Supplementary Information

Chromium Chains as Polydentate Fluoride Ligands for Lanthanides

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Synthesis

The reagents were from Aldrich and used as received.

$[(Et_2NH_2)_3Cr_6F_{11}(O_2C^tBu)_{10}]_2$ and $[(^nPr_2NH_2)_3Cr_6F_{11}(O_2C^tBu)_{10}]_2$ were prepared according S.T. Ochsenbein et al.Chem. Eur. J. 2008, **14**, 5144 – 5158.

The $[Ln(O_2C^tBu)_3(HO_2C^tBu)_3]_2$ complexes were prepared as reported in T.A. Zoan et al. J. Alloys & Comp., 1995, **225**, 396-399.

Compound 3: $[Cr_6CeF_7(O_2C^tBu)_{14}(THF)_2]$

$[(^nPr_2NH_2)_3Cr_6F_{11}(O_2C^tBu)_{10}]_2$ (2.0g, 0.54mmol), $Gd(O_2C^tBu)_3(HO_2C^tBu)_3]_2$ (2.0g, 1.33mmol) and pivalic acid (2.0g, 19.58mmol) were dissolved in toluene (100mL) and DMSO (2 g) and refluxed with stirring for 1.5h at 125ºC. Once the reaction mixture had been allowed to cool to room temperature the solvent was removed under reduced pressure and to MeCN (30 ml) was added to the residue and stirred for 0.5h. The solid was collected by filtration, washed with further MeCN and dried in air.

Column chromatography on silica gel with 1:20 EtOAc-Toluene as the eluent was used to purify the collected solid. The title compound was collected with first fraction in a very low yield. Crystals suitable for an X-ray structure study were obtained by crystallization from a mixture of THF-MeCN.

Elemental analysis calculated (%) for

$C_{78}H_{142}CeCr_6F_7O_{30}$: C 43.82, H 6.69, N 0.00; found (%) C 42.09, H 6.73, N 0.00.

Compound 4: $[Et_2NH_2)_2Cr_{12}Gd_2F_{18}(O_2C^tBu)_{26}]$,

$[Gd(O_2C^tBu)_3(HO_2C^tBu)_3]_2$ (0.5 g, 0.326 mmol), pivalic acid (1.5 g, 14.69 mmol), DMSO (1.0 g) and $[(Et_2NH_2)_3Cr_6F_{11}(O_2C^tBu)_{10}]_2$ (1.5 g , 0.427 mmol) were stirred at room temperature with THF (35 ml) for 15 min, then MeCN (20 ml) added and stirring continued for 18 hours at room temperature in a sealed flask. Then the solution was filtered and the filtrate left undisturbed for slow evaporation in a partially open flask. After 1 week a small amount of crystalline product including crystals suitable for an X-ray structure study were collected by filtration and washed with MeCN.

Yield: 0.33 g (25 %, based on Gd). Elemental analysis calculated (%) for

$C_{138}H_{258}Cr_{12}F_{18}Gd_2N_2O_{52}$: C 40.85, H 6.41, N 0.69; found (%) C 41.23, H 6.93, N 0.46.

Compound 5: $[(Et_2NH_2)_2Cr_{12}Gd_4F_{21}(O_2C^tBu)_{29}]$

$[Gd(O_2C^tBu)_3(HO_2C^tBu)_3]_2$ (1.8 g, 1.17 mmol), pivalic acid (2.0 g, 19.58 mmol), DMSO (2.0 g) and $[(Et_2NH_2)_3Cr_6F_{11}(O_2C^tBu)_{10}]_2$ (2.0 g , 0.56 mmol) were refluxed together in toluene (100 ml) for 18 hours. The solvent was then removed under reduced pressure and to the obtained residue acetonitrile (MeCN, 100 ml) was added. The mixture was filtered and the precipitate collected and washed with further MeCN and dried in air. The pure title compound was isolated by column chromatography on silica gel using Et_2O as elutant. **$[Et_2NH_2)_2Cr_{12}Gd_4F_{21}(O_2C^tBu)_{29}]$,** was present in the first fraction and crystallised from a solution of Et_2O/MeCN (10:1) by slow evaporation of the solvents at room temperature over 3 days. Large green crystals were collected by filtration washed with acetone and dried on air.

Yield: 1.52 g (56.36 %, based on Cr). Elemental analysis calculated (%) for $C_{153}H_{285}Cr_{12}F_{21}Gd_4N_2O_{58}$: Cr 13.18, Gd 13.29, C 38.83, H 6.07, N 0.59; found (%)

Cr 13.28, Gd 13.53, C 38.82, H 6.07, N 0.62.

(**Nb.** $[Et_2NH_2)_2Cr_{12}\,Ln_4F_{21}(O_2C^tBu)_{29}]$, where Ln= Sm, Eu, Tb, Dy, Ho, Er, Yb can be prepared by a similar reaction)**.**

Compounds 6 and 7: $[Et_2NH_2)_2Cr_6Y_2F_8(O_2C^tBu)_{17}]$ 6 and $[Et_2NH_2)_2Cr_{12}\,Ln_4F_{21}(O_2C^tBu)_{29}]$ 7

6. $[Y(O_2C^tBu)_3(HO_2C^tBu)_3]_2$ (1.65 g, 1.18 mmol), pivalic acid (2.0 g, 19.58 mmol), DMSO (2.0 g) and $[(Et_2NH_2)_3Cr_6F_{11}(O_2C^tBu)_{10}]_2$ (2.0 g , 0.56 mmol) were refluxed in toluene (100 ml) for 20 hours. The solvent was then evaporated under vacuum and to the residue MeCN (100 ml) was added. The mixture was filtered and the precipitate collected and washed with MeCN. The compound was later identified as **$[Et_2NH_2Cr_6Y_2F_8(O_2C^tBu)_{17}(H_2O)]$** was extracted from the residue with acetone (50 ml) and crystallised from Et_2O/ MeCN.

Yield: 0.42 g (15 %, based on Cr). Elemental analysis calculated (%) for $C_{89}H_{167}Cr_6F_8N_1O_{35}Y_2$: Cr 12.72, Y 7.25, C 43.58, H 6.86, N 0.57; found (%)

Cr 12.36, Y 7.76, C 43.76, H 7.19, N 0.55.

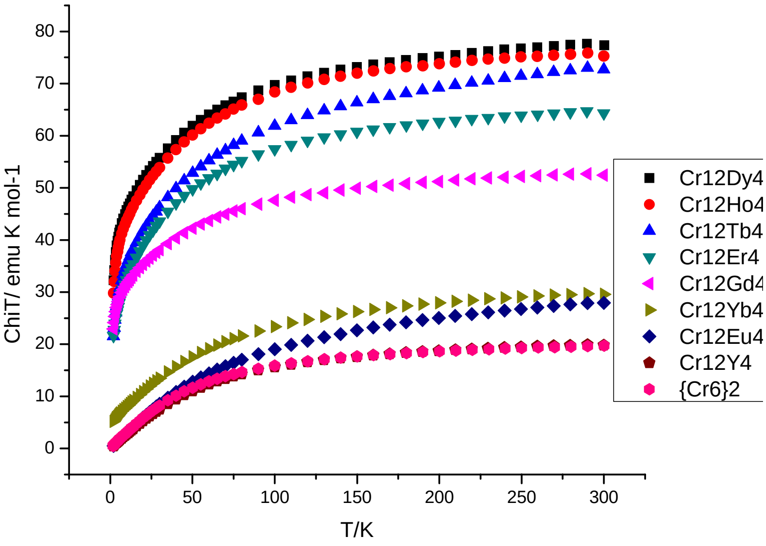
7. The remaining solid after extraction with acetone was dissolved in Et_2O (~ 50 ml), and the solution passed through silica. The filtrate was diluted slowly with MeCN (~ 50 ml), and stirred for 30 min. The resulting green microcrystalline product identified later as **$[Et_2NH_2)_2Cr_{12}Y_4F_{21}(O_2C^tBu)_{29}]$** was collected by filtration, washed with a large quantity of MeCN, then thoroughly washed with acetone, and dried in air.

Suitable crystals for an X-ray structure study were obtained from a solution of Et_2O/ MeCN (10:1) by slow evaporation of the solvents at room temperature over 3 days.

Yield: 1.55 g (61%, based on Cr). Elemental analysis calculated (%) for $C_{153}H_{285}Cr_{12}F_{21}N_2O_{58}\,Y_4$: Cr 13.99, Y 7.97, C 41.21, H 6.44, N 0.63; found (%)

Cr 13.30, Y 8.16, C 42.07, H 6.58, N 0.61.

Fig. S1 and S2. Magnetic susceptibility measurements and magnetisation measurements for $Cr_{12}Ln_4$ Complexes



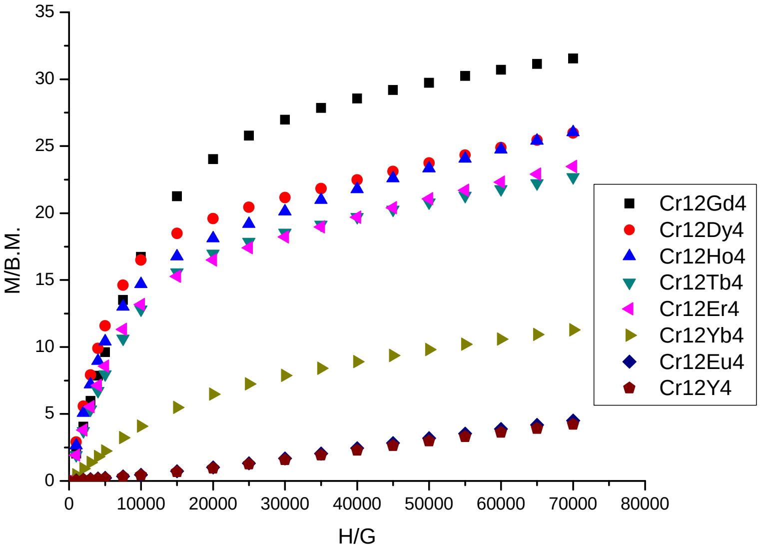


Fig. S3. EPR spectroscopy of {Cr_6} double horseshoe cf $Cr_{12}Y_4$ recorded at Q-band and 5 K.