

Analyzing the enforcement of a high-spin ground state for a metallacrown single-molecule magnet

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(Received 13 August 2015; revised manuscript received 17 March 2016; published 3 May 2016)

We have studied element-selective magnetic properties of the hetero- and homometallic metallacrowns $\text{Cu(II)}_2[12 - \text{MC}_{Y\text{N}(\text{Shi})-4}]$ ($Y = \text{Cu, Fe}$, in short CuCu_4 and CuFe_4). These metallacrowns comprise four Fe or Cu ions surrounding a central Cu ion. Using x-ray magnetic circular dichroism we have probed local symmetries, electronic configuration, orbital and spin magnetic moments of the magnetic ions. The ratio between the Cu and Fe moment of -0.11 is independent of temperature in the range of 15 K to 90 K. The Cu moment shows antiparallel to the Fe moment. For CuCu_4 we confirm the predicted $S = 1/2$ ground state. The comparison of the spectral dependence indicates a localization of the magnetic moment at the central Cu ion. The orbital to spin moment ratio is 0.03 for the Fe ion while a larger ratio of 0.12 was measured for the Cu ion in both compounds. The experimental results are compared to a mean field model and to an isotropic Heisenberg model.

DOI: 10.1103/PhysRevB.93.174404

I. INTRODUCTION

Slowly relaxing molecular magnets, denoted as single-molecule magnets, show a fascinatingly rich magnetic behavior [1–6]. This is particularly true for the case of heteronuclear systems. Potential applications of single molecule magnets include memory storage on the molecular level and building blocks of spintronic devices [7–12]. Envisioned future applications that are based on the orientation of the molecular magnetic moment and on the utilization of their quantum size effects comprise the processing of information in molecular spintronic devices and quantum computers [11].

Of particular interest are small molecular systems comprising spin frustration. The most simple arrangement are trimers with three equal spins. In this case the dominant AF coupling gives rise to doubly degenerate doublets whose degeneracy can be split by differences in molecular exchange coupling constants [13–20].

Heterometallic molecules not only bare the advantage of an additional measure to tune the intermolecular spin coupling but also allow for the selective investigation element-selective magnetic moments by x-ray magnetic circular dichroism. For example, a study of the heterometallic Cr_2Cu trimer has shown that, even in the presence of an applied magnetic field, the projection of the Cu spin is opposite to that of Cr in agreement with what is expected by spin-Hamiltonian calculations [20].

Featuring a unique combination of reliability and versatility, metallacrown complexes have been established as an exceptional class of coordination compounds [21–24]. Especially, the 12-metallacrown-4 complexes based on salicylhydroxamic acid provide a reliable and stable scaffold, which comprises a cyclic arrangement of four ring metal ions and hosts another metal guest ion at its core [25]. Moreover, the structural and chemical properties of these metallacrowns can be flexibly adjusted in a wide range by a change of bridging and secondary ligands. These complementary features turn

12-MC-4 molecules into highly promising tools for molecular spintronics [21,26–32]. 12-MC-4 complexes have so far only been used to a limited extend as the magnetic coupling in general facilitates a low-spin ground state by a near-complete cancellation of the individual spin contributions for homometallic examples in literature. Only recently, heterometallic metallacrowns featuring a high-spin state have been synthesized and characterized by magnetometry [24,33]. The corresponding idealized square magnetic model of the molecule with only two distinct coupling constants, J_1 and J_2 is indicated in Fig. 1. An analysis of the magnetic susceptibility revealed the isotropic exchange coupling parameters between neighboring magnetic moments. Accordingly, for CuFe_4 the spin ground state is $S_t = 11/2$. The energy difference to the excited states $S_t = 13/2$ and $S_t = 9/2$ is less than 0.3 meV. For CuCu_4 the spin ground state is $S_t = 1/2$ [24,33].

While the temperature and field dependence of the total moment of single molecule magnets has been studied to some extent, less attention has been paid to the molecular distribution of magnetic moments [34]. However, this information is of great importance for applications, e.g., for tailoring the coupling to ferromagnetic substrates. Here, the distribution of magnetic moments has directly been measured for the case of homometallic CuCu_4 and heterometallic CuFe_4 metallacrowns by analyzing element-selective spectral properties gained from x-ray absorption spectroscopy. The experimental results are compared to calculations on the basis of the Heisenberg model with isotropic exchange as introduced in Ref. [33] and to a mean field model considering antiferromagnetic coupling between local magnetic moments.

II. EXPERIMENTAL

The molecules investigated here have been synthesized as described in Refs. [24,33]. X-ray magnetic circular dichroism (XMCD) measurements were carried out at IFP's soft x-ray beamline WERA at the Karlsruhe synchrotron light source ANKA, using the XMCD setup of the Max Planck Institute for Intelligent Systems, Stuttgart. For the XMCD measurements

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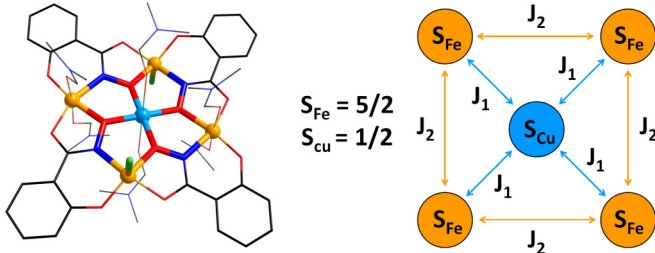


FIG. 1. Molecular structure of the CuFe_4 12-MC-4 complex (left); color scheme: Cu(II)(light blue), Fe(III) (gold), O (red), N (blue), C (black). Square magnetic model of the CuFe_4 12-MC-4 complex (right).

the CuFe_4 molecules were solved in dichloromethane. The solution was drop-casted on a freshly cleaved graphite surface. The sample was then immediately mounted in the load-lock which was pumped to ultrahigh vacuum conditions. X-ray absorption spectra (XAS) at the Fe and Cu $L_{3,2}$ edges were determined from the total electron yield as measured by the sample current at temperatures ranging from 15 K to 91 K. A magnetic field of up to 7 T was applied parallel and antiparallel to the incident photon beam with the sample normally oriented parallel to the magnetic field. The energy resolution of the x-ray monochromator was adjusted to 0.4 eV. The polarization degree is $P = 0.813$ at the Fe L -edge and $P = 0.835$ at the Cu L edge. Even after several days of absorption measurements we did not detect any changes of the spectra indicating that no radiation damage of the molecules occurred.

Element-selective magnetic moments were determined by the sum rule analysis [35,36]. The applicability of such rules is controversial due to some arbitrary assumptions concerning the number of $3d$ holes, the jj mixing effect, and the presence of the dipolar term $\langle T_z \rangle$ [20]. We have set the number of d holes to the values as determined by charge transfer multiplet calculations [37]. The jj mixing effect is considered as a correction factor for the magnetic spin moment. The correction factor is 1 in the case of the Cu^{2+} ion with $3d^9$ configuration because the single final state forbids mixing. For the Fe^{3+} ion with $3d^5$ configuration correction factors depending on the crystal field strength have been calculated [38–40]. Following the results of Piamonteze *et al.* [38] and considering the crystal field strength of $10Dq = 1.6$ eV (see Sec. III), in our case we have applied a correction factor of 1.5 for Fe. The $\langle T_z \rangle$ term is negligibly small for Fe^{3+} because of its almost spherical $3d^5$ configuration. In contrast the $\langle T_z \rangle$ term is large in the case of Cu^{2+} (see Refs. [20,38,39,41]). The angular dependence of $\langle T_z \rangle$ can be described by the Legendre polynomial $(1 - 3 \cos^2 \theta)$ [39]. In addition this angular dependence has been experimentally confirmed by Stepanow *et al.* [42] for the case of ordered Cu-phthalocyanine monolayers on Ag(100). An important precondition for the occurrence of this angular dependence is that the quadrupolar charge distribution remains largely unaffected by the magnetic spin orientation. This precondition is fulfilled in our case because the spin-orbit coupling is in general weak for the valence states of $3d$ metal ions. Then, the full operator $\langle T_i \rangle$ predominantly reflects a quadrupole term in the anisotropic spin density. In this case a new sum rule follows from the

property $\langle T_x \rangle + \langle T_y \rangle + \langle T_z \rangle = 0$: The spin moment can be determined by averaging experiments along the x , y , and z axis. Alternatively, $\langle T_z \rangle$ vanishes for a magic angle measurement or, as in our case, for polycrystalline samples (see Refs. [42,43]). Please note that this is only true in the saturated magnetic state. In the nonsaturated state $\langle T_z \rangle$ vanishes only for systems without magnetic anisotropy. According to Refs. [24,33] the temperature and field dependent magnetization can be described by an isotropic model. Consequently, we have neglected $\langle T_z \rangle$ in the following.

III. RESULTS FOR CuFe_4

Figures 2(a) and 2(b) show the XAS and XMCD spectra of the Fe and Cu $L_{3,2}$ spectra of CuFe_4 . The Fe L_3 edge reveals a pronounced shoulder below the maximum that is also visible in the corresponding XMCD spectrum. The Fe L_2 edge shows a double peak feature with a smaller peak at lower photon energy. These features are characteristic for an Fe(III) ion. The Cu XAS and XMCD spectra reveal a single peak at each L edge being characteristic for a Cu(II) ion in the $3d^9$ state with a single unoccupied d state. The XMCD spectra (Fig. 2) directly reveals the antiparallel orientation of the Fe and Cu magnetic moment, indicated by the opposite sign of the corresponding L_3 XMCD maximum. The Fe magnetic moment points parallel to the external field while the Cu moment points antiparallel to the field.

The spectra are compared with charge-transfer multiplet calculations using CTM4XAS [37]. Figure 3(a) shows the simulated XAS and XMCD spectra of the Fe(III) ion in a slightly distorted crystal field with Oh symmetry. The crystal field parameters $10Dq = 1.6$ eV and $Ds = 0.1$ eV result from a fit to the experimentally observed spectra. Figure 3(b) depicts the simulated Cu XAS and XMCD spectra for a Cu(II) ion. A crystal field with Oh symmetry is necessary to evoke a peak at the L_2 edge. A crystal field parameter of $10Dq = 0.7$ eV adjusts the peak ratio to the experimentally observed value. For comparison with the experiment the XMCD spectra have been demagnified. Please note that the calculation assumes a single transition metal ion with a fully saturated spin state whereas the molecular moments are smaller due to the intramolecular exchange interaction.

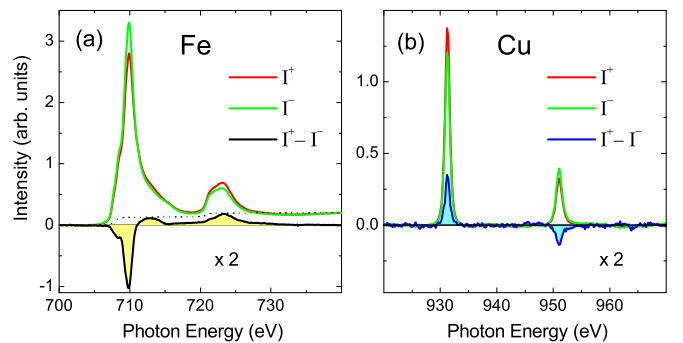


FIG. 2. X-ray absorption and XMCD spectra measured at the Fe (a) and Cu $L_{3,2}$ (b) edges for the CuFe_4 12-MC-4 metallacrown. The step function subtracted for the sum rule analysis is indicated as a dotted line. The external field is ± 7 Tesla and the temperature 22 K.

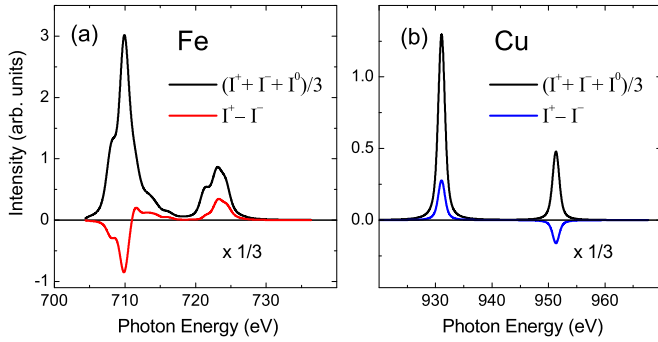


FIG. 3. X-ray absorption and XMCD spectra (full lines) simulated at the Fe (a) and Cu $L_{3,2}$ (b) edges, using CTM4XAS with the crystal field parameters $10Dq = 1.6$ eV (0.7 eV) and $Ds = 0.1$ eV (0.0 eV) for Fe (Cu).

A sum rule analysis results in values for the element-selective spin and orbital magnetic moments. Values for 20 K and an applied field of 7 T are summarized in Table I. We have considered for the number of the $3d$ holes the nominal values $N_{\text{eff}} = 5$ for Fe^{3+} and $N_{\text{eff}} = 1$ for Cu^{2+} . In particular for the Cu magnetic moment the dipolar $\langle T_z \rangle$ term of the spin moment is not negligible. In our case, however, we expect that the molecules are randomly oriented and the expectation value of the dipolar term, being proportional to $(1 - 3 \cos^2 \theta)$, would vanish for a negligibly small magnetic anisotropy. XMCD data acquired at an incident photon angle of 60 degrees results in the identical spectra as measured for normal incidence, confirming the assumption of random orientation of the molecules. For the evaluation of the Fe moment we have considered a correction factor of 1.5 because of the pronounced jj mixing [38], visible

TABLE I. Magnetic moments measured for CuCu_4 and CuFe_4 in μ_B per Fe and Cu atom, respectively, as measured at 20 K for a field of 7 T. The specific number of d holes were set to the values determined by the CTM4XAS calculations $N_h(\text{Fe}) = 5$ and $N_h(\text{Cu}) = 1$. A correction factor of 1.5 was assumed in the case of Fe because of the significant jj mixing. Magnetization in magnetic moment μ_B per molecular unit as calculated from the XMCD values, considering for Cu or Fe moments in the cyclic scaffold and one center Cu moment, are compared to the magnetization measured by superconducting quantum interference device (SQUID) magnetometry (SQUID data taken from Refs. [24,33] for the same temperature and field parameters). The error comprises statistical contributions only. Errors of the common factors polarization, N_h , and the error due to subtraction of transitions into continuous states are omitted. We estimate these errors to be on the order of 10%.

Scaffold			Center
CuCu_4	μ_{spin}	0	0.27 ± 0.02
	μ_{orb}	0	0.04 ± 0.01
	μ_{XMCD}	0.31 ± 0.02	
	μ_{SQUID}	0.32 ± 0.01	
CuFe_4	μ_{spin}	2.18 ± 0.08	-0.24 ± 0.03
	μ_{orb}	0.07 ± 0.02	0.03 ± 0.02
	μ_{XMCD}	8.7 ± 0.3	
	μ_{SQUID}	8.8 ± 0.10	

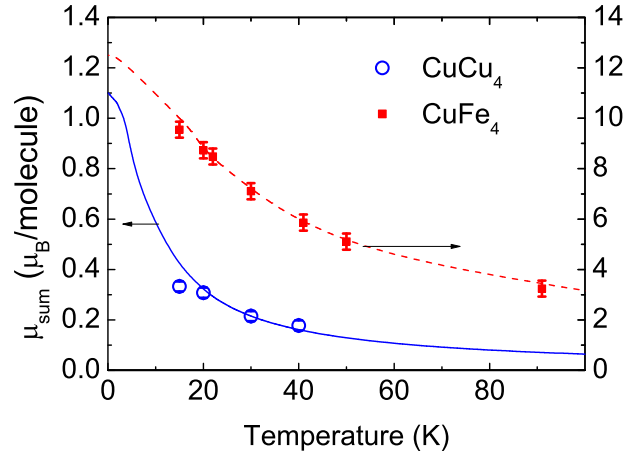


FIG. 4. Total magnetic moments for CuCu_4 (circles) and CuFe_4 (squares) as determined by the sum rule analysis for a field of 7 T, considering four moments in the scaffold and one center moment, as a function temperature. XMCD results are compared with SQUID magnetometry. SQUID data were taken from Refs. [24,33] (full and dashed lines) for the same applied field.

in the nonzero value of the XMCD signal between the L_2 and L_3 edge [44]. This mixing effect is known for metallic systems to occur for the lighter $3d$ elements [45] with decreasing spin-orbit separation of the two $L_{2,3}$ edges. With this correction factor the total magnetic moment per molecule fits to the value determined by SQUID magnetometry in Ref. [24] (see Fig. 4).

A considerable orbital magnetic moment occurs at the Cu^{2+} ion. The orbital to spin moment ratio amounts to $r = 0.12$. This indicates a significant deviation from a pure spin-1/2 state.

Measurements at an external field of ± 1 Tesla confirm that the induced magnetic moments increase linearly with external field for temperatures larger than 15 K. This fact is in full agreement with the results from SQUID magnetometry (see Ref. [24]).

Temperature-dependent and element-selective magnetic moments measured at 7 T are shown in Fig. 5. The experimental data clearly reveal the antiparallel alignment of the magnetic moment of the Cu(II) ion at the core and the magnetic moments of the Fe(III) ions in the cyclic scaffold. Furthermore, the spins of the Fe(III) ions point towards the direction of the magnetic field and overcompensate the central spin of the Cu(II) ion. These findings are valid for the whole range of the screened temperatures. Thus, the prolific effect of the heterometallic magnetic director approach can be directly observed from the element-selective moments. The ratio of the Cu and Fe moments remains remarkably constant as depicted in Fig. 6. This behavior will be discussed in more detail in Sec. V.

IV. RESULTS FOR CuCu_4

XAS and XMCD spectra for the CuCu_4 metallacrown are shown in Fig. 7. In this case the molecule comprises a ground state of $S = 1/2$, which is energetically well separated from excited states with larger spin values. In contrast to the case of CuFe_4 the spin state is very well defined at all temperatures and external fields. The saturated magnetic moments of the five Cu ions sum up to only $1 \mu_B$. Consequently, the asymmetry at the

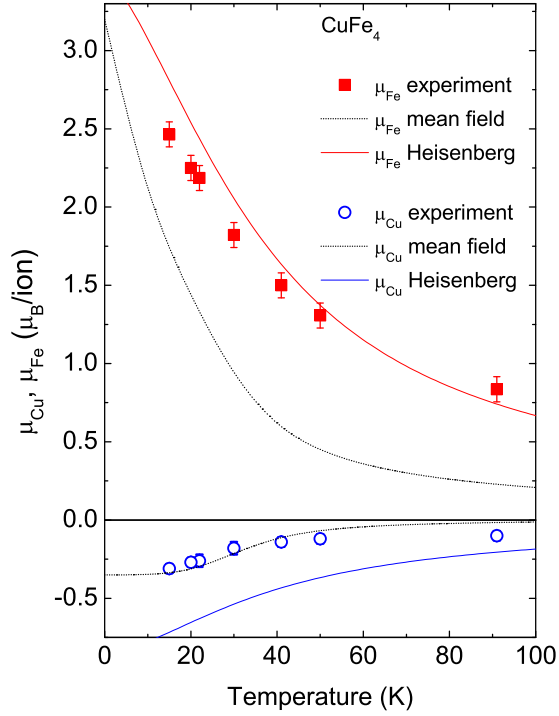


FIG. 5. Element-selective total magnetic moments as determined by the sum rule analysis versus temperature (dots and squares). Full and dashed lines indicate the temperature dependent Fe and Cu moments calculated by the mean field model.

Cu $L_{2,3}$ edge is roughly a factor of five smaller compared to the case of CuFe_4 . The temperature-dependent total magnetic moment nicely fits to the magnetic moments determined by SQUID magnetometry as reported in Ref. [24] (see Fig. 4).

The orbital to spin moment ratio of $r = 0.15$ is of the same size as in the case of CuFe_4 . This is at first glance surprising because one expects that the magnetic moment is dominated by the four Cu ions positioned in the cyclic scaffold similar to CuFe_4 . The detailed comparison of Cu spectra in CuCu_4 and CuFe_4 shown in Fig. 7 reveals a significant shift of the Cu L_3 XAS maximum by 200 meV to higher photon energy.

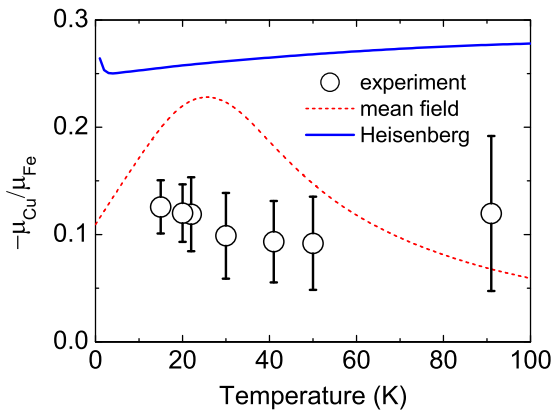


FIG. 6. Ratio of Cu and Fe moments as a function of temperature (circles). The ratio is compared with a constant spin ratio (CSR) (full blue line) and with the mean field model (MFM) (dashed red line).

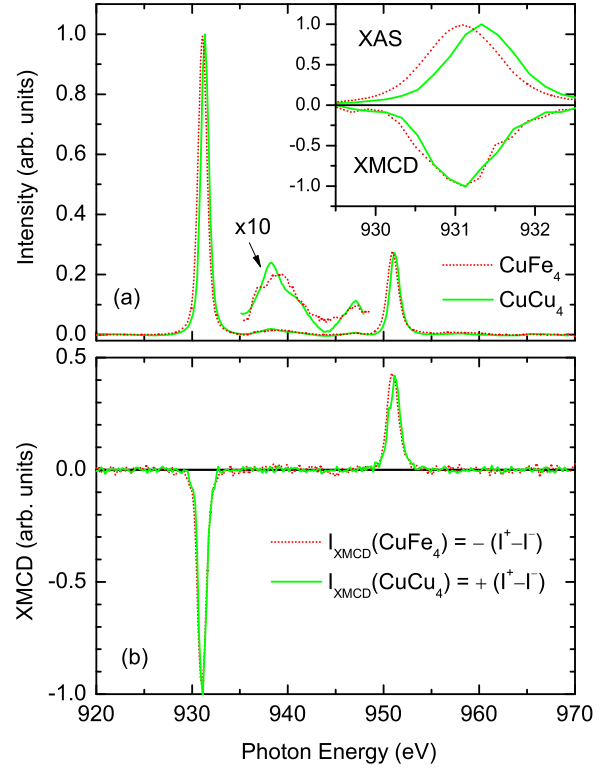


FIG. 7. X-ray absorption (a) and XMCD spectra (b) at the Cu $L_{3,2}$ edges for the CuCu_4 12-MC-4 metallacrown (full lines). The external field is ± 7 Tesla and the temperature 20 K. For direct comparison the corresponding Cu spectra as measured for CuFe_4 are shown, too (dotted lines), with reversed sign of the XMCD spectrum. All spectra are normalized to the maximum value.

Comparing with charge transfer multiplet calculations [37] this shift corresponds to a charge transfer of 0.04 electrons from the Cu(II) ions to the neighboring ions. As the XAS is dominated by the four Cu ions in the cyclic scaffold we attribute this charge transfer to occur for these four Cu ions. On the other hand, the central Cu ion occupies the same position as in CuFe_4 and is expected to show the same spectral properties.

In contrast to the XAS signal, the XMCD spectrum reveals the maximum asymmetry value at the same photon energy as in the case of CuFe_4 . From this observation we conclude that the XMCD asymmetry mainly results from the Cu ion in the center position, while the Cu ions in the cyclic scaffold do not significantly contribute to the asymmetry. Consequently, the magnetic moment of the CuCu_4 molecule is predominantly localized at the center Cu ion.

V. DISCUSSION

12-MC-4 metallacrowns comprise magnetic moments localized at one central and four adjacent $3d$ -transition metal ions (Fig. 1) in a chiral structure. The coupling of the localized magnetic moments results from the strong bonding across oxygen and nitrogen atoms. Based on magnetostructural considerations, a CuFe_4 12-MC-4 complex was first designed and then synthetically realized [24,33]. In contrast to the antiparallel alignment of the spins in the cyclic scaffold, a high spin ground state was achieved via the purposeful placement

of a Cu(II)-ion as a magnetic director inside the core of an Fe(III)-based metallacrown [33].

The occurrence of the high-spin ground state was deduced from the total magnetic moment per molecule. The temperature-dependent magnetic susceptibility reveals an increasing value of $\chi_M T$ with decreasing temperature until a maximum is reached around 40 K for the case of the heterometallic CuFe₄ compound. This finding clearly suggests an energetic preference of higher spin states. In contrast $\chi_M T$ monotonously increases with increasing temperature for the homometallic CuCu₄ 12-MC-4 metallacrown.

For CuFe₄ the mutual cancellation of the individual spin contributions is prevented by a deliberate placement of specific metal ions in the different positions in the cyclic scaffold and at the core. The central Cu(II) ion accomplishes its intended role as a magnetic director because it induces superior antiferromagnetic interactions (J_1) with the surrounding Fe(III) ions. Thus, the weaker antiferromagnetic coupling between the Fe(III) ions in the periphery (J_2) promoting the antiparallel alignment of their spins is counteracted. The analysis of the experimental temperature-dependent susceptibility data was performed by the idealized square magnetic coupling scheme shown in Fig. 1 using an isotropic Heisenberg-Dirac-Van-Vleck Hamiltonian.

The isotropic spin-Hamiltonian is given by:

$$H = -2J_1(S_1 S_2 + S_1 S_3 + S_1 S_4 + S_1 S_5) - 2J_2(S_2 S_3 + S_3 S_4 + S_4 S_5 + S_2 S_5) + \mu_B B \sum_{i=1}^5 g_i S_i, \quad (1)$$

where S_1 denotes the spin of the center ion and S_2 to S_5 the spins of the other four ions. g_i denote the corresponding isotropic g factors ($g = 2.03$ for Fe and $g = 2.16$ for Cu) as determined in Refs. [24,33].

The fit yields the values $J_1 = -6.1$ meV and $J_2 = -0.5$ meV. Although the coupling constant J_2 between the Fe spins is favorably small compared to the coupling J_1 to the central Cu spin, the impact on the spin state is not negligible because of the large Fe spin moment. The coupling constants lead to a total spin ground state of $S_t = 11/2$, which is separated from the excited $S_t = 13/2$ and $S_t = 9/2$ states by only a few meV. According to the isotropic spin-Hamiltonian for the Heisenberg-Dirac-van Vleck model, the relative energies of the spin states are linear functions of the ratio between both coupling constants J_1/J_2 [24].

The homometallic CuCu₄ 12-MC-4 metallacrown features a low-spin ground state which originates from the intrinsic magnetic connectivity. In this case all individual spins have a value of $S_i = 1/2$. In the most evident case of $J_1/J_2 < 1$, the coupling is dominated by the tangential coupling. Consequently, the spins in the cyclic scaffold are aligned antiparallel to each other, i.e., the corresponding magnetic moments cancel. The total spin ground state of $S_t = 1/2$ is then caused by the uncompensated moment S_1 located at the center ion.

In fact, a fit to the temperature-dependent magnetic susceptibility results in values of $J_1 = -19.2$ meV and $J_2 = -11.4$ meV and the radial coupling is thus stronger. But even

in this case the low-spin state is more favorable: According to the Heisenberg model a ratio $J_1/J_2 > 1$ but smaller than 4 still leads to the $S_t = 1/2$ spin ground state [33].

For the heterometallic CuFe₄ metallacrown the ratio $J_1/J_2 = 12.9$ results in the measured high-spin state $S_t = 11/2$. The maximum possible high-spin state, i.e., all peripheral moments are aligned and only the center spin shows in the opposite direction, is given by $S_t = 19/2$ and is attained at $J_1/J_2 > 20$ according to the model [Eq. (1)]. The increased intermediate spin state in CuFe₄ leads to a certain distribution of the spin state among the five centers.

The distribution of magnetic moments as observed in the experiment stays almost independent on temperature in a wide range. This finding could be tentatively explained by the symmetric distribution of energy levels for total spin states larger or lower than $S_t = 11/2$. A similar constant moment ratio has been found experimentally and explained theoretically for the case of Cr₂Cu trimer [20].

Diagonalization of the isotropic spin Hamiltonian Eq. (1) allows the calculation of the expectation values of individual spins $S_{z,i}$ as a function of field and temperature using the previously determined coupling parameters J_1 and J_2 . This theoretical result is compared with the experimental result in Fig. 5. The temperature dependence of the Fe magnetic moments is similar to the experimentally observed behavior and the absolute values are close to each other. In contrast, the spin-Hamiltonian calculation overestimates the Cu moment by more than a factor of two. A correction of the experimental values because of a finite $\langle T_z \rangle$ term in combination with a magnetic anisotropy is unlikely because at the lowest temperature the maximum field of 7 T accounts for 75% of the saturation value. Moreover, if such a correction was applied to the case of CuFe₄, the same correction would apply to the case of CuCu₄ and consequently lead to a strong deviation of SQUID magnetometry and XMCD evaluation. As a second possibility one may take into account that the spin Hamiltonian represents an approximation and more realistic models, e.g., single ion anisotropy [46–48], anisotropic coupling schemes [49,50], or even density functional theory [51,52], have to be applied.

Spin-Hamiltonian calculations for CuCu₄ also reveal a different distribution of magnetic moments in comparison to the experimental result. At low temperatures the calculated magnitude of all the Cu magnetic moments is identical and the sign of the central Cu moment is opposite to the scaffold moments. Above 25 K the central moment decreases more rapid than the scaffold moments and almost vanishes at room temperature.

As an alternative theoretical model, we consider a mean field model. We describe the temperature-dependent magnetic moments by the following set of coupled implicit mean field equations:

$$\begin{aligned} \frac{\mu_{\text{Fe}}(T)}{\mu_{\text{Fe}}(0)} &= B_{5/2} \left(\frac{\mu_{\text{Fe}}(0)(\mu_0 H + B_{\text{exch,Fe}})}{k_B T} \right), \\ \frac{\mu_{\text{Cu}}(T)}{\mu_{\text{Cu}}(0)} &= B_{1/2} \left(\frac{\mu_{\text{Cu}}(0)(\mu_0 H + B_{\text{exch,Cu}})}{k_B T} \right), \end{aligned} \quad (2)$$

with B_j denoting the Brillouin function for total angular momentum quantum number j , $\mu_0 H = 7$ T the external field, and $B_{\text{exch},i}$ referring to the effective exchange field for element

i. The effective exchange field adapted to the square model as sketched in Fig. 1 is given by:

$$B_{\text{exch,Fe}} = 1 \frac{\mu_{\text{Cu}}(T)}{g^2 \mu_B^2} J_1 + 2 \frac{\mu_{\text{Fe}}(T)}{g^2 \mu_B^2} J_2, \quad (3)$$

$$B_{\text{exch,Cu}} = 4 \frac{\mu_{\text{Fe}}(T)}{g^2 \mu_B^2} J_1,$$

where $g = 2$ indicates the neglected orbital moments and μ_B denotes the Bohr magneton. For simplicity we have chosen for the mean field model the same g -factor for all contributing magnetic moments. For the saturated magnetic moments we take into account the saturated molecular moment as determined by SQUID magnetometry (see Ref. [24]) and the experimentally determined moment ratio resulting in $\mu_{\text{Cu}}(0) = 0.35 \mu_B$ and $\mu_{\text{Fe}}(0) = 3.2 \mu_B$.

The numerical result of Eq. (2) is depicted in Fig. 5. The mean field model clearly predicts a stronger decrease of the Cu and Fe moments than observed in the experiment. Moreover, the ratio of the element-selective magnetic moments significantly depends on the temperature (see Fig. 6). At low temperatures, the Cu moment tends to remain in the fully saturated antiparallel direction. The Fe moment rapidly decreases with increasing temperature leading to an increase of the moment ratio. At high temperatures, the mean field model predicts that the Cu moment decreases more rapidly than the Fe moment and even reverses its sign at 400 K. Consequently the moment ratio decreases with increasing temperature. This behavior is descriptively explained by the high thermal energy exceeding the involved exchange energies. In this case one expects an independent thermal fluctuation of the magnetic moments eventually breaking the antiparallel alignment of Cu and Fe moments. This nonmonotonic behavior occurs for a wide range of mean field parameters. However, it is in clear contradiction to the experimentally observed constant moment ratio.

VI. SUMMARY

The element-selective magnetic properties of the hetero- and homometallic metallocrowns $\text{Cu(II)}_2[12 - \text{MC}_{YN(\text{Shi})-4}]$ ($Y = \text{Cu}, \text{Fe}$) were determined by XMCD. The present study focused on the question how the magnetic moment is distributed within the molecule and whether the individual

magnetic moments show the same temperature dependence. This is particularly interesting because the low energy spin states are separated by very small energies, and therefore external field and temperature may easily provoke excited spin states. Varying molecular moment distributions may have a strong impact for the application of single-molecule magnets.

From the analysis of spectral properties we conclude that the ground state magnetic moment of the homometallic CuCu_4 metallocrown, $\mu_{\text{Cu}}(0) = 1.1 \mu_B$, is concentrated at the center Cu ion. For the heterometallic CuFe_4 metallocrown 97% of the magnetic moment is concentrated in the cyclic scaffold, $\mu_{\text{Fe}}(0) = 3.2 \mu_B$, while the center Cu ion holds an antiferromagnetic moment of $\mu_{\text{Cu}}(0) = -0.35 \mu_B$. The ratio of magnetic moments is independent on temperature. This is a remarkable result in view of previously published results for metallic alloys, where different temperature dependencies were found and successfully described by a mean field model. A spin-Hamiltonian calculation precisely reproduces the temperature and field dependence of the total moment for both molecules. Calculated element-selective moments are in agreement with the scaffold Fe moment in CuFe_4 but overestimates the central Cu moment in CuFe_4 . In contrast to the experimental result for CuCu_4 , the spin-Hamiltonian calculations predict a larger Cu moment in the scaffold.

The orbital to spin moment ratio of 0.03 is comparatively small for the Fe ion, while a larger ratio of 0.12 was found for the Cu ion in both compounds. The larger orbital magnetic moment of the central ion reflects the lower symmetry of the effective crystal field at the center position. Tailoring the anisotropy of the crystal field in combination with a strong spin-orbit coupling might be a promising path to larger magnetic anisotropies necessary for an increase of relaxation times.

ACKNOWLEDGMENTS

The project is funded by the DFG (Germany) through SFB/TRR173 (project A09), the Stiftung Rheinland-Pfalz fuer Innovation (project 1038), and by the Center of INnovative and Emerging Materials (CINEMA). P.H. is the recipient of a fellowship through the Excellence Initiative (DFG/GSC 266). P.H. gratefully acknowledges the German National Academic Foundation (Studienstiftung des deutschen Volkes) for financial support. ANKA Angströmquelle Karlsruhe is acknowledged for the provision of beamtime. We thank the MPI-IS Stuttgart for use of their XMCD endstation at WERA.

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