susceptibility, have been simulated by spin-Hamiltonian

FIG. 4. Temperature and magnetic field dependence of the specific heat $C(T, H)$, measured for (a) Cr_8Cu_2 , (b) $\text{Cr}_{10}\text{Cu}_2$, and (c) $\text{Cr}_{12}\text{Cu}_2$ powder sample at different applied fields H . Estimated magnetic and lattice contributions to the specific heat at zero applied field (solid and dashed lines, respectively) are also reported. The magnetic contribution is estimated as the Schottky anomaly [Eq. (2)], discussed in the text.

TABLE I. Fitting parameters that enter the expressions of the lattice contribution to the specific heat (C_{latt}) and the effective Hamiltonian H_{an} defined within the lowest $S = 1$ triplet.

	r	Θ_D (K)	δ (K^{-1})	D/k_B (K)	E/k_B (K)
Cr_8Cu_2	376	138	0.50	-0.36 ± 0.07	0.17 ± 0.03
$\text{Cr}_{10}\text{Cu}_2$	448	143	0.45		
$\text{Cr}_{12}\text{Cu}_2$	504	136	0.55	-0.9 ± 0.2	0.20 ± 0.07

calculations of the form

$$H = H_{\text{ex}} + H_{\text{an}} + H_Z. \quad (3)$$

The dominant term, H_{ex} , accounts for the isotropic exchange interaction between nearest neighbors and is given by

$$H_{\text{ex}} = J_1 \sum_{k=1}^{n-1} (\mathbf{s}_{k+1} \cdot \mathbf{s}_{k+2} + \mathbf{s}_{k+n+2} \cdot \mathbf{s}_{k+n+3}) + J_2 (\mathbf{s}_{n+1} \cdot \mathbf{s}_{n+2} + \mathbf{s}_{2n+2} \cdot \mathbf{s}_1) + J_3 (\mathbf{s}_1 \cdot \mathbf{s}_2 + \mathbf{s}_{n+2} \cdot \mathbf{s}_{n+3}), \quad (4)$$

where $s_1 = s_{n+2} = 1/2$ and all other spins are $s_k = 3/2$, and the presence of two different exchange couplings (J_2 and J_3) for each Cu spin reflects the above-mentioned difference between the two Cu-Cr exchange bridges. As to the smaller, anisotropy term, we have treated it perturbatively within each of the lowest spin multiplets. In particular, the effects of anisotropy only being visible within the ground or first excited multiplets, and these always being either the singlet or the $S = 1$ triplet in the present $\text{Cr}_{2n}\text{Cu}_2$ molecules, we neglect anisotropies within $S = 2$ and use $H_{\text{an}} = \mathbb{P}_{S=1} \otimes [DS_z^2 + E(S_x^2 - S_y^2)]$, where $\mathbb{P}_{S=1}$ is the projector onto the lowest $S = 1$ triplet. Within such subspace, the analytical expressions for the eigenstates of H_{an} , as a function of the axial D and rhombic E anisotropy constants, read¹¹

$$\begin{aligned} \epsilon_0 &= D/3 + [E^2 + (g\mu_B H)^2]^{1/2}, \\ \epsilon_1 &= -2D/3, \\ \epsilon_2 &= D/3 - [E^2 + (g\mu_B H)^2]^{1/2}, \end{aligned}$$

for the $M = -1, 0, +1$ eigenstates of H_{ex} that form the lowest $S = 1$ triplet, respectively. Finally, the Zeeman term is given by $H_Z = g\mu_B B S_z$.

The calculations concerning the Cr_8Cr_2 molecule have been performed with the same set of exchange constants that are reported in the literature for the description of Cr_8Cu_2 and $\text{Cr}_{10}\text{Cu}_2$ (Refs. 5–7): $J_1 = 15$ K, $J_2 = 54$ K, and $J_3 = -10$ K. We note that the Cr-Cr exchange constant (J_1) is essentially the same for all the ring cycles;^{12,13} this is due to the fact that two adjacent Cr ions are always bridged by two carboxylates and one fluorine. The exchange Hamiltonian alone allows us to reproduce the temperature dependencies of the magnetic susceptibility (Fig. 2).

The contribution of anisotropy (H_{an}) is instead investigated through the specific-heat measurements. The best estimate is obtained by fitting all curves in magnetic field with the set of parameters reported in Table I, and with $g = 2$ [solid lines in Figs. 4(a) and 4(c)]. The corresponding patterns of the low-lying energy levels are depicted in Fig. 5. We can thus conclude that the magnetic anisotropy is relatively small as compared to exchange constants in Cr_8Cu_2 , but the zero-field splitting

FIG. 5. Patterns of the low-lying energy levels calculated with the parameters reported in Table I for (a) Cr_8Cu_2 and (b) $\text{Cr}_{12}\text{Cu}_2$.

gets more relevant for the largest heterometallic spin rings, for which the difference between the exchange energies of the multiplets gets smaller.

IV. X-RAY SPECTROSCOPIES

Local magnetization within the heterometallic spin rings can be probed through x-ray magnetic circular dichroism by exploiting its chemical selectivity. In the following we report a XMCD investigation on $\text{Cr}_{10}\text{Cu}_2$ and $\text{Cr}_{12}\text{Cu}_2$.

XAS and XMCD measurements were carried out on thick films (polycrystalline powders) of $\text{Cr}_{10}\text{Cu}_2$ and $\text{Cr}_{12}\text{Cu}_2$. Experiments were performed at the ID8 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) using a cryogenic setup that allows the cooling of the specimen at the base pressure of 1.0×10^{-10} mbar. Magnetic fields up to $\mu_0 H = 5$ T were applied by means of a superconducting coil. We employed an Apple II undulator that provides high flux (10^{13} photons/s) of polarized light. Integrity checks with XAS spectra were effectuated throughout the experiment, without finding any evidence of degradation. XAS-XMCD spectra were taken at the Cr and Cu $L_{2,3}$ edges in total yield mode, with circularly polarized light and about 100% polarization rate. The XMCD spectrum is calculated by taking the difference between two XAS spectra taken with photon helicities antiparallel ($\sigma^{\uparrow\downarrow}$) and parallel ($\sigma^{\uparrow\uparrow}$) to the magnetization of the sample (M). In order to minimize field inhomogeneities, the absorption spectra for each helicity have been taken as the average of spectra acquired with opposite directions of the applied magnetic field H .

In Fig. 6, we plot the XAS and XMCD spectra of $\text{Cr}_{10}\text{Cu}_2$ and $\text{Cr}_{12}\text{Cu}_2$. The Cr $L_{2,3}$ absorption edges present the same profile for the two compounds, with eight features which can be considered as “fingerprints” of the presence of Cr^{3+} in an

FIG. 6. (Color online) Cr (left side) and Cu (right side) $L_{2,3}$ XAS (upper panel) and XMCD spectra (lower panel), measured at 7 K and 5 T on thick film of $\text{Cr}_{10}\text{Cu}_2$ and $\text{Cr}_{12}\text{Cu}_2$. $\text{Cr}_{10}\text{Cu}_2$ curves are shifted vertically for the sake of clarity.

O_h environment.¹⁴ Similarly, the Cu $L_{2,3}$ XAS presents the same profile for the two compounds, with a single sharp peak indicating the presence of a Cu^{2+} ion in a slightly distorted O_h symmetry.¹⁵

When an external magnetic field (H) is applied, we get a competition between the antiferromagnetic coupling between nearest-neighboring ions, favoring a staggered configuration of magnetic moments at low temperature, and the Zeeman interaction, which, instead, tends to align all magnetic moments along the field direction. The $\text{Cr}_{10}\text{Cu}_2$ and $\text{Cr}_{12}\text{Cu}_2$ XMCD spectra, reported in Fig. 6 (bottom panels), provide evidence of this interplay. The negative dichroic signal at the Cr L_3 edge and the positive one at the Cr L_2 edge [$L_3(-)$ and $L_2(+)$, in short] imply that the total magnetic moment of Cr ions is parallel to H . The Cu presents a similar behavior for $L_3(-)$, $L_2(+)$, suggesting that the Cu total magnetic moment is also parallel to Cr at 7 K. This occurs in both systems and for all the monitored temperatures and external magnetic fields. The Cr- $L_{2,3}$ XMCD signal (Fig. 6, bottom panel), measured at 5 T and 7 K, turns out to be higher for $\text{Cr}_{12}\text{Cu}_2$ (9%) than that measured on $\text{Cr}_{10}\text{Cu}_2$ (7%). The situation is different for the Cu

$L_{2,3}$ edge, for which we observe a huge dichroic intensity for $\text{Cr}_{12}\text{Cu}_2$ (10.5%), while it is much lower for $\text{Cr}_{10}\text{Cu}_2$ (1.6%) hourglass. This reflects the fact that for $\text{Cr}_{12}\text{Cu}_2$ ($\text{Cr}_{10}\text{Cu}_2$) the ground state is $S = 1$ ($S = 0$), with the spins of the two Cu^{2+} ions aligned parallel (antiparallel) to each other.

Quantitative information on the Cr and Cu spin and orbital magnetic moments can be obtained by using XMCD sum rules.¹⁶ In the literature, the applicability of such rules is controversial due to some arbitrary assumptions concerning the number of 3d holes, the $j-j$ mixing effect, and the presence of the dipolar term T_z . We have already discussed the validity of the sum rules for Cr_8 , Cr_7Ni , Cr_xInNi ,^{17–21} and Cr_2Cu .²² In the following we discuss their applicability in the case of the $\text{Cr}_{2n}\text{Cu}_2$ molecules. Since each Cr^{3+} and Cu^{2+} ion in the $\text{Cr}_{2n}\text{Cu}_2$ rings is in a slightly distorted O_h symmetry and the molecules are randomly oriented, we can consider for the 3d holes numbers the nominal values ($N_{\text{eff}} = 7$ for Cr^{3+} and $N_{\text{eff}} = 1$ for Cu^{2+}). For the calculations, it is useful to define three parameters: $r = I_{L3} + I_{L2}$, which is the integral of the whole absorption spectrum, and p and q , which come from the integral of the dichroic signal, limited to the L_3 edge (p) or extended to the whole spectrum (q) (see Fig. 7). The orbital (m_o) and spin (m_s) magnetic moments can be evaluated with the following expressions:²³

$$\frac{m_o}{\mu_B} = -\frac{4q}{3r} N_{\text{eff}} \quad (5)$$

and

$$\frac{m_s}{\mu_B} = -\frac{(6p - 4q)}{r} N_{\text{eff}} \text{SC} + \frac{7T_z}{\mu_B}. \quad (6)$$

The Cr- $L_{2,3}$ and Cu- $L_{2,3}$ XAS spectra taken with both photon helicities (upper panels) and the relative dichroic signal and its integral (lower panels) measured at 7 K and 5 T for the

FIG. 7. (Color online) Upper panels: Cr (left) and Cu (right) $L_{2,3}$ XAS spectra taken with $(\sigma^{\uparrow\downarrow})$ and $(\sigma^{\uparrow\uparrow})$ circularly polarized light (red curves), and XAS integral (blue) at 5 T and 7 K for $\text{Cr}_{12}\text{Cu}_2$. Lower panels: XMCD spectra (dotted lines) and their integrals (solid lines). The p , q , and r values are calculated by removing the L_3 and L_2 edge jumps and subtracting a two-step-like function from the absorption spectrum.

$\text{Cr}_{12}\text{Cu}_2$ system are plotted in Fig. 7. The dichroic signal integral vanishes at the Cr- $L_{2,3}$ edges ($q = 0$), meaning that m_o of the Cr^{3+} ions is completely quenched by the crystal field. Conversely, m_o of Cu^{2+} ions is only partially quenched. Its value derived by the sum rules is of about 15% of m_s , for all spanned T and H . Thus, Cr ions have a spin-only gyromagnetic factor ($g_{\text{Cr}} = 2.0$), whereas $g_{\text{Cu}} = 2.25 \pm 0.1$.

We have already used a spin correction factor $\text{SC} = 1.75$ for the Cr_8 , Cr_7Ni , Cr_xInNi , and Cr_2Cu , and verified its validity by comparing the results with standard magnetization measurements.^{17–22} Since the line shape of the Cr- $L_{2,3}$ absorption spectra is here very similar, for $\text{Cr}_{2n}\text{Cu}_2$ rings we use the same SC value of 1.75 ± 0.05 . This choice is also supported by the very similar bond lengths and angles around each Cr ion in $\text{Cr}_{2n}\text{Cu}_2$, as compared to the Cr_7Ni and Cr_8 systems.

For the general case of $3d$ metals, the T_z is expected to be finite. Nevertheless, in our particular case of Cr^{3+} ions in O_h symmetry the T_z term is negligible, allowing the application of the isotropic sum rules for Cr. Conversely, for $3d^9$ systems such as Cu^{2+} ions, T_z is not negligible also in O_h symmetry. Theoretical calculations performed on Cu^{2+} ions show, for O_h and also for tetragonal (D_{4h}) distorted (elongated) symmetries, a T_z value of $-0.27\mu_B$ at 0 K, which decreases with increasing temperatures.^{24–26} Thus in the Cu spin moment sum rule, at 0 K, we have to consider a negative $7T_z$ term of about $-2\mu_B$ which is twice the m_s value: $7T_z/m_s = -2$. In the electric dipolar approximation, along the

z direction, $7T_z/m_s$ is proportional to $1 - 3\cos^2\theta$.²⁴ Thus, in our case where the molecules are randomly oriented, the average value of $7T_z/m_s$ at 0 K is approximately $-1/2$. Since our measurements are performed at 7 K and 20 K, we expect that $-1/2 < 7T_z/m_s < 0$. Thus, in order to evaluate the effect of T_z in the determination of the Cu magnetic moment, we consider the two limiting cases: the first one at 0 K, where molecules are randomly oriented ($7T_z/m_s = -1/2$), and the second one at high temperatures ($T_z = 0$).

The upper (central) panels of Fig. 8 display the separate contributions of Cr (Cu) to the total magnetic moment of the $\text{Cr}_{10}\text{Cu}_2$ and $\text{Cr}_{12}\text{Cu}_2$ rings, determined by the sum rules, as a function of $\mu_0 H$ at 7 K and 20 K. Note that for the copper ions the calculation was carried out with (open symbols) and without (filled symbols) considering T_z , in order to appreciate the differences between the two cases. In the bottom panels, the total magnetic moments derived through the sum rules are compared with bulk magnetization measurements on $\text{Cr}_{10}\text{Cu}_2$ and $\text{Cr}_{12}\text{Cu}_2$ compounds. The good agreement between these two independent estimations of the total magnetization confirms the validity of our XMCD data analysis and, more specifically, our estimation of the Cr and Cu total magnetic moments by the XMCD sum rules and the choice of the T_z value and of the SC factor. On this specific issue, it is worth noting that the effect of T_z on the Cu total magnetic moment is considerable. In fact the Cu spin magnetic moment without considering T_z is 40% higher than the value obtained by considering T_z (Fig. 8, central panels). Conversely, the importance of T_z on the total magnetic moment of the whole $\text{Cr}_{2n}\text{Cu}_2$ molecules is reduced, since the Cr contribution is predominant and the effect of T_z is a small reduction (about 5%) of the total magnetic moment (Fig. 8, lower panels).

Engelhardt and co-workers have estimated the magnetization at each spin site by performing Monte Carlo simulations of the $\text{Cr}_{10}\text{Cu}_2$ system at finite temperature and magnetic fields.⁶ Although their simulations were not performed exactly at our experimental conditions, we can try to make a comparison. So, taking into account a linear behavior of the magnetization vs $\mu_0 H$, as shown in Fig. 8, we extrapolate our results to $\mu_0 H = 10$ T and, remarkably, it turns out that the magnetization we determined by XMCD for the 10 Cr ions and that of the 2 Cu ions are in excellent agreement with those theoretically calculated in Ref. 6.

V. ENTANGLEMENT AND HETEROMETALLICITY

The $\text{Cr}_{2n}\text{Cu}_2$ molecular nanomagnets can be regarded as peculiar examples of spin rings with (predominant) antiferromagnetic coupling. Their peculiarity is related to heterometalllicity, which results from the presence of the two Cu ions within the Cr-based ring. The Cu ions can be regarded as magnetic defects, both in view of their different spin ($s_{\text{Cu}} \neq s_{\text{Cr}}$) and of their different exchange couplings to the neighboring ions ($J_{\text{Cu-Cr}} \neq J_{\text{Cr-Cr}}$). From the perspective of quantum entanglement, two main questions can arise from the study of the $\text{Cr}_{2n}\text{Cu}_2$ molecules. First, one can ask how the introduction of the defects spatially modulates spin-pair entanglement within the ring. Second, one might wonder under which conditions the two segments formed by n Cr ions can

FIG. 8. (Color online) Total magnetization (bottom panels), Cr (top panels), and Cu (intermediate panels) separate contributions, measured on $\text{Cr}_{10}\text{Cu}_2$ (left) and $\text{Cr}_{12}\text{Cu}_2$ (right).

induce quantum correlations between the distant Cu spins. In the following, we theoretically address these two questions with reference to the realistic spin Hamiltonian of the Cr_8Cu_2 molecule, and extrapolate our findings to different values of the exchange couplings.

For our purposes, the relevant part of the spin Hamiltonian is represented by its dominant term, namely the isotropic exchange: In the following, we thus set $H = H_{\text{ex}}$ [see Eq. (4)]. Additional contributions, such as dipolar interactions and crystal field anisotropies, are much smaller (see Sec. III) and do not affect the features discussed hereafter.

A. Entanglement modulation induced by the magnetic defects

The introduction of magnetic defects in an otherwise homogeneous spin system is known to spatially modulate quantum entanglement.³ In the series of Cr_7M rings, the single chemical substitution M introduces an oscillating dependence of spin-pair entanglement as a function of position.⁸ These oscillations have a different phase, depending on whether the defect spin s_M is larger or smaller than s_{Cr} , and their amplitude increases with the difference between the spin values, $|s_M - s_{\text{Cr}}|$. Here, the $\text{Cr}_{2n}\text{Cu}_2$ rings additionally offer the possibility to investigate the interplay between the modulations induced by two impurities. Besides, they allow us to highlight the role played by the exchange couplings $J_{\text{Cr-Cu}}$, which, unlike the case of the Cr_7M rings, differ significantly from $J_{\text{Cr-Cr}}$.

Hereafter, we mainly refer here to entanglement between pairs of neighboring spins. This will be discussed in terms of the negativity,²⁷ which quantifies the violation of the positive partial transpose criterion, and is defined as

$$\mathcal{N}_{ij} = \mathcal{N}(\rho_{ij}) = \left(\sum_q |\lambda_q| - \lambda_q \right) / 2, \quad (7)$$

where λ_q are the eigenvalues of the partially transposed density matrix $\rho_{ij}^{T_j}$, and ρ_{ij} is the reduced density matrix of the spins in question, s_i and s_j . If the two spins are disentangled, then $\mathcal{N}_{ij} = 0$; increasing values of $\mathcal{N}_{ij}$ correspond instead to increasingly entangled spins. In order to compute the negativity, we first derive the eigenvalues and eigenstates of the spin Hamiltonian $H = H_{\text{ex}}$ [Eq. (4)]. We then then derive—as a function of temperature T —the equilibrium density matrix ρ of the whole system, where each eigenstate of H is weighted according to the corresponding Boltzmann factor. Finally, the degrees of freedom corresponding to all the spins but s_i and s_j are traced away, leading to $\rho_{ij}(T)$.

In order to isolate the effect of the spin inhomogeneity ($s_{\text{Cu}} \neq s_{\text{Cr}}$), we start by considering the case where all J_k are identical, and take as a reference system a ring formed by $N = 10$ spins $s = 3/2$. As shown in Fig. 9(a), the value of $\mathcal{N}$ (white squares) in the $S = 0$ ground state of such homogeneous system is quite lower than its possible maximum ($\mathcal{N} = s = 3/2$), which corresponds to the case where ρ_{ij} is a spin singlet. In fact, the presence in the spin Hamiltonian of noncommuting exchange operators prevents each of them from minimizing energy and maximizing entanglement within the corresponding spin pair.⁸ The replacement of one Cr with a Cu ion ($s_6 = s_{\text{Cu}}$; orange squares) reduces the negativity of

FIG. 9. (Color online) (a) Negativity between the spins s_k and s_{k+1} as a function of heterometallicity: Cr_{10} (white squares), Cr_9Cu (orange triangles), and Cr_8Cu_2 (red squares). In all cases, the exchange couplings are all identical, and we consider the system ground state ($S = 0$, $S = 1$, and $S = 0$, respectively). (b) Negativity between the spins s_k and s_{k+1} of the Cr_8Cu_2 ring, for different values of the exchange couplings J_k : $J_1 = J_2 = J_3$ (white squares), $J_1 = J_2 = -J_3$ (green squares), $J_2/J_1 = 3.6$ and $J_3/J_1 = -2/3$ (as in the molecule, blue triangles). The negativity is computed in the ground state of each system (always with $M = 0$): This has $S = 0$, $S = 1$, and $S = 1$, respectively. The labels J_2 and J_3 denote the exchange coupling corresponding to the spin pairs that involve a Cu spin, namely $k = 1, 5, 6, 10$.

the spin pairs that involve s_{Cu} ($k = 5$ and $k = 6$) with respect to the homogeneous case, thus enhancing entanglement in the competing pairs ($k = 4$ and $k = 7$). This in turn limits entanglement in the pairs $k = 3$ and $k = 8$, giving rise to an oscillating behavior of $\mathcal{N}_{k,k+1}$ with respect to position (k). The introduction of the second Cu ion ($s_1 = s_{\text{Cu}}$)—opposite to the first one, as in the Cr_8Cu_2 molecule—reinforces such spatial modulation (red squares). This is because the two magnetic defects tend to enhance entanglement within the same spin pairs, namely (s_2, s_3) , (s_4, s_5) , (s_6, s_7) , and (s_8, s_9) . An analogous reinforcement of entanglement modulation is obtained in other rings where the two $s = 1/2$ spins are connected to each other by even-numbered chains of $s = 3/2$ spins.

In order to isolate the effect of the exchange couplings between Cu and Cr, we now compare three representative values of the pair (J_2, J_3), all referred to a Cr_8Cu_2 ring [Fig. 9(b)]. As a reference case, we report the model where all exchange couplings are identical (white squares). The change of sign in J_3 (with $|J_3| = J_2 = J_1$; green) affects spin-pair entanglement only locally. In fact, the negativity of the pairs involving the Cu spin, which was equally distributed among the two neighboring Cr spins in the previous case, is now all concentrated on the Cu-Cr pair with antiferromagnetic exchange ($k = 5$), while it vanishes in the other pair ($k = 6$). Entanglement between the Cr spins is instead scarcely affected. The realistic values of the J_k parameters (blue) increase entanglement between s_5 and s_6 ($k = 5$), where the low value of the Cu spin is compensated by the high value of the exchange constant (J_2). Such increase is achieved at the expense of the competing Cr-Cr pair ($k = 4$). These results suggest that ferromagnetic exchange couplings between the defects and the chains do not allow any clear enhancement of the modulation

effect which is induced by antiferromagnetic interactions. As to the modulus of an antiferromagnetic exchange, in order to enhance the effect of the impurity M , this should be larger (smaller) than the intrachain exchange if s_M is itself larger (smaller) than the chain spins (here s_{Cr}). A small (large) J_{Cr-Cu} exchange tends instead to quench the effect of a large (small) spin impurity.

B. Correlations and entanglement between the defect spin qubits

Equilibrium-state entanglement between distant qubits represents a potential resource in quantum communication.²⁸ In the following, we regard the two Cu ions as defect spin qubits. We estimate the classical and quantum correlations between them that are induced by the two channels, each formed by a chain of n Cr spins. As a preliminary step, we derive the reduced density matrix of the Cu spins, s_1 and s_6 , by tracing out the degrees of freedom related to the Cr spins from the ground state $|\psi_0\rangle$ of H : $\rho_{16} = \text{Tr}_{Cr}\{|\psi_0\rangle\langle\psi_0|\}$. Such reduced density matrix of the two-qubit system, expressed in the basis $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$, takes the form

$$\rho_{16} = \begin{pmatrix} 1/2 - \alpha & 0 & 0 & 0 \\ 0 & \alpha & \beta & 0 \\ 0 & \beta & \alpha & 0 \\ 0 & 0 & 0 & 1/2 - \alpha \end{pmatrix}, \quad (8)$$

where $0 \leq \alpha \leq 1/2$ and $-\beta \leq \alpha \leq \beta$ are real numbers. This simplified expression of ρ_{16} results from the time-reversal symmetry of H , and from the fact that the total-spin projection S_z is a well-defined quantity in the overall state. The former property implies that probabilities associated with states with opposite spin orientations coincide; the latter one implies instead that no coherences can exist in the reduced density matrix between states with different values of the spin projection along z , such as $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$.

Entanglement between two qubits can be quantified by the negativity. For two $s = 1/2$ spins, the value of $\mathcal{N}$ ranges from 0 (for separable states) to $1/2$ (for maximally entangled states). The negativity of two qubits in the above state ρ_{16} is given by the simple expression

$$\mathcal{N}_{16} = \text{Max}\{\alpha + |\beta| - 1/2, 0\}. \quad (9)$$

Entanglement is thus maximized by pure states such as $(|\uparrow\downarrow\rangle \pm |\downarrow\uparrow\rangle)/\sqrt{2}$ (corresponding to $\alpha = |\beta| = 1/2$), while lack of purity, such as the one resulting from occupation of the $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ states, results in $|\beta| < 1/2$ and therefore in a reduction of $\mathcal{N}$. We note in passing that the above expression of the negativity is proportional to the concurrence of the same two-qubit density matrix: $C(\rho_{16}) = 2\mathcal{N}(\rho_{16})$.

More generally, the two Cu spins can exhibit correlations, even in the absence of entanglement. In fact, entangled states are typically (though not necessarily) characterized by a degree of correlation that exceeds the one achievable in classical systems. Here, the expressions of the two-spin correlation functions, in terms of α and β , read

$$\begin{aligned} \langle s_{1,z} s_{6,z} \rangle &= 1/4 - \alpha, \\ \langle s_{1,x} s_{6,x} \rangle &= \langle s_{1,y} s_{6,y} \rangle = \beta/2, \end{aligned} \quad (10)$$

whereas, due to symmetry, $\langle s_{k,x} \rangle = \langle s_{k,y} \rangle = \langle s_{k,z} \rangle = 0$, with $k = 1, 6$. By combining the above equations, one can also express the negativity in terms of the two-spin correlation functions:

$$\mathcal{N}_{16} = \text{Max}\{2|\langle s_{1,x} s_{6,x} \rangle| - \langle s_{1,z} s_{6,z} \rangle - 1/4, 0\}. \quad (11)$$

Entanglement between the qubits in the ρ_{16} state [Eq. (8)] thus increases with in-plane correlations and with negative values of $\langle s_{1,z} s_{6,z} \rangle$.

Entanglement between the two Cu spins is limited by that between each Cu and the neighboring Cr spins. This general property of entanglement is known as *monogamy*.³ In order to highlight the relation between these two quantities, we estimate here entanglement between a Cu spin and its two inequivalent nearest neighbors by computing $\mathcal{N}(\rho_{56})$ and $\mathcal{N}(\rho_{67})$. Another form of entanglement that tends to limit that between the Cu spins is the one between two qubits (taken as a single subsystem) and the chains formed by the Cr spins. Such entanglement would in fact result in a mixed reduced density matrix ρ_{16} —even for a ring in the ground state—which is incompatible with the maximization condition for $\mathcal{N}$ (see above). Here, we quantify entanglement between (s_1, s_6) and the rest of the ring by computing the purity of ρ_{16} : $\gamma_{16} = \text{Tr}\{\rho_{16}^2\}$, which ranges from $1/4$ (when the two Cu spins are maximally entangled with the Cr spins) to 1 (when they are completely disentangled). Given the above expression of ρ_{16} [Eq. (8)], the purity reads

$$\gamma_{16} = 4\alpha^2 + 2\beta^2 - 2\alpha + 1/2. \quad (12)$$

The conditions $\mathcal{N} = 1/2$ and $\gamma_{16} = 1$ are readily seen to coincide: Both correspond to $|\beta| = \alpha = 1/2$.

In the ground state of the Cr_8Cu_2 molecule, i.e., with the realistic values of the exchange couplings J_k , the Cu spins are completely disentangled ($\mathcal{N}_{16} = 0$). Nearest-neighbor exchange interactions tend in fact to induce quantum correlations only between neighboring spins. In particular, the large value

FIG. 10. (Color online) (a) Negativity $\mathcal{N}$ of the spins s_1 and s_6 , as a function of $J_2 = -J_3 > 0$ ($S = 1$ ground state with $M = 0$, solid curve) and of $J_2 = J_3 > 0$ ($S = 0$, dotted), normalized to $J_1 > 0$. Such negativity quantifies the entanglement between the Cu spins induced by the Cr chains. (b) Correlation functions of the same two spins, $\langle s_{1,z} s_{6,z} \rangle$ (red) and $\langle s_{1,x} s_{6,x} \rangle$ (blue), as a function of $J_2 = -J_3 > 0$ (solid curves) and $J_2 = J_3 > 0$ (dotted), normalized to $J_1 > 0$.

FIG. 11. (Color online) Purity γ_{16} of the reduced density matrix of the two Cu spins, as a function of $J_2 = -J_3 > 0$ ($S = 1$ ground state with $M = 0$, solid curve) and of $J_2 = J_3 > 0$ ($S = 0$, dotted), normalized to $J_1 > 0$. The purity quantifies the overall entanglement between the spin pair (s_1, s_6) and the rest of the system. Inset: Negativity $\mathcal{N}$ of the spin pairs (s_5, s_6) (red) and (s_6, s_7) (blue). This quantifies entanglement between each Cu spin and its nearest neighbors.

of J_2 tends to entangle the Cu spins s_1 and s_6 with s_{10} and s_5 , respectively [Fig. 9(b)]. In order to disentangle the Cu spins from the neighboring Cr spins and to favor long-distance entanglement, we consider the limit of small $|J_{k>1}|/J_1$ ratios.⁹ In Fig. 10(a), we report the values of $\mathcal{N}_{16}$ for $J_2 = \pm J_3$ ranging from $0.1 J_1$ to J_1 . Finite values of the negativity are obtained for values of $|J_{k>1}|/J_1$ smaller than 0.4; $\mathcal{N}_{16}$ increases monotonically as the above ratio decreases, and approaches its maximum value when this tends to 0.1. Correlations between the x or z components of the Cu spins are instead always present [Fig. 10(b)], and increase (in modulus) with decreasing $|J_{k>1}|/J_1$. When such ratio is 0.1, both the negativity and the correlation functions suggest that the system ground state corresponds to the two Cr chains being in a singlet state, while the two Cu form a triplet state with $M_{16} = 0$ ($J_3 < 0$) or a singlet ($J_3 > 0$). This is in fact confirmed by the reduced density matrix ρ_{16} that we obtain, given by $\alpha \simeq \beta \simeq 0.43$ in the first case and by $(\alpha, \beta) \simeq (0.43, -0.36)$ in the second one. In the weak Cr-Cu coupling limit, the Cr chains thus induce an effective exchange interaction $J_{\text{Cu-Cu}}^{\text{eff}}$ between the two Cu ions. Also the correlation functions $\langle s_{1,\alpha} s_{6,\alpha} \rangle$ increase in modulus with decreasing $|J_{k>1}|/J_1$ [Fig. 10(b)]. In the case $J_3 < 0$ (solid curves), in-plane and vertical correlations tend to have opposite signs, whereas for $J_3 > 0$ (dotted) they all coincide.

As already mentioned, entanglement between the Cu ions tends to be incompatible with that between these and the Cr ions. Entanglement between the two Cu spins and the rest of the ring, quantified by the purity γ_{16} , is reported in Fig. 11 as a function of the exchange couplings. We start by considering the case $J_3 < 0$. As the ratio $|J_{k>1}|/J_1$ varies from 0.1 to 1, the two-qubit subsystem passes from being scarcely entangled ($\gamma_{16} \simeq 0.75$) to being strongly entangled ($\gamma_{16} \simeq 0.3$) with the Cr chains. A monotonic increase of entanglement with $|J_{k>1}|$ is found also between each qubit and its antiferromagnetically coupled neighbor, i.e., within the spin pair (s_5, s_6) ($\mathcal{N}_{56}$; red curve). As could be expected, no entanglement is instead present between the qubits and the ferromagnetically coupled neighbors ($\mathcal{N}_{67}$; blue). For $J_3 > 0$, the Cu subsystem is slightly more entangled with the Cr ions than in the previous case

(dotted green curve), and quantum correlations of each Cu spin are equally distributed between the two equivalent neighbors (dotted red curve in the inset).

We finally note that the combined effect of a low-spin impurity ($s_{\text{Cu}} < s_{\text{Cr}}$) and of a small $|J_{\text{Cr-Cu}}|/J_{\text{Cr-Cr}}$ ratio simultaneously maximizes both the effects considered in the present section: On the one hand, it leads to a strong spatial modulation of entanglement, and more specifically to a dimerization of the Cr chains; on the other hand, it enables a large amount of entanglement between the distant Cu spins, while suppressing entanglement between such defect spin qubits and the quantum chains.

VI. CONCLUSIONS

In conclusion, we have studied a family of $\text{Cr}_{2n}\text{Cu}_2$ compounds by low-temperature thermodynamic measurements and x-ray spectroscopies. The results clearly show that one can distinguish between the case of Cr_8Cu_2 and $\text{Cr}_{12}\text{Cu}_2$, with the $S = 1$ ground state, and that of $\text{Cr}_{10}\text{Cu}_2$, with $S = 0$. While the values of the three exchange constants have been taken from the literature, the parameters that determine the fine structure (i.e., the zero field splitting) of Cr_8Cu_2 , $\text{Cr}_{10}\text{Cu}_2$, and $\text{Cr}_{12}\text{Cu}_2$ have been estimated by means of an effective spin model, through the analysis of the Schottky anomalies in the specific-heat curves. The experimental results have been complemented by a theoretical investigation of classical and quantum correlations in the Cr_8Cu_2 ring. In particular, the spatial modulation of entanglement within the Cr chains turns out to be enhanced by the cooperative effect of the two Cu spins. A long-distance entanglement between these $s = 1/2$ spins was shown to occur in the present geometry, but only for weak Cr-Cu exchange. In such limit, the two antiferromagnetic Cr chains—with an even number of spin centers—can be approximately regarded as frozen in a singlet state, and disentangled from the Cu ions. For values of the Cr-Cu exchange that are comparable to those of the Cr-Cr exchange, the above picture has to be amended, for quantum correlations are present between spins belonging to different chemical elements, both locally (each Cu with the neighboring Cr) and globally (the two-Cu subsystem with the Cr chains).

On the basis of the present investigation, we believe that heterometallic spin rings with two (or more) spin defects can represent an interesting playground to test quantum correlations in molecular systems. Here, a number of thermodynamic quantities can be used as entanglement witnesses and allow an experimental detection of entanglement.^{29–32} In order to experimentally demonstrate entanglement between specific spin pairs within the molecule, the access to quantum correlations should be combined with the selectivity of local probes, such as NMR^{33,34} or XMCD.^{19,22} Such a challenging goal might be possibly achieved also by four-dimensional inelastic neutron scattering.³⁵

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