Supplementary Material

A. Synthetic Procedures

The reagents were from Aldrich and used as received. {Ln(hfac)$_3$·diglyme} (Ln = La, Ce, Pr; hfac = hexafluoroacetylacetonate; diglyme = bis(2-methoxyethyl)ether) were prepared as reported in: G. Malandrino and I. L. Fragala`, *Coord. Chem. Rev.*, 2006, 250, 1605. [$Cu_2(O_2CCMe_3)_4(HO_2CCMe_3)_2$] was prepared by using copper(II) carbonate basic instead of nickel (II) carbonate basic in the procedure reported for [$Ni_2(H_2O)(O_2CCMe_3)_4(HO_2CCMe_3)_4$] in G. Chaboussant, R, Basler, H.-U. Güdel, S. Ochsenbein, A. Parkin, S. Parsons, G. Rajaraman, A. Sieber, A. A. Smith, G. A. Timco, R. E. P. Winpenny, J. Chem. Soc. Dalton Trans 2004, 2757 – 2765. The Erlenmeyer Teflon ^{R} FEP flasks were supplied by Fisher.

{$[Et_2NH_2]_3[Cr_6F_{11}(O_2CCMe_3)_{10}]$}$_2$ (1).

Pivalic acid (16.0 g, 157 mmol), diethylamine (1.64 g, 22 mmol), and $CrF_3·4H_2O$ (5.0 g, 28 mmol), were stirred together at 140°C for 15 h in open Teflon flask. After cooling to room temperature, acetone (50 ml) was added to the solid and it was stirred for 5 h. Then the solid was filtered, washed with acetone and dried in air. To this product diethyl ether (75 ml) was added. The obtained extract was filtered, diluted with acetonitrile (30 ml) and stirred for 30 minutes. The resulting green microcrystalline product was filtered, washed with a large quantity of acetonitrile, then thoroughly washed with acetone, and dried in air. Yield 6.4 g (78.40 %). Elemental analysis calculated (%) for $C_{124}H_{256}Cr_{12}F_{22}N_6O_{42}$: Cr 17.60, C 42.01, H 7.28, N 2.37; found: Cr 17.32, C 42.27, H 7.52, N 2.42. X-ray quality single crystals were obtained from a solution of THF/CH_3CN (1:1) at room temperature in two days.

{$[^nPr_2NH_2]_3[Cr_6F_{11}(O_2CCMe_3)_{10}]$}$_2$ (2),

Was obtained following the same procedure as for 2 using dipropylamine instead of diethylamine.
Yield 6.1 g (71.4 %). Elemental analysis calculated (%) for $C_{136}H_{280}Cr_{12}F_{22}N_6O_{42}$: Cr 16.80, C 43.99, H 7.60, N 2.26; found: Cr 16.87, C 43.92, H 7.39, N 2.25. Suitable crystals for X-Ray structure study were obtained from a solution of pentane/acetone (2:1) by slow evaporation of the solvents at room temperature during 3 days.

{$[^iPr_2NH_2]_3[Cr_7F_{12}(O_2CCMe_3)_{12}]$}$_2$ (3),

Pivalic acid (16.0 g, 157 mmol), diisopropylamine (2.0 g, 22 mmol), and $CrF_3·4H_2O$ (5.0 g, 28 mmol), were stirred together at 140°C for 18 h. Then the obtained green viscous mass was heated at 100°C for 5 h under a N_2 flow to remove pivalic acid. After cooling to room temperature, to the solid acetone (50 ml) was added and it was stirred for 5 h, then filtered, washed with a large amount of acetone and dried in air. This product was extracted into diethyl ether (75 ml) then the solvent was evaporated, and the residue washed with acetone and dried on air. Yield 1.7 g (20.20 %). Elemental analysis calculated (%) for $C_{156}H_{316}Cr_{14}F_{24}N_6O_{50}$: Cr 17.09, C 43.98, H 7.48, N 1.97; found: Cr 16.83, C 44.31, H 7.71, N 2.13. X-ray quality single crystals were obtained by crystallization of 6 from pentane/ acetone, Et_2O/acetone or toluene/CH_3CN.

Here we report the structure of the crystals from pentane/ acetone. Elemental analysis calculated (%) for $C_{156}H_{316}Cr_{14}F_{24}N_6O_{50}$: Cr 17.09, C 43.98, H 7.48, N 1.97, F 10.70; found: Cr 17.15, C 43.99, H 7.44, N 1.86, F 10.81.

$\{[(C_8H_{15})_2NH_2]_3Cr_6F_{11}(O_2CCMe_3)_{10}\}_2$ Pivalic acid (16.0 g, 157 mmol), dioctylamine (5.3 g, 22 mmol), and $CrF_3\cdot 4H_2O$ (5.0 g, 28 mmol), were stirred together at 140°C for 15 h in open Teflon flask. After cooling to room temperature, acetone (70 ml) was added to the solid and it was stirred for 5 h. Then the solid was filtered, washed with large quantity of acetone and dried in air. To this product diethyl ether (100 ml) was added. The obtained extract was filtered*, diluted with acetone (30 ml) and concentrated by distillation up to ½ of its volume. After one week green crystals including X-ray quality were formed. The crystals were collected by filtration, washed with acetone and dried on air. Yield 3.5 g (33.8%)

Elemental analysis calculated (%) for $C_{196}H_{372}Cr_{12}F_{22}N_6O_{40}$: Cr 13.88, C 52.37, H 8.34, N 1.87; found: Cr 12.89, C 52.56, H 9.75, N 1.67.

$\{[(C_8H_{15})_2NH_2]_3Cr_3F_8(O_2CCMe_3)_4(CMe_3CCO_2H)_2\}_n$ (4)

*The remaining product on the filter after extraction of $\{[(C_8H_{15})_2NH_2]_3Cr_6F_{11}(O_2CCMe_3)_{10}\}_2$ into Et_2O, was washed several times with Et_2O (5 X 15 ml) up to light green solution, then extracted into 60 ml dichloromethane, filtered and diluted with acetone until solution become cloudy. After two weeks green crystals including X-ray quality were formed. The crystals were collected by filtration, washed with acetone, then with pentane (3 x 10 ml) and dried on air. Yield 1.1 g (7.2%) Elemental analysis calculated (%) $C_{80}H_{152}Cr_3F_8N_3O_{12}$: Cr 9.42, C 58.02, H 9.25, N 2.54; found: Cr 9.88, C 57.00, H 9.73, N 2.64.

$\{[Me_2NH_2]_3[Cr_6F_{11}(O_2CCMe_3)_{10}]\ 2.5\ H_2O\}_4$ (5),

Pivalic acid (16.0 g, 157 mmol), Dimethylammonium dimethylcarbamate (1.34 g, 10 mmol), as source of dimethylammonium cation and $CrF_3\cdot 4H_2O$ (5.0 g, 28 mmol), were stirred together at 140°C for 30 h. After cooling to room temperature, diethyl ether (20 ml) and acetone (50 ml) were added and the solution was stirred for 5 h. Then it was filtered and the filtrate diluted with acetonitrile (70 ml) and stirred for 3 days. The precipitate, which forms during this time, was filtered, washed with a large amount of acetonitrile and then extracted into Et_2O (20 ml), the extract was diluted with CH_3CN (30 ml) and stirred for 30 minutes. The green solid, which precipitated was collected by filtration, washed with a large amount of CH_3CN, and with

10 ml of acetone, and dried in air. Yield 0.32 g (2.0 %). Elemental analysis calculated (%) for $C_{224}H_{476}Cr_{24}F_{44}N_{12}O_{90}$: Cr 18.19, C 39.21, H 6.99, N 2.45; found: Cr 17.71, C 38.73, H 7.12, N 2.27. Suitable X-ray crystals were obtained from a solution of ethyl acetate: acetonitrile (1:1) at room temperature after 1 day.

$[(Et_2NH_2)\{Cr_6F_7(O_2C^tBu)_{10}(RCOCHCOR')_2\}]$ (6)

6a) R = R' = CF_3; 0.5 g (0.14 mmol) of **1** and 0.25 g (0.28 mmol) of {La(hfac)$_3$·diglyme} were dissolved in 20 ml of toluene, stirred and refluxed for 5 h. Then, the solvent was removed and the title compound was separated by column chromatography on silica gel using EtOAc/ hexane (1:1) as eluent (**6** was eluted as first product). Yield 0.34 g (61.99 %). Crystals were obtained from a solution of toluene/CH_3CN at room temperature after 1 week. Elemental analysis calculated (%) for $C_{64}H_{104}Cr_6F_{19}N_1O_{24}$: Cr 16.04, C 39.53, H 5.39, N 0.72; found: Cr 16.51, C 39.76, H 6.03, N 0.81. ES MS (sample dissolved in THF/MeOH, run in MeOH) *m/z*: - 1870 $[M - (Et_2NH_2)]^-$, + 2017 $[M + (Et_2NH_2)]^+$; + 1961 $[M + (H_3O)]^+$.

6b) R = R' = CF_3; as procedure **6a** but using 0.24 g (1.15 mmol) of Hhfac (1,1,1,5,5,5-hexafluoro-2,4-pentanedione) instead {La(hfac)$_3$·diglyme}. Yield 0.50 g (91.16 %). Crystals were obtained from a solution of toluene/CH_3CN at room temperature after 1 week. Elemental analysis calculated (%) for $C_{64}H_{104}Cr_6F_{19}N_1O_{24}$: Cr 16.04, C 39.53, H 5.39, N 0.72; found: Cr 16.24, C 39.66, H 5.42, N 0.65. ES MS (sample dissolved in THF/MeOH, run in MeOH) *m/z*: - 1870 $[M - (Et_2NH_2)]^-$, + 2017 $[M + (Et_2NH_2)]^+$; + 1961 $[M + (H_3O)]^+$.

6c) R = R' = CH_3; 0.75 g (0.21 mmol) of **1** and 0.17 g (1.71 mmol) of Hacac (2,4-pentanedione) were dissolved in 50 ml of toluene, stirred and refluxed for 24 h. Then, the solvent was removed and the title compound was separated by column chromatography on silica gel using THF/ hexane (1:2) as eluent (**6c** was eluted as second product). Yield 0.43 g (58.80 %). Elemental analysis calculated (%) for $C_{64}H_{116}Cr_6F_7N_1O_{24}$: Cr 18.05, C 44.47, H 6.76, N 0.81; found: Cr 17.91, C 44.62, H 6.93, N 0.85. ES MS (sample dissolved in THF/MeOH, run in MeOH) *m/z*: - 1654 $[M - (Et_2NH_2)]^-$, + 1802 $[M + (NH_2Et_2)]^+$; + 1751 $[M + Na]^+$; + 1694 $[M - (Et_2NH_2) + K + H]^+$; + 1678 $[M - (Et_2NH_2) + Na + H]^+$.

6d) R = C_6H_5, R' = CF_3; 0.5 g (0.14) of **1** and 0.25 g (1.15 mmol) of Hbtfa (4,4,4-Trifluoro-1-phenyl-1,3-butanedione) were dissolved in 20 ml of toluene, stirred and refluxed for 22 h. Then, the solvent was removed and the title compound was separated by column chromatography on silica gel using EtOAc/hexane (1:10) as eluent (**6d** was eluted as the second product). Yield 0.22 g (42.10 %). Elemental analysis calculated

(%) for $C_{74}H_{114}Cr_6F_{13}N_1O_{24}$: Cr 15.91, C 45.33, H 5.86, N 0.71; found: Cr 15.55, C 44.01, H 5.33, N 0.64. ES MS (sample dissolved in THF/MeOH, run in MeOH) *m/z*: - 1886 $[M - (Et_2NH_2)]^-$, + 2033 $[M + (NH_2Et_2)]^+$; + 1979 $[M + (H_3O)]^+$.

$(NH_2Et_2)[\{Cr_6F_{11}(O_2C^tBu)_{10}\}_4Na_{14}CrF_6]\bullet 6H_2O\bullet 6MeCN$ (7)

7a) 1.0 g (0.18 mmol) of **1** was dissolved in 100 ml of THF/EtOH (1:1) , then 0.66 g (10.15 mmol) of NaN_3 added and the suspension was stirred for 1 day at room temperature. Then the solvent was evaporated and the obtained solid was dissolved in 100 ml of hexane, stirred for 30 min and filtered. The filtrate was evaporated and the residue was purified by column chromatography on silica gel using THF as eluent; **7** was eluted as first product. Yield 0.75 g (80.25 %). Crystals were obtained from a solution of Et_2O/CH_3CN at 5°C after 2 day. Elemental analysis calculated (%) for $C_{216}H_{402}Cr_{25}F_{50}N_7Na_{14}O_{86}$: Cr 18.45, C 36.82, H 5.75, N 1.39, Na 4.57; found: Cr 17.98, C 37.31, H 6.07, N 1.52.

7b) The same procedure as in **7a** but by using NaOCN instead of NaN_3. Yield 0.72 g (77.04 %). Crystals were obtained from a solution of Et_2O/CH_3CN at 5°C after 1 day. Elemental analysis calculated (%) for $C_{216}H_{402}Cr_{25}F_{50}N_7Na_{14}O_{86}$: Cr 18.45, C 36.82, H 5.75, N 1.39, Na 4.57; found: Cr 18.09, C 37.51, H 6.11, N 1.41.

B. CryoSpray / Electrospray Mass Spectroscopic Measurements

Cryospray measurements at -40 °C: These experiments were carried out at concentrations of the complex in the region of 10^{-5} mol L^{-1} in THF using a Bruker microTOFQ instrument. Data was collected in positive ion mode and the spectrometer was previous calibrated with the standard tune mix to give a precision of ca. 1.5 ppm in the region of 500-3000 m/z. The standard parameters for a medium mass data acquisition were used, the end plate voltage was set to –500 V and the capillary to +4500 V.