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Published in:
Inorganic Chemistry

Link to article, DOI:
10.1021/ic300421x

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Fluoride Bridges as Structure-Directing Motifs in 3d-4f Cluster Chemistry

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Supporting Information

ABSTRACT: The use of kinetically robust chromium(III) fluorido complexes as synths for mixed 3d-4f clusters is reported. The tendency toward linear {CrIII F3–LnIII} units dictates the cluster topology. Specifically, we show that reaction of cis-[CrIII F2(NN)3]NO3 (NN = 1,10-phenanthroline ("phen") or 2,2′-bipyridine ("bpy")) with Ln(NO3)3·xH2O produces isostructural series of molecular {Ln2Cr2} squares (1–9) with technical fluoride bridges. In a parallel fashion, jack-[CrIII F3L], where L = N3,N3,N3-trimethyl-1,4,7-triazacyclononane ("Me3tacn"), reacts with Nd(NO3)3·6H2O to form a fluoride-centered penta-nuclear complex and jack-[CrIII F3L′], with L′ = 1,1,1-tris((methylamino)methyl)ethane ("Me3tame"), reacts with [Ln(hfac)3(H2O)] (hfacH = 1,1,1,5,5,5-hexafluoroacetylactone) to yield an isostructural series of {Ln3Cr2} (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 (H = J12J1, J2, formalism) and vanishingly small JCr–Gd of 0.06(0) cm−1. The large spin and small anisotropy together with weak exchange interactions in the {Gd1Cr2} (11) cluster give rise to a very large magneto-caloric effect of −ΔSm = 28.7 J kg−1 K−1 (μ0H = 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, [La{(C5Me5)2TiCl3}4]4− and [Ln{(C5Me5)2Ti2F7}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 pivate 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

Received: February 24, 2012
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-[CrF2(NN)2]+ (NN = phen, bpy), fac-[CrF3(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)2]NO3,11 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 lanthanide and no product is obtained at all for the heaviest ones (Er–Yb). The decreasing yield with increasing atomic number is accompanied by an increasing amount of an easily separable byproduct, which is not LnF3 as determined by analysis and powder diffraction. The exact nature of the byproduct has however not been determined. Freshly precipitated, and not too intensely dried, the tetranuclear compounds are isomorphous and crystallize in the tetragonal space group P4/ncc as demonstrated by the powder diffraction data for the series Ce–Dy (except Pr) in Figure 1. Upon thorough drying the crystal solvents are lost, as witnessed by elemental analyses and deterioration of the crystals. The cis-coordination of the two fluoride ions imposes a square structure on the resulting tetranuclear cluster with almost linear (169°) Ln–F–Cr bridges (cf. Figure 2). The lanthanide ion is deca-coordinated with four bidentate nitrate ligands and two bridging fluoride ligands. The coordination number is smaller than usual in bidentate nitrate complexes where coordination numbers of 11 and 12 are common, but it is also found in, for example, [Nd(NO3)4(CH3OH)2]·12. The coordination around chromium is very similar to that in the parent complex, but with slightly elongated Cr–F bond lengths 1.8816(14)/1.8844(17) Å as compared to 1.8444(10)–1.8621(10) Å in [CrF2(phen)2](ClO4)·4MeOH·H2O.13

Figure 1. Powder diffraction patterns for [(CrF2(phen)2)Ln(NO3)3]2·4MeOH·H2O (1–8). The lower trace is calculated on basis of the single crystal diffraction data for the gadolinium compound. The yields diminish steeply with increasing atomic weight 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.

Figure 2. X-ray molecular structure of the isostructural metal clusters in 6 and 3, for comparison shown with thermal ellipsoids (50% probability). Hydrogens and solvent molecules are omitted and nitrate ligands have been shown as wireframes for clarity. Color code: pink, Ln; green, Cr; yellow, F; red, O; blue, N; gray, C. Selected bond lengths (Å) and angles (deg), for 6: Cr–F: 1.8844(17); Cr–N: 2.058(2)–2.063(2); Gd–F: 2.2844(16); Gd–O: 2.506(2)–2.533(2); Cr–F–Gd: 168.61(9). For 3: Cr–F: 1.8816(14); Cr–N: 2.0550(17)–2.0615(19); Nd–F: 2.3348(15); Nd–O: 2.5326(19)–2.5651(18); Cr–F–Nd: 168.74(8).

The Cr–N distances are 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 CrLn2-planes in the packing (see the Supporting Information).

The closely related cis-[CrF2(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 [CrF₂(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: [Mn₃F₁₂(phen)₃(NO₃)₄]·12H₂O⁺ and parallels the tetra-nuclear structures with approximately linear fluoride bridges found for many metal pentafuorides. Thus, while many examples are known with doubly bridging hydroxide, oxide, and the heavier halides, fluoride clearly disfavors this structural motif. This conclusion becomes even more evident when the products resulting from reaction between trifluoro complexes of Cr(III) and lanthanoid complexes are considered. Scheme 1 depicts the structures obtained with the di- and trifluoro complexes. Thus, for both fac-[CrF₃(Me₆tame)] and fac-[CrF₃(Me₆tacn)], 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-nitrate-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(Me₆tacn)] features a most unusual central μ₂-fluoride 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)₆(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

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

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

![Figure 3. Side and top views of crystal structures of [(CrF₃(Me₆tame)]×Ln₃(hfac)₃(μ-F)₃]·7CH₃CN (Ln = Gd (11), Ho (12); left) and [(CrF₃(Me₆tacn)]×Nd₃(NO₃)₄(μ₁-F): (H₂O)]·6CH₃CN (14; right). Solvent molecules and hydrogens have been omitted for clarity. Color code: pink, Ln; green, Cr; yellow, F; red, O; blue, N; gray, C. Selected bond lengths (Å) and angles (deg), 11: Cr₁–F: 1.903(7)–1.915(7), Cr₂–F: 1.903(6)–1.912(7), Cr₁–N: 2.043(12)–2.053(12), Cr₂–N: 2.057(11)–2.066(12), Gd–F₃μ₉: 2.295(6)–2.338(7), Gd–F₃μ₅: 2.216(6)–2.244(7), Gd–O: 2.39(3)–2.49(2), Cr–F–Gd: 142.8(3)–146.6(3), Gd–F–Gd: 142.3(3)–143.9(4), 12: Cr₁–F: 1.893(4)–1.904(4), Cr₂–F: 1.892(4)–1.915(4), Cr₁–N: 2.055(8)–2.062(7), Cr₂–N: 2.044(7)–2.055(7), Ho–F₃μ₉: 2.256(4)–2.311(4), Ho–F₃μ₅: 2.189(4)–2.200(4), Ho–O: 2.35(3)–2.463(19), Cr–F–Ho: 143.3(2)–145.5(2), Ho–F–Ho: 143.3(2)–146.9(2), 14: Cr₁–F: 1.894(8)–1.936(8), Cr₂–F: 1.918(9)–1.938(8), Cr₁–N: 2.040(12)–2.095(12), Cr₂–N: 2.075(12)–2.094(13), Nd₁–F₁₂0(μ₁): 2.365(8), Nd₂–F₁₂0(μ₂): 2.434(8), Nd₃–F₁₂0(μ₃): 2.410(7), Nd₁–O: 2.489(11)–2.542(10), Nd₂–O: 2.508(11)–2.652(11), Nd₃–O: 2.499(10)–2.626(10), Nd₁–F₃μ₉: 2.297(8)–2.326(8), Nd₂–F₃μ₅: 2.342(8)–2.353(8), Nd₃–F₃μ₅: 2.372(8)–2.386(8), Cr–F–Nd: 138.5(4)–146.8(4), Nd–O–Nd: 109.4(4)–110.0(4)."

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-μ₁-hydroxido

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doi.org/10.1021/ic300421x.i Inorg. Chem. XXXX, XXX, XXX--XXX
and tri-$μ_2$-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. 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 goodnes 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$_3$)$_3$·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-framework of the Cr(III) complexes exhibits solvatochromism with Na$^+$ ions in 2-propanol.$^{16}$ It has also generally been found that Cr(III) fluoride complexes exhibit solvatochromism with hypochromic shifts upon moving to more strongly proton donating solvents.$^{16}$ It has been suggested that this effect stems from a different radial dependence of the LF $σ$- and $π$-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.$^{7}$ 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 $\{[CrF_2(phen)_2]_2Ln-(NO_3)_4\}^{+}$ and $\{[CrF_2(phen)_2Ln(NO_3)_3]\}^{+}$ as the most prominent peaks in positive ion detection mode (Supporting Information, Figure S5.1) and $\{[CrF_2(phen)_2Ln(NO_3)_4]\}^{−}$ 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.

![Figure 4](image-url)  
**Figure 4.** UV–vis spectral changes upon addition of Gd(NO$_3$)$_3$ to cis-[CrF$_2$(phen)$_2$]NO$_3$ in methanol/acetonitrile (1:4). Spectra were recorded over 30 min at room temperature (RT). Prolonged storage or further addition of Gd(NO$_3$)$_3$ results in precipitation of 6.

of this band directly measures the octahedral component of the ligand-field, the direction of the shift toward higher energies might seem counterintuitive. However, shifts of the same sign and even larger magnitude were found for fac-[CrF$_2$(Me$_6$tacn)]$^{17}$ interacting with Na$^+$ ions in 2-propanol. It has also generally been found that Cr(III) fluoride complexes exhibit solvatochromism with hypochromic shifts upon moving to more strongly proton donating solvents.$^{16}$ It has been suggested that

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Curie constants are the expected high-temperature values calculated from the free ion Gd$^3+$, with its orbitally nondegenerate $8S_{7/2}$ ground state is the preferred lanthanoid ion for modeling of magnetic properties. In Figure 7 are shown the $\chi T$ products for Cr$_2$Gd$_3$ (11) and reduced magnetization ($M$ vs $\mu_B k_B T$) 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 $J$ parameter values indicating that the Cr(III) and Gd(III) magnetic anisotropies are vanishing. The fitting yields $J_{\text{Cr-Gd}} = 0.71$ cm$^{-1}$ for 6 and $J_{\text{Cr-Cr}} = 0.14(0)$ cm$^{-1}$ and $J_{\text{Gd-Gd}} = 0.06(0)$ cm$^{-1}$ for 11. 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$^{19}$ or oxalate.$^{20}$ To the best of our knowledge, only one example of a Gd(III)$^{18}$–Cr(III) cluster with solely monatomic bridges is reported.$^{21}$ 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.$^{22}$

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 μH = 0, 10, 40, and 90 kOe. Inset: temperature dependencies of the experimental entropy for several H, as obtained from the respective heat capacity data.

From the temperature and field dependencies of the entropy (Figure 8, inset), we can easily obtain the magnetic entropy change (ΔS_m) for selected applied field changes (ΔH). 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, ΔS_m(T) = \int \left[ \frac{∂M}{∂T} \right] dH. From the isothermal M(H) curves (Supporting Information, Figure S3.4) the so-obtained temperature-dependencies of ΔS_m for μH = 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 −ΔS_m to reach the maximum value of 28.7 J kg⁻¹ K⁻¹ for T = 2.2 K and ΔH = (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.2,24 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.2a This range is of considerable technological interest because it is easily reachable by pumping liquid ⁴He.

**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
Experimental Section

Synthesis of [{CrF2(phen)2}(Ln(NO3)4)]2. All of the tetranuclear clusters were prepared by the same general protocol given here. A solution of cis-[CrF2(phen)2]NO3 (0.82 mmol) in MeOH (20 mL) was stirred at RT for 30 min and filtered twice through syringe filters with pore size 0.45 μm. The resulting solution (I) was diluted with an additional 20 mL of MeOH (for prep. of Pr and Nd compounds) or 10 mL of MeOH (for the remaining lanthanoids). A second solution (II) was made up of Ln(NO3)3·6H2O (0.81 mmol) in MeOH (10 mL). The two solutions were mixed and left for crystallization for 24 h at RT. Yields do not improve by preparation at 0 °C. The resulting mass of red crystals and white powder (the ratio between these depends on lanthanoid in question) was loosened and filtered twice through syringe filters with pore size 0.45 μm. The suspension of byproduct in MeOH was filtered twice through syringe filters with pore size 0.45 μm. The resulting solution (I) was diluted with an additional 20 mL of MeOH (for prep. of Pr and Nd compounds) or 10 mL of MeOH (for the remaining lanthanoids). A second solution (II) was made up of Ln(NO3)3·6H2O (0.81 mmol) in MeOH (10 mL). The two solutions were mixed and left for crystallization for 24 h at RT. Yields do not improve by preparation at 0 °C. The resulting mass of red crystals and white powder (the ratio between these depends on lanthanoid in question) was loosened and filtered twice through syringe filters with pore size 0.45 μm. The suspension of byproduct in MeOH was filtered twice through syringe filters with pore size 0.45 μm. The resulting solution (I) was diluted with an additional 20 mL of MeOH (for prep. of Pr and Nd compounds) or 10 mL of MeOH (for the remaining lanthanoids). A second solution (II) was made up of Ln(NO3)3·6H2O (0.81 mmol) in MeOH (10 mL). The two solutions were mixed and left for crystallization for 24 h at RT. Yields do not improve by preparation at 0 °C. The resulting mass of red crystals and white powder (the ratio between these depends on lanthanoid in question) was loosened and brought into suspension. Crystals were harvested by decantation of the byproduct in suspension. The crystals were washed repeatedly with MeOH by decantation until all the pale colored byproduct was removed, and dried on a sintered glass filter in a dynamic vacuum. Upon drying, solvast loss causes the crystals to lose their luster. A faster precipitation of the product in microcrystalline form can be achieved for Pr, Nd, and Sm by not adjusting the volume of solution 1 with additional MeOH. The suspension of byproduct in MeOH was transferred to centrifuge tubes and centrifuged, washed thoroughly with MeOH, and dried in a dynamic vacuum.

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.

{[CrF2(phen)2][Ce(NO3)4]}2 (1): Yield: 74% of theoretical based on Ce3+. Elemental analysis calcd (%) for H2C2N2O2F2Cr3Ce2H: 1.92, C 34.38, N 13.36; found: H 1.72, C 32.83, N 12.68. By-product: None.

{[CrF2(phen)2][Pr(NO3)4]}2 (2): Yield: 82% of theoretical based on Pr3+. Elemental analysis calcd (%) for H2C2N2O2F2Cr3Pr2: 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.

{[CrF2(phen)2][Nd(NO3)4]}2 (3): Yield: 87% of theoretical based on Nd3+. Elemental analysis calcd (%) for H2C2N2O2F2Cr3Nd2: 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.

{[CrF2(phen)2][Sm(NO3)4]}2 (4): Yield: 87% of theoretical based on Sm3+. Elemental analysis calcd (%) for H2C2N2O2F2Cr3Sm2: H 1.90, C 33.96, N 13.20; found: H 2.08, C 33.79, N 12.52. By-product: 0.035 g (Analysis: Found (%): H, 1.62; C, 24.41; N, 7.99). {[CrF2(phen)2][Eu(NO3)4]}2 (5): Yield: 37% of theoretical based on Eu3+. Elemental analysis calcd (%) for H2C2N2O2F2Cr3Eu2: 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). {[CrF2(phen)2][Gd(NO3)4]}2 (6): Yield: 27% of theoretical based on Gd3+. Elemental analysis calcd (%) for H2C2N2O2F2Cr3Gd2: 2.17, C 33.41, N 12.72; 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). {[CrF2(phen)2][Tb(NO3)4]}2 (7): Yield: 5.5% of theoretical based on Tb3+. Elemental analysis calcd (%) for H2C2N2O2F2Cr3Tb2: 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). {[CrF2(phen)2][Dy(NO3)4]}2 (8): Yield: 1.8% of theoretical based on Dy3+. Elemental analysis calcd (%) for H2C2N2O2F2Cr3Dy2: 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) By-product: 0.097 g (Analysis: Found (%): H, 1.67; C, 24.36; N, 7.81).

{[CrF2(phen)2][Ho(NO3)4]}2 (9): Yield: Few crystals. By-product: 0.107 g (Analysis: Found (%): H, 1.61; C, 24.09; N, 7.75). Attempted synthesis of {[CrF2(phen)2][Er(NO3)4]}2: Yield: None. By-product: 0.093 g (Analysis: Found (%): H, 1.64; C, 23.72; N, 7.65). Attempted synthesis of {[CrF2(phen)2][Yb(NO3)4]}2: Yield: None. By-product: 0.016 g (Analysis: Found (%): H, 1.24; C, 13.36; N, 5.11).

Synthesis of [{CrF2(bpy)2}[Ln(NO3)4]}2 (Ln = Nd, Sm, Eu, Gd). This synthesis proceeds similarly as for the phenanthroline analogues. Details are provided in the Supporting Information.

Synthesis of [{CrF2(Me,tame)2}Ln(hfac)3(F-)]7CH3CN (Ln = Sm (10), Gd (11), Ho (12), Yb (13)]. [(Hfac)(H2O)]2 (0.61 mmol) was dissolved in MeCN (5 mL), and the resulting solution was added to a suspension of fac-[CrF2(Me,tame)2]3H2O (0.41 mmol) in MeCN (5 mL). The mixture was stirred for 2 min and filtered. The filtrate was kept for 24 h to yield red-purple, X-ray quality crystals. Yields: 20–25% (based on Ln). When the crystals are removed from the mother liquor, desolvation takes place and the crystals deteriorate. Thoroughly dried products yield the following elemental analyses: 10: calcd (%) for H2C2N2O2F2Cr3Sm: H 2.14, C 23.35, N 3.71; found: H 2.12, C 23.15, N 3.38; 11: calcd (%) for H2C2N2O2F2Cr3Gd: H 2.12, C 23.14, N 3.68; found: H 2.07, C 23.12, N 3.37; 12: calcd (%) for H2C2N2O2F2Cr3Ho: H 2.10, C 22.91, N 3.64; found: H 1.92, C 23.17, N 3.52; 13: calcd (%) for H2C2N2O2F2Cr3Yb: H 2.08, C 22.68, N 3.61; found: H 1.98, C 22.60, N 3.30.

Synthesis of [{CrF2(Me,tame)2}Nd2(NO3)3(μ3-F)(H2O)]6CH3CN (14). A solution of fac-[CrF2(Me,tame)2] (0.100 g, 0.36 mmol) in MeCN (10 mL) was allowed to diffuse through a porous glass frit (D4) into a solution of Nd(NO3)3·6H2O (0.205 g, 0.47 mmol) in
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 calc (%) for H$_2$Cr$_6$O$_{	ext{n}}$F$_2$-Cr$_2$Nd$_2$: 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-volatages 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 120(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 (SHELXS97) and refined using the software SHELXL97 software package.3 Crystals suitable for X-ray diffraction were obtained directly from the synthetic procedure. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in the difference Fourier map and refined isotropically and constrained riding their parent atom in a fixed geometry.

For 0 < B < 9 T magnetic field range.

## SUPPORTING INFORMATION

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## REFERENCES


