

# Fluoride-Bridged $\{\text{Gd}^{\text{III}}_3\text{M}^{\text{III}}_2\}$ (M = Cr, Fe, Ga) Molecular Coolers\*\*

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Paramagnetic molecules with large spin and negligible magnetic anisotropy have received immense interests in the last few years due to the demonstration of large magneto-caloric effects (MCE).<sup>1</sup> The effect is inherently related to the magnetic entropy increase at low temperatures, which follows an adiabatic demagnetization. Particularly, it is of interest to link the magnetic centers, and shield them magnetically from adjacent molecules, by lightweight ligands to furnish high magnetic density coolers. For an exchange-coupled polynuclear complex, if only the ground spin manifold,  $S_T$ , is considered, the magnetic entropy is given by  $S_m = R \ln(2S_T + 1)$ . The type and strength of the magnetic interactions determine the way in which the entropy is gradually released with decreasing temperature, which occurs more abruptly in the temperature range where the interactions are important.<sup>1a,2</sup> Ultimately, on increasing the field change,  $\Delta B$ , the change of entropy,  $-\Delta S_m$ , reaches its maximum value, corresponding to the full entropy content of the system, viz., the entropy sum over all single-ion spins,  $S_i$ , i.e.,  $R \sum_i \ln(2S_i + 1)$ . Conclusively, it seems promising to combine  $\text{Gd}^{\text{III}}$  ( $S_{\text{Gd}} = 7/2$ ) with “magnetically isotropic” transition metal ions as  $\text{Cr}^{\text{III}}$  ( $S_{\text{Cr}} = 3/2$ ) or high-spin  $\text{Fe}^{\text{III}}$  ( $S_{\text{Fe}} = 5/2$ ), preferably connected by weak *intra*-molecular ferromagnetic interactions. Recently, Winpenny and co-

workers,<sup>3</sup> and we,<sup>4</sup> reported the first examples of polynuclear complexes incorporating fluoride-bridged  $\{\text{Cr}^{\text{III}}\text{-F-Ln}^{\text{III}}\}$  units. These systems owe their existence to the robust character of  $\text{Cr}^{\text{III}}$  ( $d^3$ ) complexes by avoiding precipitation of insoluble  $\text{LnF}_3$ .<sup>5</sup> Unfortunately, this fact imposes strong limitations on the chemistry that can be exploited and we herein demonstrate that fluoride-bridged 3d-4f polynuclear complexes can indeed also be prepared from labile transition metal fluoride complexes. As we recently communicated, the reaction of *fac*- $[\text{CrF}_3(\text{Me}_3\text{tacn})]\cdot 4\text{H}_2\text{O}$  ( $\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane) with  $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  yields a fluoride-bridged  $\{\text{Nd}_3\text{Cr}_2\}$  trigonal bipyramid (TBP). Performing the same reaction employing  $\text{Gd}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$  affords the closely related  $[\{\text{CrF}_3(\text{Me}_3\text{tacn})\}_2\text{Gd}_3\text{F}_2(\text{NO}_3)_7(\text{H}_2\text{O})(\text{CH}_3\text{CN})]\cdot 4\text{CH}_3\text{CN}$  (**1**) which can be considered as a lightweight analog of the  $[\{\text{CrF}_3(\text{Me}_3\text{tame})\}_2\text{Gd}_3\text{F}_3(\text{hfac})_6]\cdot 7\text{CH}_3\text{CN}$  ( $\text{Me}_3\text{tame} = 1,1,1$ -tris{(methylamino)methyl}ethane,  $\text{hfacH} = 1,1,1,5,5,5$ -hexafluoro-acetylacetone) TBP-shaped pentanuclear system that exhibits good cooling properties. Although this result is unsurprising, the analogous reaction with novel *fac*- $[\text{FeF}_3(\text{Me}_3\text{tacn})]\cdot \text{H}_2\text{O}$  and *fac*- $[\text{GaF}_3(\text{Me}_3\text{tacn})]\cdot 4\text{H}_2\text{O}$ , conveniently synthesized from  $\text{FeF}_3$  and  $\text{GaF}_3\cdot 3\text{H}_2\text{O}$ , respectively, yield isostructural  $\{\text{MF}_3(\text{Me}_3\text{tacn})\}_2\text{Gd}_3\text{F}_2(\text{NO}_3)_7(\text{H}_2\text{O})(\text{CH}_3\text{CN})\cdot 4\text{CH}_3\text{CN}$  (M = Fe (**2**), Ga (**3**); cf. Figure 1) without any signs of  $\text{GdF}_3$  formation. Notably, the presence of any hydroxide bridging can be safely ruled out based on electrospray mass spectra (Figures S4-6).

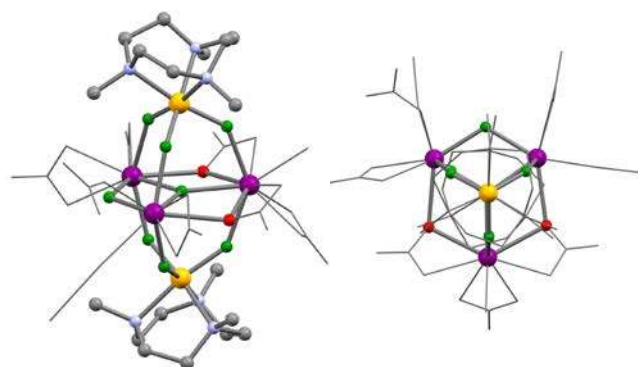
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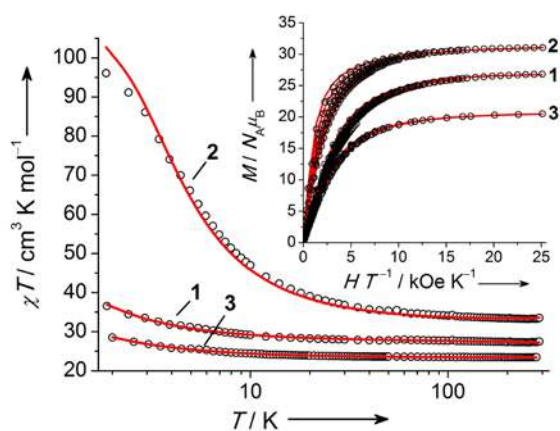
**Figure 1.** Structure of **2** shown in perspective (left) and along the Fe...Fe direction (right). Color codes: Gd, purple; Fe, orange; F, green; O, red; N, blue; C, grey. For clarity,  $\text{CH}_3\text{CN}$  molecules and the auxiliary Gd ligand sphere is shown as wireframe.

The capping *fac*- $[\text{FeF}_3(\text{Me}_3\text{tacn})]$  units ( $\angle\text{Gd-F-Fe} = 137.1(1)^\circ$ – $143.1(1)^\circ$ ) impose an approximately isosceles  $\{\text{Gd}_3\}$  triangle. Herein, two edges consist of  $\eta^1:\eta^2:\mu_2$ -bridging nitrate ions and one edge consists of a  $\mu_2$ -fluoride (cf. Figure 1). Additionally, the center furnishes a single  $\mu_3$ -fluoride bridge close to the  $\{\text{Gd}_3\}$  plane with  $\text{Gd}-(\mu_3\text{-F})-\text{Gd}$  angles of  $110.43(11)^\circ$ ,  $124.64(12)^\circ$  and  $124.93(11)^\circ$ . Compounds **2** and **3** add to the tiny family of fourth row/transition element-lanthanide, fluoride-bridged systems which, in addition to the  $\text{Cr}^{\text{III}}$  systems,<sup>3,4</sup> only encompasses  $[\text{La}\{(\text{C}_5\text{Me}_4\text{Et})_2\text{Ti}_2\text{F}_7\}_3]$  and

[Ln{(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti<sub>2</sub>F<sub>7</sub>})<sub>3</sub>] (Ln = Pr, Nd).<sup>6</sup> These latter systems, however, rely on the pronounced “hard” metal ions Ti<sup>IV</sup> and Ln<sup>III</sup>, which compete efficiently for fluoride-abstraction. Neither Fe<sup>III</sup> nor Ga<sup>III</sup> are as “hard” as Ti<sup>IV</sup> or kinetically robust as Cr<sup>III</sup>, but, surprisingly, exhibit similar reactivity towards Gd<sup>III</sup>. The lightweight structures and the larger spin possessed by high-spin Fe<sup>III</sup> over Cr<sup>III</sup>, fuelled our curiosity whether improved molecular coolers could result. The magnetic data for the isolated *fac*-[CrF<sub>3</sub>(Me<sub>3</sub>tacn)]·4H<sub>2</sub>O and *fac*-[FeF<sub>3</sub>(Me<sub>3</sub>tacn)]·H<sub>2</sub>O complexes are shown in the Supporting Information (Figure S7-8). As expected, the magnetic data are largely reminiscent of a Curie behaviour with temperature-independent  $\chi T$  products approaching the values expected for  $S_{\text{Cr}} = 3/2$  and  $S_{\text{Fe}} = 5/2$ , with a  $g$ -factor of  $g \approx 2$ . The temperature dependence of the magnetic susceptibility for **1**, **2** and **3** is shown in Figure 2 in the form of  $\chi T$  products. The field dependence of the magnetizations is given in Figure 2 (inset) and Figures S9-11. The high-temperature values of the  $\chi T$  products (**1**: 27.3 cm<sup>3</sup> mol<sup>-1</sup> K, **2**: 33.3 cm<sup>3</sup> mol<sup>-1</sup> K and **3**: 23.6 cm<sup>3</sup> mol<sup>-1</sup> K) are in good agreement with the values expected for the spin-only contributions from the uncorrelated ions. On cooling, all  $\chi T$  products increase to reach 36.6, 96.1 and 28.5 cm<sup>3</sup> mol<sup>-1</sup> K for **1**, **2** and **3**, respectively. This behavior suggests the presence of *intra*-complex ferromagnetic interactions for all compounds. The magnetic data were fitted by use of the Levenberg-Marquardt algorithm<sup>7</sup> and by numerical diagonalization of the matrix representation of the isotropic spin-Hamiltonian (1):

$$\hat{H} = g\mu_B \mathbf{B} \cdot \sum_i \hat{\mathbf{S}}_i + J_{ij} \sum_{i,j \neq i} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \quad (1)$$

where the indices  $i$  and  $j$  run through the constitutive single-ions of each compound,  $g$  is the single-ion  $g$ -factor, fixed to 2.0 for all ions,  $\hat{\mathbf{S}}$  is a spin-operator and  $J_{ij}$  is the isotropic exchange coupling parameter between the  $i^{\text{th}}$  and  $j^{\text{th}}$  centres. For **1** and **2**, the  $\chi T$  product and the low temperature variable field magnetization ( $M$  vs.  $H$ ) data can be fitted using just two parameters, namely:  $J_{\text{M-Gd}}$  and  $J_{\text{Gd-Gd}}$ , while fitting the  $\chi T$  data against spin-Hamiltonian (1) results in strongly correlated parameters. The modeling of the magnetic data of **3** affords a good estimation of the Gd-Gd exchange interaction void of complicating, additional interactions. Simultaneous fitting of the  $\chi T$  product and the  $M$  vs.  $H$  data yields  $J_{\text{Gd-Gd}} = -0.028$  cm<sup>-1</sup>. The best-fit curves are shown as solid lines in Figure 2 and in the SI.

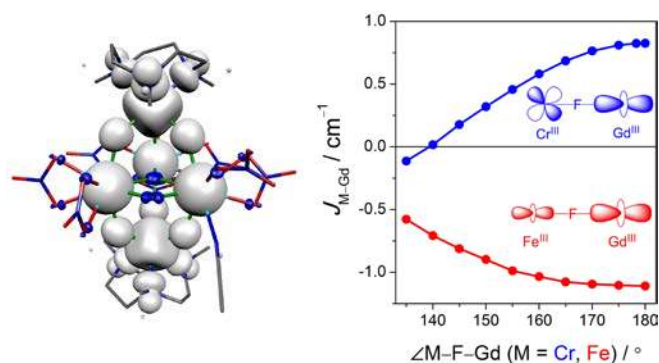


**Figure 2.** Temperature dependence of the  $\chi T$  product ( $\chi \equiv M/H$ ,  $H = 1000$  Oe) of **1**–**3**. The solid, red lines are best-fits as described in the text. Inset: Reduced magnetization and best-fits for **1**–**3** at selected low temperatures.

The data of **1** and **2** were fitted with only  $J_{\text{M-Gd}}$  as free parameter assuming transferability of  $J_{\text{Gd-Gd}}$  from **3** to **1** and **2**. For **1**, this

yielded  $J_{\text{Cr-Gd}} = -0.046$  cm<sup>-1</sup> and  $-0.036$  cm<sup>-1</sup> as obtained from the  $\chi T$  product and magnetization data, respectively. Analogously, for **2**, the best-fit  $J_{\text{Fe-Gd}}$  parameter values were  $-0.25$  cm<sup>-1</sup> (from  $\chi T$ ) and  $-0.26$  cm<sup>-1</sup> (from  $M$  vs.  $H$ ).

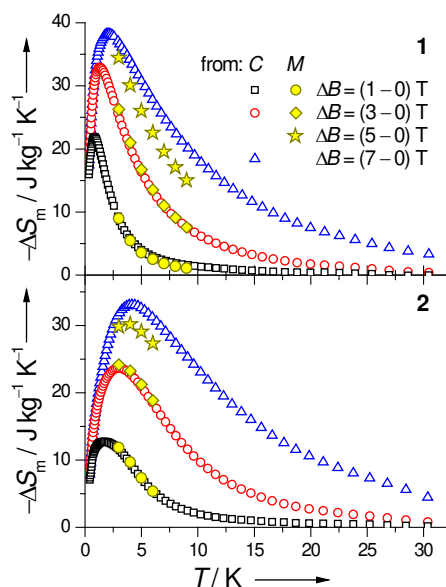
In previous studies,<sup>8</sup> we have established a magneto-structural correlation of the  $J_{\text{Cr-Gd}}$  parameter as function of the Cr-F-Gd bridging angle. The average Cr-F-Gd bridging angle of 141.5° in **1**, should according to this correlation result in a very small positive  $J_{\text{Cr-Gd}}$ . This is in reasonable agreement with the vanishing best-fit  $J_{\text{Cr-Gd}}$  parameter value. To gain insight in the magnitude and sign of the Fe<sup>III</sup>-F-Gd<sup>III</sup> interaction, DFT calculations employing the experimental geometry were undertaken. The resulting parameter values are;  $J_{\text{Fe-Gd}} = -0.35$  cm<sup>-1</sup> and  $J_{\text{Gd-Gd}} = -0.02$  cm<sup>-1</sup>, also in good agreement with the experimental findings and previous theoretical studies.<sup>9</sup>



**Figure 3.** DFT-computed spin densities (left) for complex **2** drawn with isosurface value of 0.003  $a_0^{-3}$  ( $a_0 = \text{Bohr length}$ ) and DFT-based magneto-structural correlations (right) developed for the model complex described in the text.

Further, we performed calculations on the dinuclear model [Fe<sup>III</sup>F<sub>2</sub>(py)<sub>4</sub>Gd<sup>III</sup>(hfac)<sub>4</sub>] (py = pyridine) to develop a magneto-structural model for the Fe<sup>III</sup>-F-Gd<sup>III</sup> unit mimicking our approach for the Cr<sup>III</sup> analog.<sup>8</sup> This simple approach is justified by the equality of the average Fe-F (1.91 Å) and Cr-F (1.91 Å) bond distances in **1** and **2**. DFT calculations yield a ferromagnetic coupling ( $J = -1.1$  cm<sup>-1</sup>) for the dinuclear model in contrast to the Cr<sup>III</sup> analog where an antiferromagnetic coupling was calculated. As discussed by Ruiz and co-workers, the interaction of the 3d orbitals of transition metals with the 5d orbitals of Gd<sup>III</sup> plays a key role in controlling the sign of the magnetic interaction.<sup>10</sup> Previously, we established the mechanism of magnetic coupling for generic 3d-Gd<sup>III</sup> pairs where the crucial role of empty 5d orbitals of Gd<sup>III</sup> was illustrated.<sup>11</sup> Specifically, the occupation of 5d orbitals is linked to the sign of the coupling constant, with larger occupation leading to more ferromagnetic interaction, in structurally related compounds.<sup>11b</sup> For Cr<sup>III</sup>, with ( $t_{2g}$ )<sup>3</sup> configuration, interaction with Gd<sup>III</sup> 5d orbitals is relatively smaller as compared to Fe<sup>III</sup> where the  $e_g$  orbitals promote stronger delocalization and interaction with the Gd<sup>III</sup> 5d orbitals. The differential occupancy is evident also from the NBO calculations (see SI for details). The overlap between 3d and 4f orbitals, which generally contributes to antiferromagnetic coupling, is also detected to be significantly less for the Fe<sup>III</sup>-Gd<sup>III</sup> pair compared to Cr<sup>III</sup>-Gd<sup>III</sup> analogues (cf. SI, Table S3). The angular dependence of  $J_{\text{Fe-Gd}}$  in {Fe<sup>III</sup>-F-Gd<sup>III</sup>} (cf. Figure 3 (b)) shows the magnitude of the ferromagnetic  $J_{\text{Fe-Gd}}$  to increase with the bridging angle, while for {Cr<sup>III</sup>-F-Gd<sup>III</sup>} an opposite trend was established.<sup>8</sup> As the angle increases, the interaction of the Fe<sup>III</sup>  $d_{z^2}$  orbital with Gd<sup>III</sup> 5d orbitals is expected to be large, leading to stronger ferromagnetic coupling

for the Fe<sup>III</sup>-Gd<sup>III</sup> pair. For the Cr<sup>III</sup>-Gd<sup>III</sup> pair at larger angles, the spin-bearing orbitals of Cr<sup>III</sup> and the Gd<sup>III</sup> d-orbitals become orthogonal leading to a decrease in the interaction and less (more) ferromagnetic (antiferromagnetic) coupling. The spin density (cf. Figure 3 (a)) analysis reflects the points discussed where Cr<sup>III</sup> has gained spin density while there is significant reduction on the Fe<sup>III</sup> (3.09 vs. 4.28 for Cr<sup>III</sup> and Fe<sup>III</sup> respectively). This suggests a spin-polarization mechanism for the Cr<sup>III</sup>-Gd<sup>III</sup> unit and both spin-polarization and a delocalization mechanism operational for Fe<sup>III</sup>-Gd<sup>III</sup>. This is visually, directly observable in the significant departure from spherical shape of the spin-density distribution around Fe<sup>III</sup>.



**Figure 4.** Magnetic entropy changes,  $-\Delta S_m$ , corresponding to the labeled magnetic field changes,  $\Delta B$ , for **1** (top) and **2** (bottom), as obtained from specific heat,  $C$ , and magnetization,  $M$ , data. Cf. Figure S15 for a zoom of the low-temperature region.

The different magnitude of  $J_{\text{Cr-Gd}}$  and  $J_{\text{Fe-Gd}}$  is also evidenced in the experimental specific heat of **1** and **2**, respectively, depicted in Figure S12 together with the calculated Schottky anomalies for the paramagnetic ions at the corresponding fields (solid lines). Indeed, while for **1** the *intra*-molecular magnetic interactions are already decoupled for fields larger than  $\sim 1$  T, for **2**, fields larger than  $\sim 7$  T are necessary. A prominent feature in **2** is the kink at  $T_c = 0.65$  K that we ascribe to a magnetic phase transition, driven by dipolar interactions. We notice that the magnetic entropy at  $T_c$  amounts to about  $\sim 3.2 k_B$  per molecular spin (Figure S12), which is close to the value corresponding to the highest possible spin per molecule obtained in case of ferromagnetic alignment, i.e.,  $k_B \ln(2S_T + 1) = 3.47 k_B$ , where  $S_T = 3S_{\text{Gd}} + 2S_{\text{Fe}} = 31/2$ . Thus, we conjecture that the phase transition takes place concomitantly with the establishment of *intra*-molecular alignment of spins. Indeed,  $T_c$  is of the same order as the dipolar interaction energy between nearest-neighbor  $S_T = 31/2$  molecules, i.e.,  $\mu^2/r^3 \approx 0.3$  K, where  $r \approx 12$  Å is the *inter*-molecular distance. Contrary,  $J_{\text{Cr-Gd}}$  in **1** is not sufficiently strong to compete with thermal fluctuations. Thus, neither an *intra*-molecular ordering nor a phase transition is observed for **1**.

The MCE is evaluated by obtaining the isothermal magnetic entropy changes  $-\Delta S_m$  from the entropy data. We also use the magnetization data (Figures S9-12) for the same purpose by means of the Maxwell relation  $\Delta S_m(T) = \int [\partial M(T, B) / \partial T]_B dB$ . From Figure 4, we report that the maximum  $-\Delta S_m$  values for the largest  $\Delta B$  (from

7 T to 0 T) are  $38.3 \text{ J kg}^{-1} \text{K}^{-1}$  ( $T = 2.0$  K) and  $33.1 \text{ J kg}^{-1} \text{K}^{-1}$  ( $T = 4.2$  K) for **1** and **2**, respectively. The maximum entropy value involved, corresponding to  $3S_{\text{Gd}}$  and  $2S_{\text{Cr}}$  ( $S_{\text{Fe}}$ ) is calculated as  $43.4$  ( $47.1$ )  $\text{J kg}^{-1} \text{K}^{-1}$  for **1** (**2**). Therefore, for  $\Delta B$  larger than the field needed to fully overwhelm the magnetic interactions involved, a larger  $-\Delta S_m$  should occur in **2** rather than **1**. Otherwise, one would expect a larger  $-\Delta S_m$  in the case of weaker magnetic correlations, as experimentally observed for  $\Delta B \leq 7$  T. Indeed, a weaker coupling promotes a relatively larger number of low-lying excited spin states, thus favoring a larger field-dependence of the MCE. Finally, we point out that the experimental  $-\Delta S_m$  of **1** is extremely large for a 3d-4f complex and comparable to the best magnetic molecular coolers at liquid-helium temperatures.<sup>12</sup>

In summary, a small family of unusual fourth-row metal ion-lanthanide complexes with bridging fluoride ions is reported. The combination of lightweight auxiliary ligands and tunable interaction by choice of metal ion makes these systems interesting modules for low-temperature cooling applications.

**Keywords:** fluoride · magnetic refrigeration · lanthanides · magnetic properties · DFT

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