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ARTICLE TYPE

## Enforcement of a high-spin ground state for the first 3d heterometallic 12-metallacrown-4 complex†

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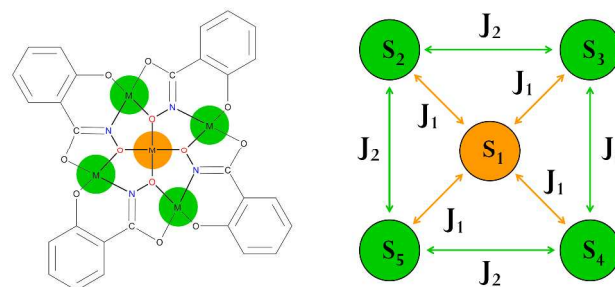
**Cu(II)(DMF)<sub>2</sub>Cl<sub>2</sub>[12-MC<sub>Fe(III)N(Shi)-4</sub>](DMF)<sub>4</sub>·2DMF has been synthesized as the first heterometallic transition metal 12-MC-4 complex. The purposeful placement of specific metal ions in the different sites of the metallacrown attains the establishment of a high-spin ground state. Inducing the anticipated superior exchange interactions, the central Cu(II) guest ion averts the common mutual cancellation of the spins, as it is observed in corresponding homometallic compounds.**

Since their discovery in 1989,<sup>1–3</sup> the class of metallacrown complexes have proven to combine a variety of beneficial chemical and structural features in a most singular way.<sup>4,5</sup> Especially for the 12-MC-4 compounds based on salicylhydroxamic acid (H3Shi), the reliable formation and high stability of the basic scaffold has been established.<sup>6–8</sup> As these complexes at the same time reveal a great stereochemical versatility and allow for a facile exchange and functionalization of secondary or bridging ligands, they have a highly promising potential in magnetochemical research. So far, however, the 12-MC-4 complexes have remained of limited application within the community as they in general lack a high-spin ground state.<sup>9–14</sup> This also holds true for Mn(II)(OAc)<sub>2</sub>[12-MC<sub>Mn(III)N(Shi)-4</sub>](DMF)<sub>6</sub>, which has been identified as a SMM.<sup>15</sup> Here, the low-spin ground state is compensated by the single-ion anisotropy contributions due to the beneficial planar structure of metallacrowns. In general, a major reason for the absence of a high-spin ground state in the reported 12-MC-4 metallacrowns consists in the intrinsic magnetic connectivity (Fig. 1). Because the antiferromagnetic radial magnetic interactions are of similar strength as the tangential exchange couplings, a near-complete cancellation of the spins is observed in these systems.<sup>9,10</sup>

Herein, we present the first results of a complementary heterometallic approach for metallacrowns. The purposeful placement of specific transition metal ions in the different sites of the metallacrown targets a more distinct differentiation of the coupling strengths. Indeed, an increased spin ground state is accomplished for the CuFe<sub>4</sub> cluster which is shown here as the first 3d heterometallic 12-MC-4 complex.

Designed according to magneto-structural considerations (see below), the heterometallic compound [CuFe<sub>4</sub>(Shi)<sub>4</sub>(Cl)<sub>2</sub>(DMF)<sub>6</sub>]·2DMF or, following the notation by Pecoraro et al., Cu(II)(DMF)<sub>2</sub>Cl<sub>2</sub>[12-MC<sub>Fe(III)N(Shi)-4</sub>](DMF)<sub>4</sub>·2DMF was synthesized via the reaction of salicylhydroxamic acid with the corresponding metal chloride

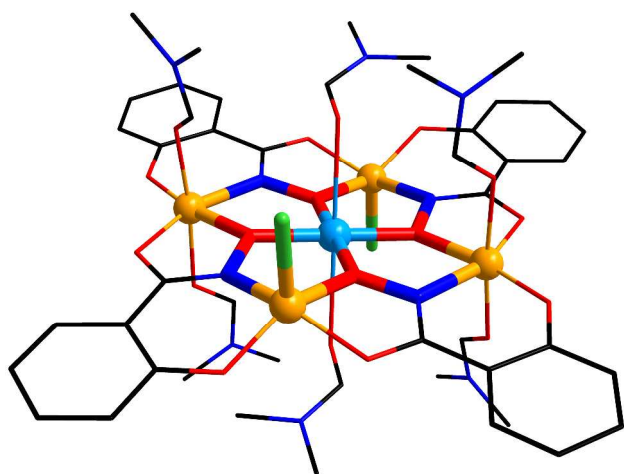
salts and triethanolamine in dimethylformamide (DMF). The formation of the cyclic scaffold by the Fe(III) ions had been anticipated due to the extraordinarily high affinity of the hydroxamic acid moiety towards this species.<sup>16–18</sup> By contrast, the encapsulation of the Cu(II) ion at the core was fostered by avoiding common bridging anions like carboxylate ligands. Cu(II)(DMF)<sub>2</sub>Cl<sub>2</sub>[12-MC<sub>Fe(III)N(Shi)-4</sub>](DMF)<sub>4</sub>·2DMF (**1**) and the homometallic metallacrown (HNEt<sub>3</sub>)<sub>2</sub>Cu(II)[12-MC<sub>Cu(II)N(Shi)-4</sub>](**2**), as supplementary counterexample for the magnetic properties, were fully characterized by X-ray crystallography, elemental analysis, infrared spectroscopy, UV-Vis spectroscopy, atomic absorption spectroscopy (**1**), Mößbauer spectroscopy (**1**), ESI mass spectrometry and SQUID-magnetometry.



**Fig. 1** Basic 12-MC-4 motif with different metal-binding sites at the core (orange) and in the surrounding scaffold (green), and a corresponding idealized square magnetic model with a radial ( $J_1$ ) and tangential ( $J_2$ ) coupling constant.

The neutral metallacrown complex in the crystal structure of compound **1** is centrosymmetric and obeys the regular 12-MC-4 constitution (Fig. 2). Here, the peripheral scaffold comprises four Fe(III) ions whereas a Cu(II) ion is encapsulated at the core of the cluster. The Fe(III) ions are linked by four salicylhydroxamate ligands forming the cyclic host of the metallacrown with the characteristic repetition unit [Fe-O-N-]. Thus, each ligand coordinates two ring metal ions in a bidentate fashion. While the iminophenolate moiety is involved in a six-membered chelate ring, the hydroxamate group binds to another iron ion in a five-membered chelate ring. Adjacent salicylhydroxamate trianions are coordinated in a transoid arrangement and with complementary moieties at a shared ring metal ion. The Cu(II) guest ion resides in the inner cavity on a centre of inversion and is bound by the hydroxamate oxygen donor atoms. Two of the iron ions on opposite sides of the ring adopt a square pyramidal coordination

sphere with a chloride counter ion on the apical position ( $\tau = 0.058$ ).<sup>19</sup> The remaining Fe(III) ions have an octahedral coordination environment featuring a trans arrangement of secondary dimethylformamide (DMF) ligands. Another pair of DMF molecules occupies the axial sites of the central Cu(II) guest ion, which reveals a strongly Jahn-Teller elongated octahedral coordination geometry. Giving rise to a so called sofa configuration,<sup>6,7</sup> a small deviation from planarity of the basic motif is caused by a slight tilting of the salicylhydroximate main ligands out of the least-square plane of the metal ions. The complex is disordered over two positions about the copper ion on the centre of inversion with a rate of over 97% for the majority orientation. Additionally, two disordered dimethylformamide solvent molecules per metallacrown fill the cavities between adjacent complexes. Crystal structure information (Tab. S1), a numbering scheme (Fig. S1), packing diagrams (Fig. S2, S3), selected interatomic distances (Tab. S2) and bond angles (Tab. S3) are given in the ESI together with the data for the elemental analysis, atomic absorption spectroscopy, and spectroscopic data for the full characterization.



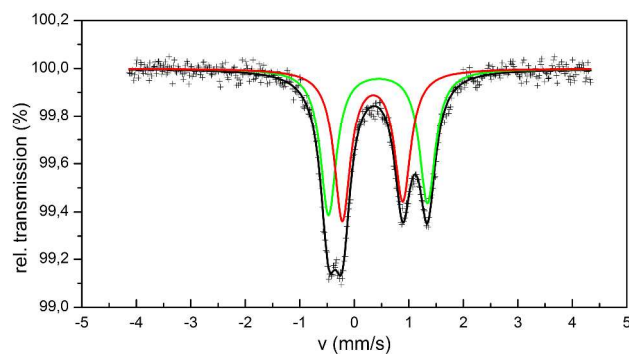
**Fig. 2** Molecular structure of Cu(II)(DMF)<sub>2</sub>Cl<sub>2</sub>[12-MC<sub>Fe(III)N(Shi)</sub>-4](DMF)<sub>4</sub> in crystals of **1**; colour scheme: light blue - Cu(II), yellow - Fe(III), green - Cl, red - O, dark blue - N, black - C.

The presence of Fe(III) ions in two distinguishable coordination spheres is additionally verified by Mössbauer spectroscopy. As shown in Fig. 3 two well resolved signals with quadrupolar splittings are observed. While the isomer shifts ( $\delta_{IS}$  0.4343 mm s<sup>-1</sup> and 0.3336 mm s<sup>-1</sup> for doublet A and B, respectively) differ only slightly for both iron sites, the size of the quadrupolar splitting clearly differs. The  $\Delta E_Q$  values 1.816 mm s<sup>-1</sup> (site A) and 1.108 mm s<sup>-1</sup> (site B) reflect the different chemical environments of the nuclei that are affecting the electric field gradients. Integration of the signals yields the expected 1:1 ratio for the two Fe(III) sites.

Worth mentioning is that the ESI mass spectrum in a 1:1 mixture of DMF and acetonitrile indicates the integrity of the basic motif of **1** not only in solution but even in the gas phase. It comprises peaks at 1126 and 1141 m/z which can be assigned to the molecular ions  $\{(\text{Cu(II)(Cl)}_2[12\text{-MC}_{\text{Fe(III)N(Shi)}}-4](\text{DMF})_2)+\text{Na}\}^+$  and  $\{\text{Cu(II)Cl}[12\text{-MC}_{\text{Fe(III)N(Shi)}}-4](\text{DMF})_3\}^+$ .

The crystal structure of **2** (Fig. S4) contains the well-known pentanuclear complex dianion Cu(II)[12-MC<sub>Cu(II)N(Shi)</sub>-4]<sup>2-</sup> which

also matches the regular 12-MC-4 metallacrown motif.<sup>6,20</sup> All five sites at the core and the cyclic scaffold are occupied by Cu(II) ions which adopt square planar coordination spheres and hence do not bind any secondary ligands. A sofa-configuration is also observed for this complex. The triethyl ammonium counter ions interact via hydrogen bonds with peripheral oxygen atoms of the hydroximate ligands on opposite sides of the 12-MC-4 cluster. For the full characterization data see ESI (Tab. S1-3; Fig. S5-7).



**Fig. 3** Mössbauer spectrum of **1**; solid lines represent the result of the entire fit (black), the fit for doublet 1 (green) and doublet 2 (red).

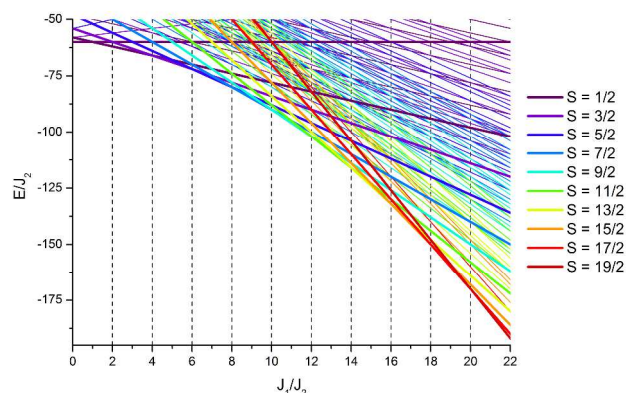
The reported homometallic 12-MC-4 metallacrown complexes in general feature a low-spin ground state which originates from the intrinsic magnetic connectivity.<sup>9-14,15</sup> In Fig. 1, the corresponding idealized square magnetic model with only two distinct coupling constants is shown. Here, the parameter  $J_1$  characterises the radial interaction between the central guest ion and the metal ions in the cyclic host whereas  $J_2$  quantifies the magnetic interaction within the ring. According to the isotropic spin-Hamiltonian for the Heisenberg-Dirac-van-Vleck model below, the relative energies of the spin states are linear functions of the ratio between both coupling constants  $J_1/J_2$ .<sup>10</sup>

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_1\hat{S}_5) - 2J_2(\hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \hat{S}_4\hat{S}_5 + \hat{S}_2\hat{S}_5)$$

The energetic preference of low-spin states for the common case of overall antiferromagnetic interactions is best rationalized by the simple example of a homometallic copper 12-MC-4 metallacrown with all individual spins  $S_i = 1/2$  (Fig. S11). For a dominant tangential coupling below a ratio of  $J_1/J_2 = 1$ , a total spin ground state of  $S_t = 1/2$  is adopted which represents the case of an alternating spin alignment in the cyclic scaffold (Fig. S12-14). A state with  $S_t = 1/2$  remains lowest in energy until a ratio of  $J_1/J_2 = 4$  is exceeded and a parallel alignment among the peripheral spins with opposite orientation towards the central spin is present in the  $S_t = 3/2$  ground state. For real copper 12-MC-4 systems, intermediate ratios around  $J_1/J_2 = 2$  are observed.<sup>10,11-14,21</sup> Hence, an  $S_t = 1/2$  ground state is present in spite of stronger magnetic coupling along the radial than the tangential interaction pathway. In Fig. 5, the temperature-dependent magnetic susceptibility data of the homometallic complex  $(\text{HNEt}_3)_2\text{Cu(II)}[12\text{-MC}_{\text{Cu(II)N(Shi)}}-4]$  **2** are shown in the  $\chi_{MT}$  vs. T plot. At room temperature, the experimental  $\chi_{MT}$  product of 1.00 cm<sup>3</sup> K mol<sup>-1</sup> is distinctly smaller than the calculated spin-only value of 1.88 cm<sup>3</sup> K mol<sup>-1</sup> for five uncoupled Cu(II) ions with  $S_i$

= 1/2 and  $g = 2.0$ . Lowering the temperature, the  $\chi_M T$  values decline to a plateau at  $0.44 \text{ cm}^3 \text{ K mol}^{-1}$  between 10 and 40 K evidencing an isolated  $S_i = 1/2$  spin ground state. Below 10 K, a decrease of the  $\chi_M T$  product is again observed, which can be attributed to weakly antiferromagnetic intermolecular interactions mediated by  $\pi$ - $\pi$  interactions. The shortest distances for Cu(II) ions of adjacent metallacrowns are found to be only 6.05 Å and 6.92 Å. Analyzing these data by the aforementioned magnetic model, the best fit result of  $g = 2.16$ ,  $J_1 = -155.2 \text{ cm}^{-1}$ ,  $J_2 = -92.3 \text{ cm}^{-1}$  and  $J_1/J_2 = 1.7$  is obtained, in good agreement with reported values for comparable compounds.<sup>10,11–14,21</sup> In the corresponding energy level diagram, the low-spin ground state of  $S_i = 1/2$  is well separated from two excited  $S_i = 1/2$  states by 125.8 and 184.5  $\text{cm}^{-1}$  whereas the lowest lying  $S_i = 3/2$  spin state is 213.8  $\text{cm}^{-1}$  higher in energy (Fig. S15). The well isolated ground state is further confirmed by magnetization measurements as the curves match the anticipated Brillouin function (Fig. S16, S17).

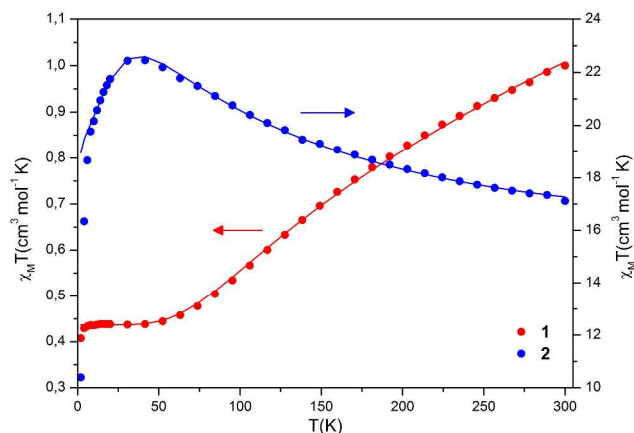
Targeting a high-spin ground state despite the given magnetic connectivity, a reinforcement of the radial ( $J_1$ ) versus the tangential exchange interaction ( $J_2$ ) supports the star-shaped sub-pattern within the square magnetic model (Fig. S18). In that respect, it is worth mentioning that a large number of star-shaped molecules with a high-spin ground state has been reported in spite of antiferromagnetic interactions.<sup>22–27</sup> As the tangential and radial coupling constants of homometallic 12-MC-4 complexes in general lack a sufficient differentiation, we applied a heterometallic approach placing specific metal ions at the core and ring sites. Following the considerations described above, we assigned a Cu(II) guest ion to the task of a central magnetic director as its natural magnetic orbital  $d_{x^2-y^2}$  points directly towards basal donor atoms and can induce extraordinary strong antiferromagnetic exchange interactions in an appropriate arrangement.<sup>28–30</sup> On the other hand, Fe(III) ions were chosen to build up the cyclic host providing high single-ion spin contributions as well as suitable sets of magnetic orbitals. In summary, a target molecule Cu(II)[12-MC<sub>Fe(III)N(Shi)-4</sub>] was designed in order to attain a high-spin metallacrown.



**Fig. 4** Coupling constants ratio-dependent normalized energy level diagram for a generalized Cu(II)[12-MC<sub>Fe(III)N(Shi)-4</sub>] system with antiferromagnetic radial ( $J_1$ ) and tangential ( $J_2$ ) interactions; occurring spin ground states are highlighted.

Analyzing this Cu(II)[12-MC<sub>Fe(III)N(Shi)-4</sub>] system on the basis of the square magnetic model, the number of states significantly increases from 10 to 286 due to the placement of individual spins

$S_i = 5/2$  in the cyclic scaffold (Fig. S19). However, as for the Cu<sub>5</sub> metallacrown, the alternating orientation of the peripheral spins with an  $S_i = 1/2$  ground state is present in the region of dominant radial interaction for ratios  $J_1/J_2 < 1$ . At a ratio  $J_1/J_2 = 4$ , an  $S_i = 3/2$  state becomes lowest in energy and, continuing the reinforcement of the radial interaction, the value of the actual spin ground state successively increases by 1 for every enhancement of the ratio of the coupling constants by 2, as can be seen in Fig. 4. Finally, a maximum parallel spin orientation in the ring with  $S_i = 19/2$  is attained at the upper limit of  $J_1/J_2 = 20$  (Fig. S20). However, increased spin ground states are accessible already for significantly lower ratios between the radial and tangential coupling constant than  $J_1/J_2 = 20$  (Fig. 4).



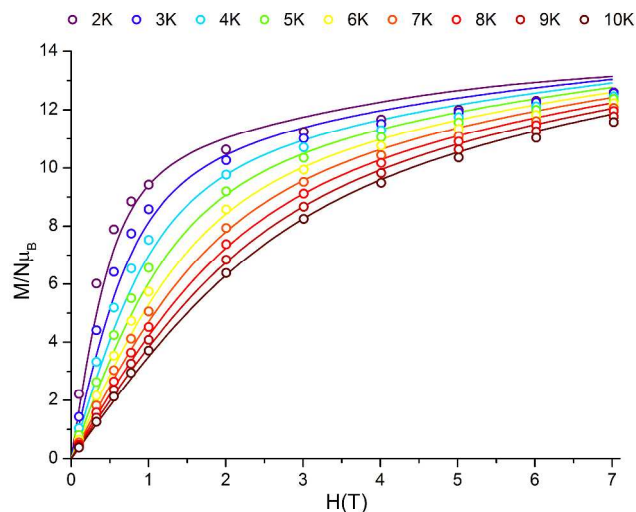
**Fig. 5** Temperature dependence of the  $\chi_M T$  product for **1** and **2**; the solid lines refer to the best fit results of the experimental data.

Having followed the concept discussed, we realized the target system through the synthesis of Cu(II)(DMF)<sub>2</sub>Cl<sub>2</sub>[12-MC<sub>Fe(III)N(Shi)-4</sub>](DMF)<sub>4</sub>·2DMF (**1**). Its temperature-dependent magnetic susceptibility data are given on the basis of a  $\chi_M T$  vs.  $T$  plot in Fig. 5. The experimental  $\chi_M T$  product of  $17.12 \text{ cm}^3 \text{ K mol}^{-1}$  at room temperature is in agreement with the expected spin-only value of  $17.88 \text{ cm}^3 \text{ K mol}^{-1}$  for four non-interacting Fe(III) ions ( $S_i = 5/2$ ) and one Cu(II) ion ( $S_i = 1/2$ ). On decreasing the temperature, the  $\chi_M T$  values increase until a maximum of  $22.45 \text{ cm}^3 \text{ K mol}^{-1}$  is reached around 40 K. This finding clearly suggests an energetic preference of higher spin states. At lower temperatures, the  $\chi_M T$  product decreases again. The final drop below 10 K might indicate zero-field splitting as significant parameters  $D$  have been reported for square pyramidal coordinated Fe(III) ions.<sup>31–33</sup> However, distances of 7.10 and 7.42 Å between Fe(III) ions of adjacent metallacrowns do not exclude intermolecular magnetic interactions either.

The interpretation of the magnetic data was again performed via the aforementioned square magnetic model (Fig. 1). Despite the lack of an exact  $C_4$  symmetry and the different coordination spheres of the distinguishable Fe(III) ions, this simplification is justified because the Cu-O-Fe angles as well as the distances relevant for the exchange interaction resemble each other. Apart from the steep decline below 10 K, the best fit curve reproduces the initial increase, the reaching of a maximum and the final decrease of the  $\chi_M T$  product on cooling very well. The obtained parameters are  $J_1 = -49.2 \text{ cm}^{-1}$  for the radial and  $J_2 = -3.8 \text{ cm}^{-1}$  for the tangential coupling constant. The average  $g$ -value over all



five metal ions is found to be 2.03, perfectly in agreement with the numerical average of expected g-values of 2.0 for four Fe(III) ions and 2.2 for one Cu(II) ion. According to the coupling constants ratio-dependence of the energy levels (Fig. 4) the value of  $J_1/J_2 = 13$  means an  $S_t = 11/2$  spin ground state. However, as shown in Fig. S21 and S22 the next excited  $S_t = 13/2$  and  $S_t = 9/2$  states are only 3.3 and 4.2  $\text{cm}^{-1}$  higher in energy.



**Fig. 6** Field dependence of the reduced magnetization ( $M/N\mu_B$  vs.  $H$ ) plot of **1** for different temperatures between 2 and 10 K; solid lines represent simulations according to the best fit result of the temperature dependence of the  $\chi_M T$  product.

Using the optimized fit parameters from the temperature-dependent susceptibility for a simulation, the field dependence of the reduced magnetization ( $M/N\mu_B$  vs.  $H$ ) is reproduced quite well (Fig. 6, S23). Both types of magnetic measurements clearly confirm the achievement of a high-spin ground state.

## Conclusions

Based on investigations in magnetic properties of homometallic 12-MC-4 metallacrowns, we have developed a heterometallic approach in order to overcome the commonly observed low-spin ground state for these systems. We have designed and realized the first 3d heterometallic 12-MC-4 molecule  $\text{Cu(II)(DMF)}_2\text{Cl}_2[12\text{-MC}_{\text{Fe(III)N(Shi)}^-4}](\text{DMF})_4 \cdot 2\text{DMF}$  by avoiding potential bridging ligands. The purposeful placement of a Cu(II) guest ion at the core of an iron based cyclic host indeed enforces a high-spin ground state due to dominating magnetic interactions between the Cu(II) centre and the Fe(III) ions. Thus, we confirmed that the reliability and flexibility of 12-MC-4 metallacrowns can be combined with advanced magnetic features in a targeted way. Although slow magnetic relaxation has not been observed for the present  $\text{Cu(II)[12-MC}_{\text{Fe(III)N(Shi)}^-4}]$  complex, the versatility of metallacrowns provides various synthetic opportunities for subtle modifications. Hence, our current synthetic efforts aim at the magnetic anisotropy via the exchange of secondary ligands. A refined magnetic model of the novel heterometallic metallacrown will be possible via XMCD measurements.

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## Notes and references

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- <sup>b</sup> Graduate School Materials Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany
- † Electronic Supplementary Information (ESI) available: [Experimental details; synthesis; X-ray crystallography - crystal structure information (Tab. S1), selected interatomic distances and angles (Tab. S2-3), molecular structure of **2** (Fig. S4), numbering schemes with thermal ellipsoids (Fig. S1, S5), packing diagrams (Fig. S2, S3, S6, S7); elemental analysis - data; infrared spectroscopy - data; UV-Vis spectroscopy - data, spectra (Fig. S8, S9); atomic absorption spectroscopy - data; mößbauer spectroscopy - data, spectrum (Fig. S10), ESI-mass spectrometry - data; magnetism - energy level diagrams (Fig. S12-15, S19-S22), magnetization curves (Fig. S16, S17, S23), spin alignment illustrations (Fig. S11, S18)]. See DOI: 10.1039/b000000x/
- ‡ **Crystal data.** **1**  $\text{C}_{52}\text{H}_{72}\text{Cl}_2\text{CuFe}_4\text{N}_{12}\text{O}_{20}$ ,  $M = 1543.04$ , triclinic,  $a = 11.7510(5)$ ,  $b = 12.8013(5)$ ,  $c = 12.8605(5)$  Å,  $\alpha = 96.9260(10)$ ,  $\beta = 111.4130(10)$ ,  $\gamma = 110.2760(10)^\circ$ ,  $U = 1620.39(11)$  Å<sup>3</sup>,  $T = 173$  K, space group P-1 (no.2),  $Z = 1$ , 35651 reflections measured, 7811 unique ( $R_{\text{int}} = 0.0466$ ) which were used in all calculations. The final  $wR(F^2)$  was 0.0779 (all data). **2**  $\text{C}_{40}\text{H}_{48}\text{Cu}_3\text{N}_6\text{O}_{12}$ ,  $M = 1122.58$ , monoclinic,  $a = 9.5697(7)$ ,  $b = 18.8080(13)$ ,  $c = 11.8032(9)$  Å,  $\alpha = 90$ ,  $\beta = 107.039(2)$ ,  $\gamma = 90^\circ$ ,  $U = 2031.2(3)$  Å<sup>3</sup>,  $T = 173$  K, space group P2<sub>1</sub>/c (no.14),  $Z = 2$ , 19690 reflections measured, 4967 unique ( $R_{\text{int}} = 0.0825$ ) which were used in all calculations. The final  $wR(F^2)$  was 0.0795 (all data). CCDC 984042 and 984043.
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TOC

## Enforcing a high-spin ground state for a 12-metallacrown-4 complex via a heterometallic magnetic director approach†

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Applying a novel magnetic director approach, we have realized  $\text{Cu(II)(DMF)}_2\text{Cl}_2[12\text{-MC}_{\text{Fe(III)N}(\text{Shi})\text{-4}](\text{DMF})_4 \cdot 2\text{DMF}$  as the first heterometallic transition metal 12-MC-4 complex in order to equip this type of compound with a high-spin ground state.

