Understanding the magnetism of {Fe$_2$Ln} dimers, step-by-step+

S. G. Baca,a,b J. van Leusen,b M. Speldrichb and P. Kögerlera,b,c

A magnetochemical comparison between the (Fe$_2$$^{II}$Ln$_2$$^{III}$)-type coordination clusters [Fe$_4$M$_2$(OH)$_2$(N$_3$)$_2$(bdea)$_4$(O$_2$CCMe$_3$)$_5$(H$_2$O)]NO$_3$·2(EOFH) (M = Dy, Y) and [Fe$_4$M$_2$(OH)$_2$(N$_3$)$_2$(bdea)$_4$(O$_2$CCMe$_3$)$_4$(NO$_3$)$_2$](3(EOFH) (M = Gd, Eu; H$_2$bdea = N-butyldiethanolamine), of which (Fe$_4$Dy$_2$) reveals slow molecular magnetization relaxation up to 6 K, allows assessment of the exchange coupling governing the clusters’ multiplet patterns.

Though research on single molecule magnets (SMMs) has reached its peak with most of the underlying spin physics now well understood,1 the investigation of heterometallic d/f-based SMMs remains a challenging and attractive goal. In lanthanide-containing SMMs exhibiting very large zero-field splitting,2 which apparently increases the probability of relaxation mechanisms that effectively limit the threshold temperature for the detection of magnetization hysteresis – either of thermal or quantum tunneling origin – are still not completely understood, and these compounds exhibit a surprisingly wide range of relaxation phenomena.2 All this has prompted an extensive effort to assess the magnetism of polynuclear 4f but also heterometallic d/f coordination clusters,3 in order to gain a deeper insight into the relaxation pathways. Until now research on polyheterometallic 3d/4f SMMs was mainly focused on Mn/Ln, Co/Ln, and Ni/Ln heterometallic systems.4 Although some Fe$^{III}$/Ln$^{III}$ heterometallic coordination clusters have also been reported,5 only a few of them exhibit slow magnetization relaxation in the absence of a static field, i.e. SMM characteristics.6,7 This surprisingly frequent absence of slow magnetization relaxation here might be caused by the stray fields produced by the Fe$^{III}$ spin centers, which apparently increases the probability of relaxation via quantum tunneling mechanisms.

At the same time, modeling the thermodynamic magnetic properties of more complex 3d/4f spin structures, such as the susceptibility, requires taking into account all microscopic aspects, in particular single ion effects and spin–spin interactions, which frequently lead to over-parameterization issues. In order to minimize the number of magnetically relevant independent fitting parameters, a comparison between nearly isosctructural complexes of increasing magnetic complexity allows us to stepwise ascertain the ligand field parameters and exchange energies even of 3d/4f compounds comprising magnetically complex spin centers such as Dy$^{III}$.

In this context, we explored the potential of our strategy6 for using both structure-directing aminoalcohols and carboxylates for the synthesis of heterometallic coordination cluster families based on archetypal triangular (M$^{III}$)$_3$(H$_2$O) fragments.7 Here we present the synthesis, structures and magnetic properties of four hexanuclear heterometallic cluster compounds: [Fe$_4$Dy$_2$(OH)$_2$(N$_3$)$_2$(bdea)$_4$(O$_2$CCMe$_3$)$_5$(H$_2$O)]NO$_3$.2(EOFH) (1), which exhibits slow magnetization relaxation and non-zero out-of-phase ac susceptibility up to 6 K, and nearly identical analogues comprising diamagnetic Y$^{III}$ ions, [Fe$_4$Y$_2$(OH)$_2$(N$_3$)$_2$(bdea)$_4$(O$_2$CCMe$_3$)$_5$(H$_2$O)]NO$_3$.2(EOFH) (2), or spin-only Gd$^{III}$ ions, [Fe$_4$Gd$_2$(OH)$_2$(N$_3$)$_2$(bdea)$_4$(O$_2$CCMe$_3$)$_4$.NO$_3$.2(EOFH)] (3). Another compound virtually isosctructural to 3 but incorporating Eu$^{III}$ ions, [Fe$_4$Eu$_2$(OH)$_2$(N$_3$)$_2$(bdea)$_4$(O$_2$CCMe$_3$)$_4$.NO$_3$.2(EOFH)] (4), has also been prepared.

The reaction of the µ-oxo-centered trinuclear iron pivalate with sodium azide and lanthanide(III)/yttrium(III) nitrate in the presence of N-butyldiethanolamine (H$_2$bdea) in a 2 : 1 : 1 : 2 ratio in ethanol solution produced crystals of 1–4 in relatively high yields (53%, 21%, 40% and 46% based on Fe, respectively). All compounds remain thermally stable up to ca. 200 °C. Single-crystal X-ray diffraction analysis‡ reveals that all

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1. Institute of Applied Physics, Academy of Sciences of Moldova, 5 Academiei str., Chisinau, MD-2028, Moldova
2. Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, D-52074 Aachen, Germany. E-mail: paul.koegerler@ac.rwth-aachen.de
3. Peter Grüning Institute, PGI-6, Research Centre Jülich, D-52425 Jülich, Germany
4. Electronic supplementary information (ESI) available: Synthesis, characterization, X-ray diffraction, magnetochemical analysis details, additional structural plots and thermal stability data. CCDC 937876, 959015–959017. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6qi00095a

‡ Crystal data for 1: Ca$_4$H$_{13}$Dy$_2$Fe$_4$N$_2$O$_{33}$, Mr = 1981.15 g mol$^{-1}$, triclinic, space group $P1$, $a = 14.4435(9)$, $b = 17.3351(11)$, $c = 18.0251(12)$ Å, $\alpha = 92.765(10)$, $\beta = 104.869(2)$, $\gamma = 96.595(2)$, $V = 4332.9(5)$ Å$^3$, $Z = 2$, $R_1 = 0.0548$ ($I > 2\sigma(I)$), $wR_2 = 0.1246$ (for 14 285 unique reflections and 1040 refined parameters). 2: Ca$_4$H$_{13}$Fe$_4$N$_2$O$_{33}$, Mr = 1833.97 g mol$^{-1}$, triclinic, space group $P1$, $a = 14.423(4)$,
complexes crystallize in the space group $P$1 and feature the coordination cluster monocation $[\text{Fe}_4\text{M}_2(\text{OH})_2(\text{N}_3)_3(\text{bdea})_4(\text{O}_2\text{CCMe}_3)_3(\text{H}_2\text{O})_3]^{\text{M} = \text{Dy, Eu}}$, a nitrate counteranion and two ethanol solvate molecules in 1 and 2, or the neutral $[\text{Fe}_4\text{M}_2(\text{OH})_2(\text{N}_3)_3(\text{bdea})_4(\text{O}_2\text{CCMe}_3)_3(\text{NO}_3)_2]^{\text{M} = \text{Gd, Eu}}$ cluster and three ethanol solvates in 3 and 4. As complexes 1 and 2 as well as 3 and 4 are isostructural, we limit the structural description to 1 and 3. The cationic complex in 1 consists of a hexanuclear oxido-linked core fragment of four FeIII and two DyIII ions and can be regarded as two nearly identical Fe$_2$Dy$_2$ triangles condensed via two μ$_2$-hydroxio groups (Fig. 1), with a Dy⋯Dy distance of 3.871(6) Å.

Four bridging pivate groups and four doubly deproto- nated N-butylidethanolamine ligands additionally bridge the Fe$_2$Dy$_2$ triangles $[\text{Dy}⋯\text{Fe}, 3.392(12)$ and $3.404(11)$ Å] and the metal sites within each triangle motif $[\text{Fe}⋯\text{Fe}, 3.169(17)$–$3.172(17)$ Å; Fe⋯Dy, 3.450(12)–3.542(12) Å]. The central $[\text{Fe}_4\text{Dy}_2(\mu_3-\text{O})_2]^{-}$ fragment can alternatively be decomposed into four edge-sharing $[\text{M}_2\text{M}(\mu_3-\text{O})_3]$ triangles: Fe1Fe2Dy2, Dy1Dy2Fe1, Dy1Dy2Fe3, and Fe3Fe4Dy1. Two (end-on) azide ligands (to Fe2/Fe4), one monodentate carboxylate and a water molecule (to Dy1/Dy2) complete the metal coordination spheres. Each N-butylidethanolamine group links two FeIII and two DyIII atoms: two polycarboxylates residues act as hexadentate ligands via one N atom and μ$_3$-O and μ$_2$-O atoms and the remaining two bde$_2^{-}$-act as pentadentate ligands via one N atom and two μ$_2$-O linkages. All Fe(n) ions adopt distorted octahedral environ- ments: Fe1 and Fe3 are NO$_5$ coordinated by a μ$_3$-OH group $[\text{Fe}⋯\text{M}_2(\text{OH})_2(\text{N}_3)_3(\text{bdea})_4(\text{O}_2\text{CCMe}_3)_3(\text{H}_2\text{O})_3]^{\text{M} = \text{Dy, Eu}}$, a carboxylate oxygen $[\text{Fe}⋯\text{O}_{\text{carb}}]$, 1.943(5)/1.969(5) Å, a carboxylate oxygen $[\text{Fe}⋯\text{O}_{\text{carb}}]$, 1.967(6)/1.953(6) Å as well as three alkoxo oxygen atoms (one μ$_3$-O and two μ$_2$-O) from two bde$_2^{-}$ groups $[\text{Fe}⋯\text{O}_{\text{alk}}]$, 1.968(5)–2.069(5) Å and a nitrogen atom from one polycarboxaline $[\text{Fe}⋯\text{N}], 2.218(7)/2.196(7)$ Å; Fe2 and Fe4 are NO$_5$ coordinated by a carboxylate oxygen atom $[\text{Fe}⋯\text{O}_{\text{carb}}]$, 2.027(6)/2.046(6) Å, three alkoxo oxygen atoms (one μ$_3$-O, two μ$_2$-O) of two bde$_2^{-}$ groups $[\text{Fe}⋯\text{O}_{\text{alk}}]$, 1.949(5)–2.055(5) Å, a bde$_2^{-}$N atom $[\text{Fe}⋯\text{N}_{\text{alk}}]$ 2.212(7)/2.215(6) Å and an azide-N atom $[\text{Fe}⋯\text{N}_{\text{azide}}]$, 1.992(8)/1.990(8) Å. Both DyIII ions are eight-coordinated: two μ$_2$-OH groups, two oxygen atoms from two carboxylates, two alkoxo μ$_3$-O and one μ$_1$-O atoms from two bde$_2^{-}$; Dy1 additionally binds to a monodentate pivate, Dy2 to H$_2$O $[\text{Dy}⋯\text{O}, 3.204(5)–2.364(5)$ Å. The coordinated water molecule and monodentate pivate as well as the outer-sphere nitrate anion and two solvate ethanol molecules engage in extensive intra- and intermolecular hydrogen bonding in 1. In particular, one of the OH$^-$ groups forms a strong intramolecular O⋯H⋯O hydrogen bond $[2.608(8)$ Å] with the uncoordinated carboxylate oxygen (O2⋯O4), whereas the second hydroxide forms an intermolecular O⋯H⋯O hydrogen bond $[2.777(8)$ Å] with the nitrate anion (O1⋯O22, see Fig. S2).

Very similar to 1, the charge-neutral coordination cluster in 3 also consists of a hexanuclear oxido-linked core fragment of four FeIII and two GdIII ions or two nearly identical Fe$_2$Gd tri- angles bridged by two μ$_3$-OH groups $[\text{Gd}⋯\text{Gd}, 4.053(1)$ Å, Fig. S5]. The difference stems from apical ligands coordinated to the two LnIII ions: in 3, these are two chelated NO$_3^{-}$ anions vs. monodentate pivate acid and H$_2$O in 1. As a result, both GdIII sites are O$_x$-coordinated (Fig. 2); Gd–O, 2.316(8)–2.650(8) Å. The coordination environment of the four FeIII atoms is similar to 1 [NO$_3$ for Fe1 and Fe3, N$_2$O$_4$ for Fe2 and Fe4; Fe–O, 1.965(7)–2.079(7) Å; Fe–N, 1.993(8)–2.254(9) Å].

Magnetometric analyses of 1–4 (Fig. 3) – with the ultimate goal of modeling the magnetically complex $\{\text{Fe}_4\text{Dy}_2\}$

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Fig. 1 Structure of the $\{\text{Fe}_4\text{Dy}_2\}$ complex in 1. Color scheme: O, red; C (carboxylate), light gray; C (bdea), dark gray; N (azide), light blue; N (bdea), dark blue. Only the hydrogen positions of the μ$_3$-OH groups are shown for clarity.

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Fig. 2 Comparison of the structure of the $\{\text{Fe}_4\text{Dy}_2\}$ complex in 1 (left) and the $\{\text{Fe}_4\text{Gd}_2\}$ complex in 3 (right), in an approx. perpendicular view to that in Fig. 1. Highlighted are the terminal ligands (H$_2$O and monodentate pivate in 1, nitrate in 3) resulting in eight- and nine-coordinated lanthanide centers. All terminal organic residues, azide and hydrogen omitted for clarity.
species 1 – employed the computational framework CONDON that implements a 'full model' Hamiltonian and thus accounts for all microscopic aspects necessary to model the complex 3d–4f spin structure, in particular the relevant single-ion effects and coupling interactions (see the ESI† for computational details). To quantify these effects, we analyzed the magnetic susceptibility data considering ligand-field effects, spin–orbit coupling, and external magnetic field. Standard values are employed for spectroscopic parameters (e.g. Racah energies B and C or spin–orbit coupling energies). CONDON alternatively implements an effective isotropic spin model that is used for comparison where applicable. Note that the presence of at least three different exchange pathways (all mediated by μ₃-O bridges) precludes the unambiguous direct determination of their associated exchange energies (J₁, J₂, J₃, J₄, or the molecular field parameter λ_mf; see coupling scheme) based on χ_m(B,T) data. Furthermore, the computational requirements for a full model of the hexanuclear {Fe₄Ln₂} cluster mandate a simplification to the coupling scheme that is herein divided into two identical {Fe₄Ln} triangles (see Fig. 1), the interaction of which is accounted for by a molecular field term. To address these issues the following strategy was employed: we start with the magnetically simplest system {Fe₄Y₂} containing diamagnetic Y³⁺ to extract the parameters of the Fe³⁺ centers which are adopted for all other systems. Next, {Fe₄Gd₂} is analyzed as a purely isotropic spin system; these results are compared to full-model calculations based on the two-triangle coupling scheme, in order to validate the latter. Finally, full-model calculations are applied to {Fe₄Dy₂}, {Fe₄Eu₂} serves as an additional reference point for this approach.

Given the nearly identical geometries, the nearest-neighbor Fe–Fe coupling (J₂) is assumed to vary minimally between 1–4 and can be directly determined from the {Fe₄Y₂} species (2). Based on the angular overlap model, implemented and parameterized in the program wxJFinder, these variations should not exceed ±10% for the individual Fe–O(H)–Fe exchange pathway geometries in 1–4. Here, any inter-triangle Fe⋯Fe exchange coupling (which would involve extended –O–Y–O–exchange pathways) can be neglected and the Heisenberg-type intra-molecular exchange interaction pattern (Hₜₐₜ = 2JₜₐₜSₜSₐ) is simplified to that of a spin dimer. The tetragonally distorted FeO₆ coordination environments in 1–4 are best described as D₄h symmetric; for this assumption the Fe³⁺ ligand field parameters derived from a least-squares fit for 2 are B₀² = −3500 cm⁻¹, B₂₀ = 24000 cm⁻¹, and B⁴₀ = 19000 cm⁻¹ (in Wybourne notation) and J₂ = −6.5 cm⁻¹ (SQ = 1.0%; Fig. 3). These Bᵦ values are used as constants in the fitting procedures of 1, 3, and 4. As is evident from the susceptibility temperature dependence (at 0.1 Tesla; Fig. S9†) with a maximum at 55 K and a minimum at 5 K, a small paramagnetic impurity is present and it can also be quantified (ρ = 0.2%). Analyzing 2 as a purely isotropic spin system (χₑₓ = gₘₑₙ = 2.0) results in a slightly worse fit but yields the same J₂ value of −6.5 cm⁻¹ (SQ = 1.8%, ρ = 0.25%; Fig. S10†).

Next, we swap diamagnetic Y³⁺ for spin-only Gd³⁺ centers, i.e. moving from 2 to 3. The low-field χT curve of 3 decreases from 29.6 cm³ K mol⁻¹ and reaches a minimum of around 16.6 cm³ K mol⁻¹ at 8.0 K. Approximating {Fe₄Gd₂} as an isotropic spin system, a least-squares fit to a Heisenberg-type Hamiltonian (see coupling scheme, Fig. 3) yields J₁ = −(0.38 ± 0.12) cm⁻¹, J₂ = −(6.5 ± 0.1) cm⁻¹, J₃ = +(0.20 ± 0.06) cm⁻¹ and J₄ = +0.03 ± 0.01 cm⁻¹ (SQ = 1.2%; see the ESI† for correlation analysis). We note that the converged J₂ value is identical to that for 2, as expected for the nearly identical exchange pathway geometries. The weak Gd⋯Gd contact (J₃) is found to be approx. one order of magnitude smaller than the Gd⋯Fe contacts; weak ferromagnetic interactions are also documented for μ₃-hydroxo-bridged Fe⋯Gd³⁺ and Gd⋯Gd³⁺ examples.

As mentioned above, modeling the Fe³⁺ and Gd³⁺ centers in {Fe₄Gd₂} with their full single-ion effects mandates restrictions to the exchange coupling scheme in the model Hamiltonian: the {Fe₄Gd₂} cluster is described as a dimer of triangles, where all inter-triangle exchange interactions are represented by the molecular field approximation $\chi = \chi' - \lambda_{mf}$ where $\chi'$ represents the susceptibility contribution of the two uncoupled {Fe₄Gd₂} triangles. This model then yields $B₀² = −200$ cm⁻¹, $B₂₀ = −1900$ cm⁻¹, and $B⁴₀ = 205$ cm⁻¹ for Gd³⁺ and $J₂ = 0.42$ cm⁻¹, $J₄ = −6.5$ cm⁻¹ and $\lambda_{mf} = +0.042$ mol cm⁻³ (SQ = 1.9%). Both models for 3 are in excellent agreement, see Fig. S11† with identical values for $J₂$ and ferromagnetic inter-triangle coupling (i.e. $\lambda_{mf} > 0$).

The {Fe₄Eu₂} species (4) with its nearly temperature-independent paramagnetic Eu³⁺ centers ($m_y = 0$, see Fig. S9†) further corroborates that the $J₂$ value is nearly independent of

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**Fig. 3** Top: Coupling scheme for the (Fe₄Ln₂) core structure with four exchange constants ($J_{1-4}$). Bottom: Temperature dependence of $\chi T$ for 1 (Dy, blue), 2 (Y, black), 3 (Gd, red), and 4 (Eu, green) at 0.1 Tesla. Open circles: experimental data, lines: least-squares fit to the employed model Hamiltonian (see text). Dashed lines: sum of (uncoupled) single ion effects of each (Fe₄Ln₂) entity.
the lanthanide in the \{Fe_4Ln_2\} family. The $\chi$ vs. $T$ curve (0.1 Tesla) shows a maximum at 55 K and a minimum at 5 K, i.e. the same as those for 2. Thus, in a first-order approximation we adopted the coupling scheme for 2, augmented by the additive contributions of the two Eu$^{III}$ centers. A least-squares fit ($SO = 1.0\%$) then yields $B_0^1 = -150 \text{ cm}^{-1}$, $B_0^6 = -1940 \text{ cm}^{-1}$, $B_0^5 = 208 \text{ cm}^{-1}$ (if parameters for Eu$^{III}$) and confirms $J_2 = -6.7 \text{ cm}^{-1}$.

The magnetism of the \{Fe$_4$Dy$_2$\} species (1), with the Dy$^{III}$ ions in a non-coordinated coordination environment, is strongly dependent on both the single-ion effects, in particular the thermal population of higher Dy$^{III}$ multiplet states, and the Fe...Fe and Fe...Dy interactions. The increase in $\chi T$ with decreasing temperatures below 8 K that is also observed for several traditional iron(III) complexes, further supports the presence of Dy$^{III}$ magnetic interactions. The increase in $\chi T$ with decreasing temperatures below 8 K that is also observed for 2 is caused by very weak ferromagnetic inter-triangle interactions. Akin to 2, the \{Fe$_4$Dy$_2$\} unit is modeled as a dimer of identical isosceles triangles, in order to allow the usage of the Russell–Saunders ground term for each Dy$^{III}$ ion and Fe$^{III}$ ion (note that the full \{Fe$_4$Dy$_2$\} system would require 3.2 TByte random access memory for matrix diagonalization). The assumption of $D_{4d}$-symmetric Dy$^{III}$O$_8$ environments in 1 was found to be an adequate approximation, a less-symmetric ligand field (correspondingly parameterized by a higher number of independent ligand field parameters) did not significantly increase the fitting quality. For 2, intra-triangle exchange interactions are described by Heisenberg coupling; all inter-triangle interactions were modeled via the molecular field approximation. A least-squares fit ($SO = 1.6\%$) results in $B_0^1 = -300 \text{ cm}^{-1}$, $B_0^6 = -1850 \text{ cm}^{-1}$, and $B_0^5 = 210 \text{ cm}^{-1}$ for Dy$^{III}$ and $J_1 = -0.48 \text{ cm}^{-1}$, $J_2 = -6.7 \text{ cm}^{-1}$, and $\lambda_{mf} = +0.075 \text{ mol cm}^{-1}$. Note that $J_2$ converges very close to the corresponding values for 2–4 and that the Fe...Dy exchange energy ($J_1$) as expected is very similar to the Fe...Gd exchange in 2. The derived If parameters for Dy$^{III}$ correspond to a zero-field splitting of the free-ion $j = 15/2$ ground state multiplet into $m_j$ levels, where the lowest states with $m_j = \pm 11/2$ are 7.9 cm$^{-1}$ below the next-highest $m_j = \pm 9/2$ states (Fig. 4a). The energetic separation to the $m_j = \pm 1/2$ states, relevant for thermal magnetization relaxation processes, is 240.4 cm$^{-1}$.

Therefore, alternating-current magnetic susceptibility measurements with no dc bias were analyzed in order to determine if these splitting patterns lead to an effective slowing-down of the relaxation of the magnetization upon an external field change. Frequency-dependent peaks are observed in the out-of-phase response and indicate that \{Fe$_4$Dy$_2$\} exhibits single-molecule characteristics up to 6 K, although this is close to the thermal quantum regime (Fig. S12 and S13†). The corresponding real (in-phase) $\chi'$ and the imaginary (out-of-phase) components $\chi''$ were fitted to a Cole–Cole equation (Fig. 4b).† The resulting average relaxation times of the magnetization, $\tau$, allow the parameterization of common relaxation process types. The observed spread in $\alpha$ (0.03–0.24) indicates several relaxation pathways, and we determined that a combined Orbach–Raman relaxation, $\tau = 1/(\tau_0^{-1} \exp[-\Delta E/k_B T] + \tau_R^{-1})$, allows for a more adequate determination of relaxation parameters (Fig. S14†). This results in an attempt time $\tau_0 = (1.01 \pm 0.89) \times 10^{-7} \text{ s}$, an effective relaxation barrier $\Delta E = (18.4 \pm 2.7) \text{ cm}^{-1}$, i.e. less than a tenth of the $m_j = \pm 11/2$–$\pm 1/2$ splitting, and Raman parameters $n = 6.6 \pm 0.4$ and $C = (0.06 \pm 0.23)$ K$^{-n}$ s$^{-1}$. We note that the Orbach parameters are similar to previously reported \{Fe$_4$Dy$_2$\} species. The Raman parameter $n$ is lower than 9, i.e. the value expected for Kramers ions, but such lower values (4–9) have been reported previously and may be due to e.g. optical phonons.†

Conclusions

In conclusion, the four hydroxide-bridged \{Fe$_2$M\} dimer complexes in 1–4 enable us to analyze their magnetic characteristics in a stepwise, comparative ansatz. In particular, the full magnetochemical analysis of the susceptibility data of the \{Fe$_4$Dy$_2$\} species requires exploiting the clusters’ close structural relationship in order to avoid over-parametrization issues. The \{Fe$_4$Dy$_2$\} compound (1) exhibits slow magnetization relaxation, i.e. SMM behavior, which we link to the zero-field splitting of the Dy$^{III}$ ground multiplet. Contrasting all previous work on Fe$^{III}$/Dy$^{III}$ complexes, herein we were able to also model the Fe–Fe and Fe–Dy coupling energies: antiferromagnetic interactions are dominant, yet weaker inter-triangle interactions appear ferromagnetic. Finally, we cautiously note that our magnetochemical interpretation, based solely on susceptibility data derived from microcrystalline samples, only allows for an assessment within the limitations of the various employed models. Numerous attempts to isolate larger single crystal specimens for single-crystal anisotropy measurements unfortunately remained fruitless.

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