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Fluoride Bridges as Structure-Directing Motifs in 3d-4f Cluster Chemistry

Torben Birk,† Kasper S. Pedersen,† Christian Aa. Thuesen,† Thomas Weyhermüller,‡ Magnus Schau-Magnussen,† Stergios Piligkos,† Högni Weihe,† Susanne Mossin,§ Marco Evangelisti,¶ and Jesper Bendix§

†Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark
‡Max Planck Institute for Bioinorganic Chemistry, D-45470 Mülheim an der Ruhr, Germany
§Department of Chemistry, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
¶Instituto de Ciencia de Materiales de Aragón, Departamento de Física de la Materia Condensada, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain

Supporting Information

ABSTRACT: The use of kinetically robust chromium(III) fluoride complexes as synthons for mixed 3d-4f clusters is reported. The tendency toward linear \( \{ \text{Cr}^{III} - \text{F} - \text{Ln}^{III} \} \) units dictates the cluster topology. Specifically, we show that reaction of \( \text{cis-}[\text{Cr}^{III} \text{F}_2(\text{NN})_2] \text{NO}_3 \) (\( \text{NN} = 1,10\)-phenanthroline (“phen”) or 2,2′-bipyridine (“bpy”)) with \( \text{Ln}^{III}(\text{NO}_3)_3 \cdot \text{xH}_2\text{O} \) produces isostructural series of molecular \( \{ \text{Ln}_3\text{Cr}_2 \} \) squares (1–9) with linear fluoride bridges. In a parallel fashion, \( \text{fac-}[\text{Cr}^{III} \text{F}_3 \text{L}] \), where \( \text{L} = \text{N,N,N′-trimethyl-1,4,7-triazacyclononane} \) (“Me₃tacn”), reacts with \( \text{Nd(NO}_3)_3 \cdot \text{6H}_2\text{O} \) to form a fluoride-centered penta-nuclear complex and \( \text{fac-}[\text{Cr}^{III} \text{F}_3 \text{L}'] \), with \( \text{L}' = \text{1,1,1-tris-(methylamino)methylethane} \) (“Me₃tame”), reacts with \( \text{[Ln-(hfac)} \text{H}_2\text{O} \text{]} \) (hfacH = 1,1,1,5,5,5-hexafluoroacetylacetone) to yield an isostructural series of \( \{ \text{Ln}_3\text{Cr}_2 \} \) (10–14) trigonal bipyramids with no central ligand. The formation of the latter is accompanied by a partial solvolysis of the Cr(III) precursor but without formation of insoluble LnF₃. The magnetic properties of the gadolinium containing clusters allow quantification of fluoride-mediated, antiferromagnetic Gd–Cr exchange interactions of magnitude between 0.14 cm⁻¹ and 0.71 cm⁻¹ (\( \tilde{H} = J_{12}\text{S}_1\cdot\text{S}_2 \) formalism) and vanishingly small \( J_{\text{Gd-Gd}} \) of 0.06(0) cm⁻¹. The large spin and small anisotropy together with weak exchange interactions in the \( \{ \text{Gd}_3\text{Cr}_2 \} \) (11) cluster give rise to a very large magneto-caloric effect of \( -\Delta S_m = 28.7 \text{ J kg}^{-1} \text{ K}^{-1} \) (\( \mu_0H = 90 \) to 0 kOe).

INTRODUCTION

Interest in high-nuclearity clusters incorporating lanthanoid ions has been boosted by the quest for magnetically anisotropic molecular systems as single-molecule magnets,† and, more recently, the increasing focus on nanoscopic coolers§ has established a need for molecular entities exhibiting very-large spin ground states. Presently, the vast majority of mixed 3d-4f clusters are bridged by large organic ligands or smaller entities such as hydroxide or especially alkoxides whereas valence-isoelectronic fluoride bridges are exceedingly scarce.¶ Reported examples of fluoride-bridging included, until recently, only systems with diamagnetic Ti(IV) ions, namely, \( \{ \text{La-} \{(\text{C}_5\text{Me}_4\text{Et})_3\text{TiF}_3 \} \} \) and \( \{ \text{Ln-} \{(\text{C}_5\text{Me}_4\text{Et})_3\text{TiF}_3 \} \} \) (Ln = Pr, Nd)§ in which the 12-coordinate lanthanoid ion is exclusively surrounded by fluoride ions. Recently, fluoride-bridged systems were augmented by lanthanoid-containing wheels or fused wheels featuring fluoride bridges in conjunction with pivalate bridges between chromium(III) and lanthanoids. As discussed by Winpenny and co-workers, the synthesis of fluoride-bridged 3d-4f clusters is hampered by the strong affinity of lanthanoid(III) ions for fluoride resulting in competitive formation of highly insoluble LnF₃. The above-mentioned titanium complexes probably owe their existence to the comparable affinity of “hard” Ti(IV) and the lanthanide ion for fluoride. Thus, the successful isolation of those polynuclear systems is most likely irrelevant for the majority of other transition metal ions. However, relying on kinetics rather than thermodynamics the use of kinetically robust transition metal (TM) fluoride complexes, for example, of chromium(III), may be a generally feasible approach provided the synthesis can be carried out relatively fast and at moderate temperatures. In the synthesis of mixed 3d-4f clusters topological control is difficult to achieve because of the flexibility in coordination number and geometry of the lanthanoid ions and frequent solvent coordination. There are

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very few accessible mono- or diatomic bridges which have not been extensively explored. Its simplicity, spectroscopic innocence, relatively low basicity, and preference for "hard" metal ions make fluoride an attractive bridging ligand for mixed transition metal-lanthanoid complexes. Furthermore, the tendency toward pseudolinear bridging established in transition metal chemistry could facilitate prediction and design of specific molecular topologies, if it can be shown to carry over into lanthanoid chemistry. To exploit the latter property of the fluoride ligand, it is necessary to target simple systems with unsupported fluoride bridges. This will also allow for a quantification of the magnetic interaction via the fluoride bridge, which was not possible in the wheels wherein the fluoride bridge coexists with one or two pivalate bridges.

Useful building blocks for polynuclear fluoride-bridged 3d-4f systems would be robust di- or trifluorido complexes of Cr(III) preferably with polydentate coligands and soluble in organic solvents. Such difluorido precursors are well described in literature with the auxiliary ligand sphere consisting of amines or imines, for example, cis-[CrF2(phen)2]NO3. Additionally, neutral trifluorido analogues can be obtained by minor modifications of published synthetic procedures. Here we describe the syntheses and properties of a class of simple chromium(III)-lanthanide clusters starting from di- and trifluorido complexes of chromium: cis-[CrF3(NN)]2+ (NN = phen, bpy), fac-[CrF5(Me3tame)], and fac-[CrF3(Me3tacn)].

## RESULTS AND DISCUSSION

We have recently, demonstrated the formation of bimetallic fluoride bridged linear rods or squares obtained by using robust trans-[CrF2(py)4]+ (py = pyridine)10 or cis-[CrF2(phen)3]+11 respectively, as building blocks. This type of reactivity is generalizable, and 1:1 assembly reactions in methanolic solution of cis-[CrF2(phen)2]NO3 and Ln(NO3)3·aq yield tetranuclear clusters, which crystallize as solvates with the general formula [(CrF2(phen)2)(Ln(NO3)3)2·4MeOH·H2O (Ln = Ce–Nd, Sm–Ho (1–9)). Yields diminish pronouncedly with increasing atomic number of the lanthanoid and amounts to less than 2% for the Dy-compound (cf. Experimental Section). The low-angle part of the powder diffraction also demonstrates the Dy-compound to contain a crystalline impurity. The Cr–N distances at 2.0550(17)–2.063(2) Å in the same range as found in the monomeric precursor: 2.0566(15)–2.0934(15) Å. The crystallographic symmetry, which connects different clusters by 4-fold screw-axes ensures all clusters to be oriented with parallel Cr–Ln2-planes in the packing (see the Supporting Information).

The closely related cis-[CrF3(bpy)2]+ reacts analogously and furnishes structurally similar fluoride-bridged tetranuclear clusters. However, these systems are void of solvents of crystallization and crystallize with lower symmetry in orthorhombic I222 (cf. Supporting Information). It is note-
worthy, that the cis configuration of the fluoride ligands in [CrF₃(phen)_2]⁺ does not suffice to introduce chelate binding toward the lanthanoid ions. A similar result has recently been observed for a homometallic tetranuclear manganese(II) cluster: [MnII(O₂CMe)_4]⁺(NO₃)·12H₂O₁⁴ and parallels the tetra-nuclear structures with approximately linear fluoride bridges found for many metal pentafluorides. Thus, while many examples are known with doubly bridging hydroxido, oxide, and the heavier halides, fluoride clearly disfavors this structural motif. This conclusion becomes even more evident when the products resulting from reaction between trifluorido complexes of Cr(III) and lanthanoid complexes are considered. Scheme 1 depicts the structures obtained with the di- and tris-

**Scheme 1. Structure Diagrams of the Polynuclear Complexes Obtained from Di- and Trifluorido Chromium(III) Building Blocks***

![Scheme 1. Structure Diagrams of the Polynuclear Complexes Obtained from Di- and Trifluorido Chromium(III) Building Blocks](image)

The complete absence of chelating binding towards the lanthanoid centers illustrates the tendency of fluoride bridges to avoid bending.

trifluorido complexes. Thus, for both fac-[CrF₃(Me₃tame)] and fac-[CrF₃(Me₃tacn)], pentanuclear structures were obtained from acetonitrile solutions using respectively [Ln-(hfac)₃(H₂O)₂] (Ln = Sm (10), Gd (11), Ho (12), Yb (13); hfacH = 1,1,1,5,5,5-hexafluoroacetylacetone) and Nd-(NO₃)₃·6H₂O as lanthanoid sources. Both types of structures consist of triangular arrangements of the lanthanoid ions bridged in the equatorial plane by either bidentate and bridging nitrate (μ-nitrito-1,2xO:1κO) ligands or fluoride ligands. These triangles are then capped above and below the plane by tridentate, but nonchelating, {LCrF₃} moieties. Additionally, the system derived from fac-[CrF₃(Me₃tacn)] features a most unusual central μ₂-fluorido ligand bridging all three neodymium centers symmetrically. This bridging mode is very rare, but not completely unprecedented in transition metal chemistry where examples of planar μ₂-F bridging fluoride exist in, for example, [Ni₂(μ₂-F)(CF₃CO₂)₃(CF₃CO₂H)₃]⁺. The overall 3-fold symmetry of the clusters is broken by different equatorial coordination environments of the lanthanoids and associated small variations in Ln−F bond lengths toward the {CrF₃} moieties.

Crystal structures of the pentanuclear systems are shown in Figure 3. An important feature of the structures is the additional bridging fluoride ligands (μ₁ or μ₂), which demonstrates that even quite robust Cr(III) fluoride complexes are susceptible to fluoride abstraction by lanthanoid ions under mild conditions (cf. Experimental Section). However, despite of this, formation of very insoluble LnF₃ was never observed under the experimental conditions used to prepare these polynuclear complexes. Although the Cr−F−Ln bridges in 11, 12, and 14 are significantly bent at angles of 138.6−146.8°, it is striking that the facial trifluorido complexes avoid chelate binding of a single lanthanoid ion despite the lability and size of the lanthanoid ions. This is again paralleled by the transition metal fluoride chemistry where tri-μ₂-fluorido complexes are scarce in comparison with the abundance of tri-μ₂-hydroxido complexes.
and tri-$\mu_2$-chlorido complexes. In combination these observations attest to a pronounced preference for linear bridging by fluoride, which pertains to systems with lanthanoid ions. This geometric preference is reminiscent of the behavior of cyanide as a bridging ligand and it might, therefore, render robust fluoride complexes, appealing building blocks for assembly of polynuclear systems with targeted topologies. In the structures of 11 and 12, Cr=F–Ln and Ln=F–Ln bridging angles are very similar and both close to 140°. However, this similarity should not be overinterpreted since the trigonal bipyramidal structures in combination with the metal-fluoride bond lengths restrict the bridging angles, which are thus compromises between linear bridging and optimal bond lengths. Since the preparations invariably involve hydrated starting materials, it could be speculated, that some of the fluorides alternatively could be assigned as isoelectronic hydroxide ligands. The X-ray structures of 11 and 12 were both solved with hydroxide in place of the equatorial fluoride bridges with very little effect on the goodness of the modeling, which only slightly, but not statistically significantly favors fluoride bridges. However, electrospray mass spectrometry (vide infra) only reveals intact clusters and fragments with fluoride bridges and thus rules out the presence of hydroxide bridges.

The polynuclear solid state structures described above are not merely consequences of crystal packing, but reflect association also in solution. When methanolic solutions of cis-[CrF$_2$(phen)$_2$]NO$_3$ and Gd(NO$_3$)$_2$aq are mixed to yield solutions with different ratios of Gd/Cr (ranging from 0 to 2), there is an associated color change from red-purple to orange. The ligand-field (LF) spectrum of Cr(III) changes, resulting in a blue shift of the first spin-allowed band, $^4T_2$(O)$\leftrightarrow^4A_2$(O), of 460 cm$^{-1}$ (cf. Figure 4). Since the position of this effect stems from a different radial dependence of the LF $\sigma$- and $\pi$-parameters for fluoride. However, DFT modeling of the interaction between neutral trifluorido complexes of Cr(III) and Na$^+$ in vacuum as well as in solution revealed a pronounced breakdown of the commonly assumed additivity of ligand-field contributions. Thus the actual decrease of the donor strength of fluoride upon ligation or solvation is more than compensated by an increased donation from the auxiliary amine, or as demonstrated here, imine ligands. The change in absorption spectrum results in isosbestic points suggesting only two spectroscopically distinct coordination environments of the chromium(III) as the Gd/Cr-ratio is increased.

The nature of the species in solution can be gauged by electrospray mass spectrometry of reaction mixtures before precipitation. For the tetranuclear compounds, this technique identifies fragments of composition [(CrF$_2$(phen)$_2$)$_2$Ln(NO$_3$)$_4$] and [CrF$_2$(phen)$_2$Ln(NO$_3$)$_3$]$^+$ as the most prominent peaks in positive ion detection mode (Supporting Information, Figure S5.1) and [CrF$_2$(phen)$_2$Ln(NO$_3$)$_3$]$^+$ in negative ion detection mode for Ln = Ce (1), Sm (4), and Gd (6). These ions are all likely fragments of the tetranuclear structures determined in the solid state and in agreement with the UV–vis spectroscopy points to extensive association in solution before precipitation.

Although very insoluble in acetonitrile, the isolated pentanuclear complexes (10–13) can be redissolved to a small extent in this solvent, and the resulting solutions yield mass spectra, which can unambiguously be correlated to the solid state structure. Thus, three peaks are present in positive ion detected electrospray mass spectra of such solutions of 10–13 (cf. Supporting Information, Figure S6.1–S6.4). These peaks correspond to compositions of {M-hfac$^-$}, {M+Na$^+$}, and {M-LnF$_2$-hfac$_2$}$^+$, where M denotes the neutral pentanuclear cluster. The isotope pattern of the {M-hfac$^-$}-peak for 12 is shown in Figure 5 together with that of the intact cluster plus a sodium ion. For both entities simulations corresponding to all bridging ligands being fluoride have been included. The perfect reproduction of the isotope pattern (as found for the isostructural clusters with different lanthanoid ions: 10, 12, and 13) rules out hydroxide ligands and demonstrate exclusive fluoride bridging in these clusters.

As the first examples of unsupported fluoride bridges between 3d and 4f ions, the magnetic properties of these systems are as of interest. The temperature dependencies of the $\chi T$ product for some of the tetranuclear square structures are shown in Figure 6. At high-temperature (300 K) the $\chi T$ values (2: 6.3 cm$^3$ K mol$^{-1}$; 3: 6.2 cm$^3$ K mol$^{-1}$; 4: 4.0 cm$^3$ K mol$^{-1}$) are in agreement with the values expected for two chromium(III) (S = 3/2, g ≈ 2) and two lanthanoid ions (Pr: $^4I_{15/2}$ $g_I = 4/3$; Nd: $^4I_{9/2}$ $g_I = 8/11$; Sm: $^4H_{15/2}$ $g_I = 27/7$). With decreasing temperature the value for $\chi T$ drops slightly for all compounds because of the progressive depopulations of ligand-field states (Stark sublevels).

Furthermore, for 2 a steep drop occurs below $\sim$10 K which is not observed for 3 and 4 where the $\chi T$ goes to a local minimum ($\sim$13 K) and then increases rapidly on lowering temperature. For TM compounds this behavior is a signature of a ferrimagnetic spin arrangement; however, in this case it may be a result of weak ferromagnetic Ln–Cr (Ln = Nd, Sm) interactions masked by the above-mentioned decrease of $\chi T$ on descending temperature. Notably, this behavior parallels that observed for oxalate-bridged Cr–Ln systems with the same lanthanoid ions.$^{17}$ The magnetization curves do not show any
Curie constants are:

\[
\chi = C_T T^{-1} + \chi_M \quad \text{(eq 1)}
\]

Temperature dependence of the \( \chi T \) product for 2, 3, and 4.
The expected high-temperature values calculated from the free ion Curie constants are:

1. \( 3.86 \text{ cm}^3 \text{ K mol}^{-1} \)
2. \( 2.0 \text{ cm}^3 \text{ K mol}^{-1} \)
3. \( 6.95 \text{ cm}^3 \text{ K mol}^{-1} \)
4. \( 6.88 \text{ cm}^3 \text{ K mol}^{-1} \)

Supporting Information.

Figure 6. Temperature dependence of the \( \chi T \) product for 2, 3, and 4.
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Supporting Information.

Figure 7. Fits of the \( \chi T \) product for 6 (Cr$_2$Gd$_2$-square) and 11 (Cr$_2$Gd$_3$-bipyramid) to the spin-Hamiltonian of eq 1. The resulting parameter values are:

- Cr$_2$Gd$_2$: \( J_{\text{Cr-Gd}} = 0.71 \text{ cm}^{-1} \)
- Cr$_2$Gd$_3$: \( J_{\text{Cr-Gd}} = 0.14(0) \text{ cm}^{-1} \)
- Gd$_2$-Gd: \( J_{\text{Gd-Gd}} = 0.06(0) \text{ cm}^{-1} \)

The \( g \) factors were fixed to \( g_{\text{Cr}} = g_{\text{Gd}} = 2.0 \).

For Cr$_2$Gd$_2$ (11):

\[
\hat{H} = \mu_B \mathbf{B} \left[ g_{\text{Cr}} (\hat{S}_{\text{Cr1}} + \hat{S}_{\text{Cr2}}) + g_{\text{Gd}} (\hat{S}_{\text{Gd1}} + \hat{S}_{\text{Gd2}} + \hat{S}_{\text{Gd3}}) \right] + J_{\text{Cr-Gd}} (\hat{S}_{\text{Cr1}} \hat{S}_{\text{Gd1}} + \hat{S}_{\text{Gd1}} \hat{S}_{\text{Cr2}} + \hat{S}_{\text{Cr2}} \hat{S}_{\text{Gd2}} + \hat{S}_{\text{Gd2}} \hat{S}_{\text{Cr1}})
\]

The \( g \) factors were fixed to \( g_{\text{Cr}} = g_{\text{Gd}} = 2.0 \). The \( \chi T \) and reduced magnetization \( M_B \) vs \( T \) data (Supporting Information) were fitted simultaneously. No zero-field splitting (ZFS) terms were included in the models but fitting of the \( \chi T \) data only gave the same parameter values indicating that the Cr(III) and Gd(III) magnetic anisotropies are vanishing. The fitting yields \( J_{\text{Gd-Gd}} \approx 0.71 \text{ cm}^{-1} \) for 6 and \( J_{\text{Gd-Gd}} \approx 0.14(0) \text{ cm}^{-1} \) for 11.\textsuperscript{18} The magnetic exchange coupling across the fluoride bridges is found to be comparable in magnitude (0.14–0.71 cm$^{-1}$) to that observed for 3d-Gd interactions with other small bridges as cyanide\textsuperscript{19} or oxalate\textsuperscript{20}. To the best of our knowledge, only one example of a Gd(III)–Cr(III) cluster with solely monatomic bridges is reported\textsuperscript{21}. In this hydroxide bridged (GdCr$_4$) cluster the Gd–Cr interaction is indeed antiferromagnetic, but its magnitude was not extracted. The very pronounced difference in magnitude of the coupling in 6 and 11 in conjunction with other results obtained by us, suggests that coupling decreases steeply with bending of the fluoride bridges.\textsuperscript{22}

The quite weak couplings in 11 together with isotropic Gd(III) and Cr(III) with holohedrized octahedral coordination.
environment and concomitant small ZFS suggest that these systems should possess a large number of electronic states which are nearly degenerate with the ground state. This situation makes 11 a good candidate for the observation of a large Magneto-Caloric Effect (MCE), that is, the change of the magnetic entropy and related adiabatic temperature following a change in the applied magnetic field. This effect is at the basis of the magnetic refrigeration technique and therefore a large MCE is industrially in demand.

The magnetocaloric properties of 11 have been investigated by means of heat capacity (C) experiments, which represent the most suitable probe for the indirect determination of MCE.\(^{24}\) In Figure 8 is shown the experimental C, normalized to the gas constant \(R\), collected for \(\vec{\mu} H = 0, 10, 40,\) and 90 kOe. Inset: temperature dependencies of the experimental entropy for several \(H\), as obtained from the respective heat capacity data.

\(\text{Figure 8. Temperature dependencies of the heat capacity (C) of 11 normalized to the gas constant } R, \text{ collected for } \vec{\mu} H = 0, 10, 40, \text{ and 90 kOe. Inset: temperature dependencies of the experimental entropy for several } H, \text{ as obtained from the respective heat capacity data.}\)

At high temperatures the heat capacity is dominated by nonmagnetic contributions arising from thermal vibrations of the lattice, which can be modeled with the Debye function (solid line in Figure 8) yielding a value of \(\Theta_D = 18.0 \text{ K}\) for the Debye temperature, which is in the range of values observed for this class of molecular compounds.\(^{23}\) At low temperatures the heat capacity is dominated by an applied-field sensitive contribution, which shifts to higher temperatures by increasing \(H\). From the experimental heat capacity, the temperature dependence of the entropy is obtained by integrating \(\int C/T \, dT\), leading to the temperature dependencies of the entropy which are depicted in the inset of Figure 8 for the corresponding applied fields. In the cases of \(\vec{\mu} H = 0\) and 10 kOe, the lack of data points below approximately 0.3 K forced us to add a constant value to the corresponding entropy curves to match the limiting values at high temperature. This procedure is justified by the entropy calculations performed on the C data obtained for higher fields, whose temperature dependencies are well within our experimentally accessible temperature window. As we shall see below, this procedure does not jeopardize our evaluation of the MCE of 11. We also notice that the so-obtained zero-field entropy increases sharply reaching an approximate value of 8 RT at low temperatures. The 1 K < \(T < 5 \text{ K}\) temperature range is characterized by a slow increase of the zero-field entropy, passing from \(\sim 8 \text{ RT}\) to \(\sim 9 \text{ RT}\), respectively. Above roughly 5 K, the zero-field entropy starts again to steadily increase because of the dominant lattice contribution (see Figure 8). The 8–9 R plateau could be understood assuming that, for this temperature range, all magnetic interactions are decoupled to large extent. Therefore, under this assumption, we expect the entropy to approach the maximum value for noninteracting single-ion spins, that is, \(3 \times R_{\mu} \ln(2 S_{\text{tot}} + 1) + 2 \times R \ln(2 S_{\text{f}} + 1) = 9 R\), where \(S_{\text{tot}} = 7/2\) and \(S_{\text{f}} = 3/2\), in good agreement with the experimental data.

Figure 9 shows the experimental \(S_{\text{ff}}\) (Figure 9). This is a remarkable MCE that sets the corresponding applied field changes (\(\Delta H\)). Note that the estimation of the lattice contribution is irrelevant for our calculations, since we deal with differences between total entropies at different magnetic field strengths. The resulting magnetic entropy changes are summarized in Figure 9. Besides heat capacity, magnetization (\(M\)) data can also be employed for estimating the magnetic entropy change by making use of the Maxwell relation, \(\Delta S_{\text{ff}}(T) = \int \left[ \partial M/\partial T \right] \, dH\). From the isothermal \(M(T)\) curves (Supporting Information, Figure S3.4) the so-obtained temperature-dependencies of \(\Delta S_{\text{ff}}\) for \(\mu_0 \Delta H = 10,\) 40, and 50 kOe are displayed in Figure 9. The nice agreement with the data obtained from C, proves that our experimental uncertainty in the low-temperature zero-field entropy does not affect the evaluation of the MCE of 11.

We experimentally observe \(-\Delta S_{\text{ff}}\) to reach the maximum value of 28.7 J kg\(^{-1}\) K\(^{-1}\) for \(T = 2.2\) K and \(\Delta H = (90–0)\) kOe (Figure 9). This is a remarkable MCE that sets 11 among the best performing molecular magnetic refrigerants recently reported in the literature.\(^{5,24}\) Our results suggest that 11 could potentially be employed as a magnetic refrigerant for the low-temperature range starting from 2 K and downward, that is, the starting temperature for an adiabatic demagnetization process.\(^{22}\) This range is of considerable technological interest because it is easily reachable by pumping liquid \(^4\)He.

\(\text{CONCLUSION}\)

In conclusion, assembly of polynuclear lanthanoid complexes employing robust chromium(III)-fluoride complexes is a convenient route to small heterometallic complexes with fluoride bridges. These polynuclear complexes constitute the first examples of unsupported fluoride-bridges between a paramagnetic transition metal and a lanthanide ion. The propensity of fluoride for linear bridging established for

\(\text{Figure 9. Temperature dependencies of the magnetic entropy change (}\Delta S_{\text{ff}}\text{) for 11, as obtained from the respective heat capacity (C) and magnetization (\(M\)) data, for selected field changes (\(\Delta H\)), as labeled.}\)
polynuclear transition metal systems is manifest also in mixed 3d-4f systems. The resulting, structurally simple systems allowed for modeling of the magnetic properties and for the first quantification of magnetic coupling between 3d and 4f centers across a fluoride bridge. This coupling was found to be numerically similar to that for cyanide or oxalate bridges, while the lack of systems with isoelectronic hydroxide or alkoxide bridges between chromium and gadolinium prevents direct comparison with these bridging ligands. The coupling appears to decrease pronouncedly with the bending of the fluoride bridges. This can be favorably exploited for achieving a large MCE, since a relatively large number of magnetic degrees of freedom become available at low temperature because of the low-lying excited spin states promoted by the weak coupling. The weakest intracluster interactions are achieved in the bipyramidally shaped \( \text{Gd}_2\text{Cr}_2 \) (11) complex. Indeed, for 11 we report a remarkably large MCE at low temperatures, which results also from the large net magnetic moment of the molecule, combined with its negligible anisotropy. Furthermore, 11 has a relatively large metal/ligand mass ratio that is an important advantage since the nonmagnetic ligands contribute passively to the MCE.

## EXPERIMENTAL SECTION

**Synthesis.** Materials. Ce(NO\(_3\))\(_3\)·6H\(_2\)O (Puriss, p.a., Fluka), Pr(NO\(_3\))\(_3\)·H\(_2\)O (99.9%, Alfa Aesar), Nd(NO\(_3\))\(_3\)·6H\(_2\)O (99.9%, Alfa Aesar), Sm(NO\(_3\))\(_3\)·6H\(_2\)O (99.9%, Alfa Aesar), Eu(NO\(_3\))\(_3\)·6H\(_2\)O (99.9%, Alfa Aesar), Tb(NO\(_3\))\(_3\)·H\(_2\)O (99.9%, Aldrich), Dy(NO\(_3\))\(_3\)·5H\(_2\)O (99.9%, Aldrich), Ho(NO\(_3\))\(_3\)·5H\(_2\)O (99.9%, Aldrich), Er(NO\(_3\))\(_3\)·5H\(_2\)O (99.9%, Alfa Aesar), Yb(NO\(_3\))\(_3\)·H\(_2\)O (99.9%, Alfa Aesar), 1,10-phenanthroline (Alfa Aesar), and the solvents MeOH (Lab Scan.), 2-methoxyethanol (HPLC grade 99.9%), and EtOH (99%, 4 × 100 mL) was stirred at RT for 30 min and filtered to the MCE.

**Inorganic Chemistry**

Yields and analytical data for the individual compounds are given below. Note, that drying has resulted in partial solvent loss. For all compounds except that of Gd, the calculated values are given for the solvent free composition.

- **[CrF\(_2\)(phen)\(_3\)][Ce(NO\(_3\))\(_3\)]** (1): Yield: 74% of theoretical based on Ce\(_{III}\). Elemental analysis calcd (%) for H\(_2\)Ce\(_3\)N\(_3\)O\(_7\)F\(_4\)Cr\(_2\): H 1.92, C 34.38, N 13.36; found: H 1.72, C 32.83, N 12.36. By-product: None.
- **[CrF\(_2\)(phen)\(_3\)][Pr(NO\(_3\))\(_3\)]** (2): Yield: 82% of theoretical based on Pr\(_{III}\). Elemental analysis calcd (%) for H\(_2\)Ce\(_3\)N\(_3\)O\(_7\)F\(_4\)Cr\(_2\): H 1.92, C 34.34, N 13.35; found: H 1.94, C 33.44, N 12.44. By-product: Present, but small amount.
- **[CrF\(_2\)(phen)\(_3\)][Nd(NO\(_3\))\(_3\)]** (3): Yield: 87% of theoretical based on Nd\(_{III}\). Elemental analysis calcd (%) for H\(_2\)Ce\(_3\)N\(_3\)O\(_7\)F\(_4\)Cr\(_2\): H 1.91, C 34.21, N 13.30; found: H 2.05, C 34.24, N 12.69. By-product: Present, but small amount.
- **[CrF\(_2\)(phen)\(_3\)][Sm(NO\(_3\))\(_3\)]** (4): Yield: 87% of theoretical based on Sm\(_{III}\). Elemental analysis calcd (%) for H\(_2\)Ce\(_3\)N\(_3\)O\(_7\)F\(_4\)Cr\(_2\): H 1.90, C 33.96, N 13.20; found: H 2.08, C 33.79, N 12.52. By-product: None.
- **[CrF\(_2\)(phen)\(_3\)][Gd(NO\(_3\))\(_3\)]** (5): Yield: 37% of theoretical based on Eu\(_{III}\). Elemental analysis calcd (%) for H\(_2\)Ce\(_3\)N\(_3\)O\(_7\)F\(_4\)Cr\(_2\): H 1.90, C 33.90, N 13.18; found: H 1.97, C 33.59, N 12.10. By-product: 0.070 g (Analysis: Found (%): H, 1.76; C, 26.85; N, 9.16).
- **[CrF\(_2\)(phen)\(_3\)][Gd(NO\(_3\))\(_3\)]** (6): Yield: 87% of theoretical based on Eu\(_{III}\). Elemental analysis calcd (%) for H\(_2\)Ce\(_3\)N\(_3\)O\(_7\)F\(_4\)Cr\(_2\): H 1.97, C 33.59, N 12.10; found: H 2.06, C 33.53, N 12.25. By-product: 0.05 g (Analysis: Found (%): H, 1.64; C, 25.02; N, 7.99).
- **[CrF\(_2\)(phen)\(_3\)][Tb(NO\(_3\))\(_3\)]** (7): Yield: 5.5% of theoretical based on Tb\(_{III}\). Elemental analysis calcd (%) for H\(_2\)Ce\(_3\)N\(_3\)O\(_7\)F\(_4\)Cr\(_2\): H 1.88, C 33.62, N 13.07; found: H 1.85, C 33.07, N 12.06. By-product: 0.082 g (Analysis: Found (%): H, 1.63; C, 24.41; N, 7.81).
- **[CrF\(_2\)(phen)\(_3\)][Dy(NO\(_3\))\(_3\)]** (8): Yield: 1.8% of theoretical based on Dy\(_{III}\). Elemental analysis calcd (%) for H\(_2\)Ce\(_3\)N\(_3\)O\(_7\)F\(_4\)Cr\(_2\): H 1.87, C 33.48, N 13.02; found: H 1.79, C 32.09, N 12.19. The isolated crystalline product is contaminated with a crystalline impurity (cf. Figure 1).

- **Attempted synthesis of \([CrF\(_2\)(phen)\(_3\)][Er(NO\(_3\))\(_3\)]\)): Yield: None. By-product: 0.093 g (Analysis: Found (%): H, 1.64; C, 24.36; N, 7.81).

- **[CrF\(_2\)(phen)\(_3\)][Ho(NO\(_3\))\(_3\)]** (9): Yield: Few crystals. By-product: 0.107 g (Analysis: Found (%): H, 1.61; C, 24.09; N, 7.75).

- **Attempted synthesis of \([CrF\(_2\)(phen)\(_3\)][Yb(NO\(_3\))\(_3\)]\)): Yield: None. By-product: 0.016 g (Analysis: Found (%): H, 1.24; C, 13.36; N, 5.11).

- **Synthesis of \([CrF\(_2\)(bpy)\(_3\)][Ln(NO\(_3\))\(_3\)]\):** **(Ln = Nd, Sm, Eu, Gd).** This synthesis proceeds similarly as for the phenanthroline analogues. Details are provided in the Supporting Information.
MeCN (20 mL) at 5 °C. Over a period of days pink rod-shaped crystals develop. These are very often hollow and encapsulate some of the mother liquor. Upon drying they lose solvent and crumble. The best elemental analyses were obtained by gently crushing of the crystalline product, repeated washing with MeCN, and storage below 0 °C. Elemental analysis calcld (%) for H$_{6}$C$_{60}$N$_{20}$O$_{25}$F$_{7}$Cr$_{2}$Nd$_{3}$: H 3.53, C 20.33, N 15.80; found: H 3.58, C 20.08, N 15.47.

**Physical Measurements.** Elemental analysis for C, H, and N was performed with a CE Instrument: FLASH 1112 series EA, at the microanalytical laboratory, University of Copenhagen. UV/vis spectra were recorded on a Perkin-Elmer, Lambda 2 UV/vis spectrophotometer. Electrospray mass spectra were recorded on a micromass Q- Tof spectrometer employing cone-voltages in the range 20–45 V from solutions with concentrations in the nominal range 5–50 μM.

**X-ray Crystallography.** All single-crystal X-ray diffraction data were collected at 121(1) K on a Nonius KappaCCD area-detector diffractometer, equipped with an Oxford Cryostreams low-temperature device, using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved using direct methods (SHELXL97) and refined using the SHELXL97 software package.20,21 Crystals suitable for X-ray diffraction were obtained from crystals produced with the Mercury program ver. 2.4 from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. The molecular structure diagrams were produced with the Mercury program ver. 2.4 from The Cambridge Crystallographic Data Center. Powder X-ray crystallographic data were collected on a STOE Stadi-P powder diffractometer equipped with PSD-detector using Cu Kα (λ = 1.54060 Å) radiation monochromated with curved germanium. Data were subtracted by a background using the software of the STOE WinXPOW software ver. 1.10. Theoretical powder diffractograms were generated from the single crystal structure by use of the software “Mercury CSD 2.2” from The Cambridge Crystallographic Data Center.22

**Magnetic Measurements.** The magnetic measurements were performed on a MPMS-XL Quantum-Design SQUID magnetometer located at University of Copenhagen. All measurements were performed on polycrystalline samples immobilized in a frozen n-eicosane matrix to avoid torquing. The susceptibilities were corrected for diamagnetic contributions from the sample holder, n-eicosane, and the sample by means of Pascal’s constants. Alternating current (ac) susceptibility measurements were measured with various frequencies in the range 1–1500 Hz with an ac field amplitude of 3 Oe with and without an applied static field (H$_{0}$ = 2 kOe). The modeling was performed with MagProp22 and home-written software. Heat capacity measurements using the relaxation method down to ~0.3 K on powder samples were carried out by means of a commercial setup for the 0 < B$_{0}$ < 9 T magnetic field range.

**REFERENCES**


(18) Although numerically small, inclusion of both parameters, \( J_{\text{Co-Gd}} \) and \( J_{\text{Ce-Gd}} \), is statistically warranted since they by the fitting both have relative uncertainties well below 10% and a mutual correlation coefficient of 0.078.


(22) Pedersen, K. S.; Thuesen, C. Aa.; Schau-Magnussen, M.; Bendix, J., manuscript in preparation.
