

Molecular Refrigeration

Fluoride-Bridged  $\{Gd^{III}_3M^{III}_2\}$  ( $M = Cr, Fe, Ga$ ) Molecular Magnetic Refrigerants\*\*

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**Abstract:** The reaction of *fac*- $[M^{III}F_3(Me_3tacn)] \cdot xH_2O$  with  $Gd(NO_3)_3 \cdot 5H_2O$  affords a series of fluoride-bridged, trigonal bipyramidal  $\{Gd^{III}_3M^{III}_2\}$  ( $M = Cr$  (**1**),  $Fe$  (**2**),  $Ga$  (**3**)) complexes without signs of concomitant  $GdF_3$  formation, thereby demonstrating the applicability even of labile fluoride-complexes as precursors for 3d–4f systems. Molecular geometry enforces weak exchange interactions, which is rationalized computationally. This, in conjunction with a lightweight ligand sphere, gives rise to large magnetic entropy changes of  $38.3 \text{ J kg}^{-1} \text{ K}^{-1}$  (**1**) and  $33.1 \text{ J kg}^{-1} \text{ K}^{-1}$  (**2**) for the field change  $7 \text{ T} \rightarrow 0 \text{ T}$ . Interestingly, the entropy change, and the magnetocaloric effect, are smaller in **2** than in **1** despite the larger spin ground state of the former secured by intramolecular Fe–Gd ferromagnetic interactions. This observation underlines the necessity of controlling not only the ground state but also closely lying excited states for successful design of molecular refrigerants.

Paramagnetic molecules with large spin and negligible magnetic anisotropy have received immense interest in the last few years owing to the demonstration of large magnetocaloric 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 a high magnetic density, which ultimately favors a large MCE.<sup>[1c]</sup> 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, namely, the entropy sum over all single-ion spins  $S_i$ , that is,  $R \sum_i \ln(2S_i + 1)$ . It thus seems promising to combine  $Gd^{III}$  ( $S_{Gd} = 7/2$ ) with “magnetically isotropic” transition-metal ions, such as  $Cr^{III}$  ( $S_{Cr} = 3/2$ ) or high-spin  $Fe^{III}$  ( $S_{Fe} = 5/2$ ), preferably connected by weak intramolecular 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  $\{Cr^{III}-F-Ln^{III}\}$  units. These systems owe their existence to the robust character of  $Cr^{III}$  ( $d^3$ ) complexes by avoiding precipitation of insoluble  $LnF_3$ .<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 reported, the reaction of *fac*- $[CrF_3(Me_3tacn)] \cdot 4H_2O$  ( $Me_3tacn = N,N',N''$ -trimethyl-1,4,7-triazacyclononane) with  $Nd(NO_3)_3 \cdot 6H_2O$  yields a fluoride-bridged  $\{Nd_3Cr_2\}$  trigonal bipyramid (TBP).<sup>[4b]</sup> Performing the same reaction employing  $Gd(NO_3)_3 \cdot 5H_2O$  affords the closely related  $[\{CrF_3(Me_3tacn)\}_2Gd_3F_2(NO_3)_7(H_2O)(CH_3CN)] \cdot 4CH_3CN$  (**1**), which can be considered as a lightweight analogue of the  $[\{CrF_3(Me_3tame)\}_2Gd_3F_3(hfac)_6] \cdot 7CH_3CN$  TBP-shaped pentanuclear system that exhibits good cooling properties ( $Me_3tame = 1,1,1$ -tris{(methylamino)methyl}ethane,  $hfacH = 1,1,1,5,5,5$ -hexafluoroacetylacetonone). Although this result is unsurprising, the analogous reaction with novel *fac*- $[FeF_3(Me_3tacn)] \cdot H_2O$  and *fac*- $[GaF_3(Me_3tacn)] \cdot 4H_2O$ , conveniently synthesized from  $FeF_3$  and  $GaF_3 \cdot 3H_2O$ , respectively, yields isostructural  $[\{MF_3(Me_3tacn)\}_2Gd_3F_2(NO_3)_7(H_2O)(CH_3CN)] \cdot 4CH_3CN$  ( $M = Fe$  (**2**),  $Ga$  (**3**); Figure 1) without any signs of  $GdF_3$  formation. Notably, the presence of any hydroxide bridging can be safely ruled out based on electrospray mass spectra (Supporting Information, Figures S4–S6).

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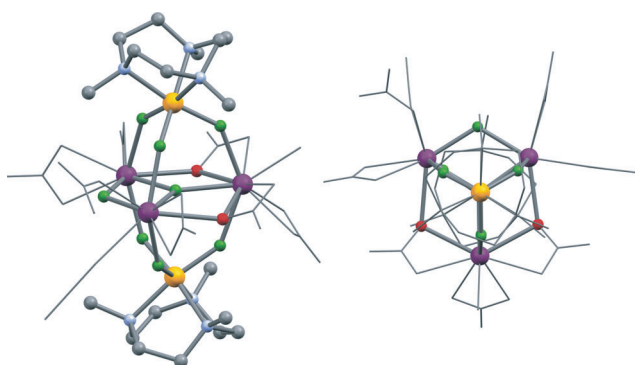
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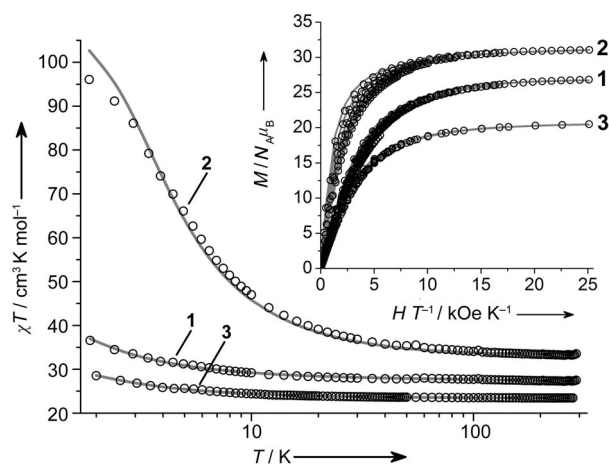
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**Figure 1.** The structure of **2** shown in perspective (left) and along the Fe...Fe direction (right). Gd purple, Fe yellow, F green, O red, N blue, C gray. For clarity, the auxiliary Gd ligand sphere is shown as a wire-frame.

The capping *fac*-[FeF<sub>3</sub>(Me<sub>3</sub>tacn)] units (angle Gd-F-Fe = 137.1(1)°–143.1(1)°) impose an approximately isosceles {Gd<sub>3</sub>} triangle. Two edges consist of η<sup>1</sup>:η<sup>2</sup>:μ<sub>2</sub>-bridging nitrate ions and one edge consists of a μ<sub>2</sub>-fluoride (Figure 1). Additionally, the center furnishes a single μ<sub>3</sub>-fluoride bridge close to the {Gd<sub>3</sub>} plane with Gd-(μ<sub>3</sub>-F)-Gd angles of 110.43(11)°, 124.64(12)°, and 124.93(11)°. Compounds **2** and **3** add to the tiny family of fourth row/transition element–lanthanide, fluoride-bridged systems, which, in addition to the Cr<sup>III</sup> systems,<sup>[3,4]</sup> only encompasses [La{(C<sub>5</sub>Me<sub>4</sub>Et)<sub>2</sub>Ti<sub>2</sub>F<sub>7</sub>}<sub>3</sub>] 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 refrigerants 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 (Figures S7, S8). As expected, the magnetic data are largely reminiscent of a Curie behavior 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 dependencies of the magnetizations are given in Figure 2 (inset) and in the Supporting Information, Figures S9–S11. The high-temperature values of the  $\chi T$  products (**1** 27.3 cm<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>, **2** 33.3 cm<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>, and **3** 23.6 cm<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>) 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<sup>-1</sup> for **1**, **2**, and **3**, respectively. This behavior suggests the presence of intra-complex ferromagnetic interactions for all of the 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):

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



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

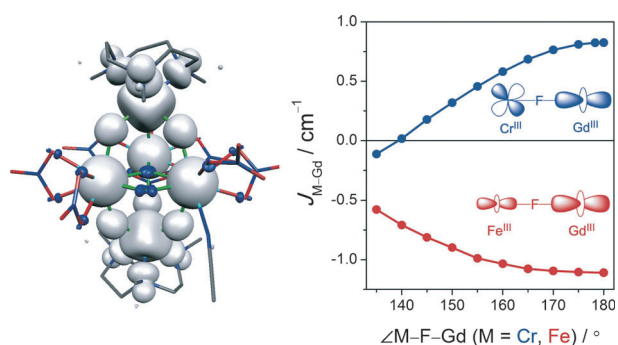
where the indices  $i$  and  $j$  run through the constitutive single ions of each compound,  $g$  is the single-ion  $g$ -factor, fixed to 2.0 for all ions,  $\hat{\mathbf{S}}$  is a spin operator, and  $J_{ij}$  is the isotropic exchange coupling parameter between the  $i$ th and  $j$ th centers. For **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 Supporting Information. The data of **1** and **2** were fitted with only  $J_{\text{M-Gd}}$  as the 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  $J_{\text{Cr-Gd}}$  value. 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>, which are also in good agreement with the experimental findings and previous theoretical studies.<sup>[9]</sup>

Furthermore, 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> analogue.<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) bonds in **1** and **2**. DFT calcu-

lations yield a ferromagnetic coupling ( $J = -1.1 \text{ cm}^{-1}$ ) for the dinuclear model, in contrast to the  $\text{Cr}^{\text{III}}$  analogue 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  $\text{Gd}^{\text{III}}$  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  $\text{Gd}^{\text{III}}$  pairs where the crucial role of empty 5d orbitals of  $\text{Gd}^{\text{III}}$  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  $\text{Cr}^{\text{III}}$ , with  $(t_{2g})^3$  configuration, interaction with  $\text{Gd}^{\text{III}}$  5d orbitals is relatively smaller as compared to  $\text{Fe}^{\text{III}}$  where the  $e_g$  orbitals promote stronger delocalization and interaction with the  $\text{Gd}^{\text{III}}$  5d orbitals. The differential occupancy is evident also from the NBO calculations (see the Supporting Information for details). The overlap between 3d and 4f orbitals, which generally contributes to antiferromagnetic coupling, is also detected to be significantly less for the  $\text{Fe}^{\text{III}}\text{-Gd}^{\text{III}}$  pair compared to  $\text{Cr}^{\text{III}}\text{-Gd}^{\text{III}}$  analogues (Supporting Information, Table S3). The angular dependence of  $J_{\text{Fe-Gd}}$  in  $\{\text{Fe}^{\text{III}}\text{-F-Gd}^{\text{III}}\}$  (Figure 3) shows the magnitude of the ferromagnetic  $J_{\text{Fe-Gd}}$  to increase with the bridging angle, while for  $\{\text{Cr}^{\text{III}}\text{-F-Gd}^{\text{III}}\}$  an opposite trend was established.<sup>[8]</sup> As the angle increases, the interaction of the  $\text{Fe}^{\text{III}}$   $d_{z^2}$  orbital with  $\text{Gd}^{\text{III}}$  5d orbitals is expected to be large, leading to stronger ferromagnetic coupling for the  $\text{Fe}^{\text{III}}\text{-Gd}^{\text{III}}$  pair. For the  $\text{Cr}^{\text{III}}\text{-Gd}^{\text{III}}$  pair at larger angles, the spin-bearing orbitals of  $\text{Cr}^{\text{III}}$  and the  $\text{Gd}^{\text{III}}$  d-orbitals become orthogonal, leading to a decrease in the interaction and less (more) ferromagnetic (antiferromagnetic) coupling. The spin density analysis (Figure 3) reflects the points discussed where  $\text{Cr}^{\text{III}}$  has gained spin density while there is significant reduction on the  $\text{Fe}^{\text{III}}$  (3.09 vs. 4.28 for  $\text{Cr}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$ , respectively). This suggests a spin-polarization mechanism for the  $\text{Cr}^{\text{III}}\text{-Gd}^{\text{III}}$  unit and both spin-polarization and a delocalization mechanism operational for  $\text{Fe}^{\text{III}}\text{-Gd}^{\text{III}}$ . This is visually directly observable in the significant departure from spherical shape of the spin-density distribution around  $\text{Fe}^{\text{III}}$ .

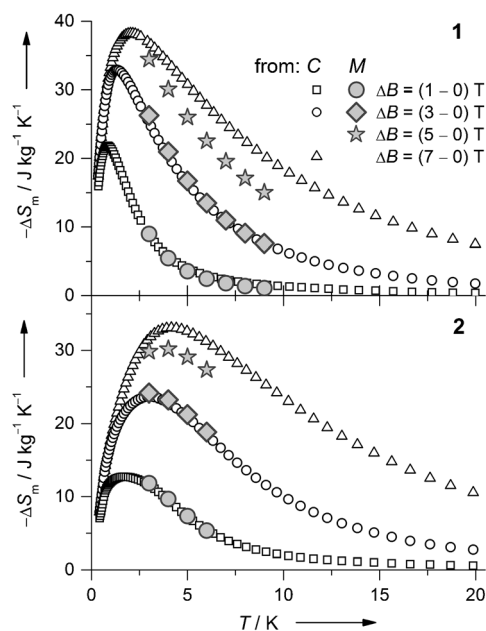
The different magnitude of  $J_{\text{Cr-Gd}}$  and  $J_{\text{Fe-Gd}}$  is also observed in the experimental specific heat of **1** and **2**, respectively (Supporting Information, Figure S12) together



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

with the calculated Schottky anomalies for the paramagnetic ions at the corresponding fields (solid lines). Indeed, while for **1** the intramolecular magnetic interactions are already decoupled for fields larger than 1 T, for **2**, fields larger than 7 T are necessary. A prominent feature in **2** is the kink at  $T_c = 0.65 \text{ K}$  that we ascribe to a magnetic phase transition that is driven by dipolar interactions. We notice that the magnetic entropy at  $T_c$  amounts to about  $3.2 k_B$  per molecular spin (Supporting Information, Figure S12), which is close to the value corresponding to the highest possible spin per molecule obtained in case of ferromagnetic alignment, that is,  $k_B \ln(2S_T + 1) = 3.47 k_B$ , 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 intramolecular alignment of spins. Indeed,  $T_c$  is of the same order as the dipolar interaction energy between nearest-neighbor  $S_T = 31/2$  molecules, that is,  $\mu^2/r^3 \approx 0.3 \text{ K}$ , where  $r \approx 12 \text{ \AA}$  is the intermolecular distance. In contrast,  $J_{\text{Cr-Gd}}$  in **1** is not sufficiently strong to compete with thermal fluctuations. Thus, neither an intramolecular 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 (Supporting Information, Figures S9–S11) 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, the maximum  $-\Delta S_m$  values for the largest  $\Delta B$  (from 7 T to 0 T) are  $38.3 \text{ J kg}^{-1} \text{ K}^{-1}$  ( $T = 2.0 \text{ K}$ ) and  $33.1 \text{ J kg}^{-1} \text{ K}^{-1}$  ( $T = 4.2 \text{ K}$ ) 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 cumulative effect of magnetic interactions



**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. See the Supporting Information, Figure S15 for a zoom of the low-temperature region.

involved, a larger  $-\Delta S_m$  should occur in **2** rather than **1**. Otherwise, a larger  $-\Delta S_m$  would be expected 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 refrigerants at liquid-helium temperatures.<sup>[12]</sup>

In summary, a small family of unusual fourth-row metal–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.

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