

## SUPPLEMENTARY EXPERIMENTAL DATA.

The reagents were from Aldrich and used as received. Complexes were prepared in Teflon flasks supplied by Fisher

**[HNEt(cy-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>][Cr<sub>9</sub>NiF<sub>12</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>18</sub>] 1.** CrF<sub>3</sub>·4H<sub>2</sub>O (5.0 g, 28 mmol), *N*-Ethyldicyclohexylamine, (cy-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>NEt (2.47 g, 11.8 mmol), 2NiCO<sub>3</sub> · 3Ni(OH)<sub>2</sub> · 4H<sub>2</sub>O (0.5 g, 0.9 mmol) and Me<sub>3</sub>CCO<sub>2</sub>H (15.0 g, 147 mmol) were heated while stirring at 140°C for 8.0 h. The flask was cooled to room temperature and acetone (50 ml) was added and stirred for 15 mins. The microcrystalline product was filtered, washed with a large quantity of acetone, dried in air, and then dissolved in hot hexane (100 ml), filtered and the filtrate evaporated to dryness. The product was crystallized from a THF/ toluene mixture by slow cooling of the solution and partial evaporation of the solvents. The crystals rapidly desolvate giving a green powder. Yield 1.45 g (17%, calculated from CrF<sub>3</sub>·4H<sub>2</sub>O).

Elemental analysis (%): calcd for C<sub>104</sub>H<sub>190</sub>Cr<sub>8</sub>F<sub>12</sub>N<sub>1</sub>NiO<sub>36</sub>: Cr 16.80, Ni 2.11, C 44.85, H 6.88, N 0.50, F 8.19; found: Cr 17.08, Ni 2.10, C 44.77, H 7.17, N 0.47, F 8.32.

Electrospray mass spectroscopy (ES-MS) (sample dissolved in THF, run in MeOH) *m/z*: - 2574 [M - NH Et(cy-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup>; + 2807 [M+Na]<sup>+</sup>

**[HNMe(cy-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>][Cr<sub>9</sub>NiF<sub>12</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>18</sub>] 2** and **[HNMe(cy-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>][Cr<sub>8</sub>Ni<sub>2</sub>F<sub>12</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>18</sub>] 3** are products of one synthesis.

**[HNMe(cy-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>][Cr<sub>9</sub>NiF<sub>12</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>18</sub>] 2.** CrF<sub>3</sub>·4H<sub>2</sub>O (5.0 g, 28 mmol), *N*-Methyldicyclohexylamine, MeN(cy-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub> (2.6 g, 13 mmol), 2NiCO<sub>3</sub> · 3Ni(OH)<sub>2</sub> · 4H<sub>2</sub>O (0.5 g, 0.9 mmol) and Me<sub>3</sub>CCO<sub>2</sub>H (15.0 g, 147 mmol) were heated while stirring at 140°C for 0.5 h then the temperature was increased to 160°C for 4 h. The flask was cooled to room temperature and acetone (50 ml) was added and stirred for 15 mins. The microcrystalline product was filtered, washed with a large quantity of acetone and dried in air. It was then dissolved in hot hexane (350 ml) filtered and the filtrate concentrate by distillation to 80 ml and diluted with 1,4 dioxane (20 ml). The slow evaporation of solvent at ambient temperature in two weeks, to a volume of *ca.* 40 ml produced X-ray quality green crystals that were collected by filtration and washed with 1,4-dioxane. The crystals rapidly desolvate giving a green powder. Yield 1.77 g (21%, calculated from CrF<sub>3</sub>·4H<sub>2</sub>O).

Elemental analysis (%): calcd for C<sub>103</sub>H<sub>188</sub>Cr<sub>9</sub>F<sub>10</sub>N<sub>1</sub>NiO<sub>36</sub>: Cr 16.89, Ni 2.12, C 44.65, H 6.80, N 0.51; found: Cr 17.07, Ni 2.15, C 45.30, H 6.83, N 0.48.

ES-MS (sample dissolved in THF, run in MeOH )  $m/z$ : - 2574  $[M - NH Me(cy-C_6H_{11})_2]^-$  ; + 2793  $[M+Na]^+$

**[HNMe(cy-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>]<sub>2</sub>[Cr<sub>8</sub>Ni<sub>2</sub>F<sub>12</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>18</sub>] 3** was obtained as a byproduct in the synthesis of **2** and isolated by column chromatography on silica gel. The microcrystalline initial product was extracted with hexane (as above), and the residue dissolved in toluene then added to a column. Using toluene as the eluent, **2** was eluted first. Then using THF as eluent, a green solution of **3** was collected. The solvent was evaporated under reduced pressure to 50 ml and MeCN (5 ml) was added. Slow concentration of the solution at ambient temperature in N<sub>2</sub> in one week to a volume of 30 ml produced X-ray quality green crystals that were collected by filtration and washed with MeCN. The crystals rapidly desolvate giving a green powder. Yield 1.1 g (17%, calculated from 2NiCO<sub>3</sub> · 3Ni(OH)<sub>2</sub> · 4 H<sub>2</sub>O).

Elemental analysis (%): calcd for C<sub>116</sub>H<sub>214</sub>Cr<sub>8</sub>F<sub>12</sub>N<sub>2</sub>Ni<sub>2</sub>O<sub>36</sub>: Cr 13.98, Ni 3.95, C 46.84, H 7.25, N 0.94; found: Cr 13.51, Ni 3.99, C 45.54, H 7.39, N 0.75.

ES-MS (sample dissolved in THF, run in MeOH )  $m/z$ : - 2777  $[M - NH Me(cy-C_6H_{11})_2]^-$  .

**[H<sub>2</sub>N<sup>t</sup>Bu<sup>is</sup>Pr][Cr<sub>8</sub>CdF<sub>9</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>18</sub>] 4**. CrF<sub>3</sub>·4H<sub>2</sub>O (5.0 g, 28 mmol), N-tert-Butylisopropylamine <sup>t</sup>BuNH<sup>is</sup>Pr (1.3 g, 11 mmol), and Me<sub>3</sub>CCO<sub>2</sub>H (15.0 g, 147 mmol) were heated while stirring at 140 °C for 2.0 h, then CdCO<sub>3</sub> (0.7 g, 4.1 mmol) was added. The temperature was then increased to 160 °C and the flask heated for a further 15 hours. The flask was cooled to room temperature and acetone (50 ml) was added and stirred for 30 mins. The microcrystalline product was filtered, washed with a large quantity of acetone, dried in air and extracted in hot THF (100 ml), filtered and the filtrate diluted with acetonitrile (40 ml), which gave crystalline product. This was collected by filtration then recrystallized from ethylacetate to obtain X-ray quality green crystals in two days by slow cooling and partial evaporation of the solution in N<sub>2</sub>. Yield 2.9g (32%, calculated from CrF<sub>3</sub>·4H<sub>2</sub>O).

Elemental analysis(%): calcd for C<sub>97</sub>H<sub>180</sub>Cd<sub>1</sub>Cr<sub>8</sub>F<sub>9</sub>N<sub>1</sub>O<sub>36</sub>: Cr 15.78, Cd 4.26, C 44.20, H 6.88, N 0.53; found: Cr 15.93, Cd 4.50, C 44.72, H 6.80, N 0.48.

ES-MS (sample dissolved in THF, run in MeOH )  $m/z$ : - 2519  $[M - H_2^tBuN^{is}Pr]^-$  ; -2634  $[M-H]^-$  ; + 2534  $[M-O_2CCMe_3]^+$  ; +2635  $[M]^+$  ; +2638  $[M+Na]^+$ .

**[H<sub>2</sub><sup>t</sup>BuN<sup>is</sup>Pr][Cr<sub>8</sub>NiF<sub>9</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>18</sub>] 5** and compound **[H<sub>2</sub><sup>t</sup>BuN<sup>is</sup>Pr][Cr<sub>9</sub>NiF<sub>10</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>20</sub>] 6** are products of one synthesis and slight variations in the reaction are required to increase the yield of **6**.  
**Variant A.** CrF<sub>3</sub>·4H<sub>2</sub>O (5.0 g, 28 mmol), <sup>t</sup>BuNH<sup>is</sup>Pr (1.3 g, 11 mmol), and Me<sub>3</sub>CCO<sub>2</sub>H (15.0 g, 147 mmol) were heated while stirring at 140 °C for 1.5 h before the addition of 2NiCO<sub>3</sub> · 3Ni(OH)<sub>2</sub> · 4H<sub>2</sub>O (0.5 g, 0.9 mmol). The temperature was then increased to 160 °C and the flask heated for a further 8

hours. The flask was cooled to room temperature and acetone (50 ml) was added and stirred for 30 min. The microcrystalline product was filtered, washed with a large quantity of acetone, dried in air and extracted in hot THF (100 ml), filtered and the filtrate diluted with acetonitrile (40 ml) that leads to crystallization in one week of large hexagonal prisms of **5** as a major product and a small quantity of square blocks. X-ray diffraction analyses for both crystals show that they have different cell parameters and compound **6** forms the square blocks. Products were filtered and separated by recrystallisation from ethylacetate, a solvent in which **5** has a much higher solubility than **6**. Slow evaporation of the ethylacetate filtrate gave only hexagonal prisms of **5** that rapidly desolvate. Yield 1.5g ( 17 % ) (calculated from  $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$  )

Elemental analysis (%): calcd for  $\text{C}_{97}\text{H}_{180}\text{Cr}_8\text{F}_9\text{N}_1\text{NiO}_{36}$ : Cr 16.11, Ni 2.27, C 45.12, H 7.03, N 0.54; found: Cr 16.04, Ni 2.26, C 45.10, H 6.83, N 0.50.

ES-MS (sample **5** dissolved in THF, run in MeOH )  $m/z$ : - 2465  $[\text{M} - \text{H}_2^t\text{BuN}^{\text{is}}\text{Pr}]^-$  ; + 2581  $[\text{M}]^+$  ; + 2604  $[\text{M}+\text{Na}]^+$  .

The square blocks were washed with ethylacetate and dried in air. Insufficient quantity of **6** was obtained in this synthesis for elemental analyses.

ES-MS (sample **6** dissolved in THF, run in MeOH )  $m/z$ : - 2738  $[\text{M} - \text{H}_2^t\text{BuN}^{\text{is}}\text{Pr}]^-$  ; + 2877  $[\text{M}+\text{Na}]^+$

**Variant B.**  $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$  (5.0 g, 28 mmol),  $^t\text{BuNH}^{\text{is}}\text{Pr}$  (1.05 g, 9.1 mmol), and  $\text{Me}_3\text{CCO}_2\text{H}$  (30.0 g, 294 mmol) were heated while stirring at 140°C for 1.5 h, then  $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  (0.3 g, 0.5 mmol) was added. The temperature was then increased to 160 °C and the flask heated for a further 52 hours. The flask was cooled to room temperature and acetone (50 ml ) was added and stirred for 30min . The microcrystalline product was filtered, washed with a large quantity of acetone, dried in air and dissolved (practically completely) in hot THF (150 ml), filtered and the filtrate evaporated to dryness. Toluene (50 ml ) was added to the product, stirred for 1h, and then the microcrystalline product was filtered, washed with toluene and dried in air. The product was then dissolved in hot ethylacetate (125 ml) and filtered. The hot filtrate was diluted with acetonitrile (25 ml) which led to crystallization in three days of exclusively hexagonal prisms of **5**. Yield 3.5g ( 53 % ) (calculated from of  $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4 \text{H}_2\text{O}$  )

Elemental analysis (%): calcd for  $\text{C}_{97}\text{H}_{180}\text{Cr}_8\text{F}_9\text{N}_1\text{NiO}_{36}$ : Cr 16.11, Ni 2.27, C 45.12, H 7.03, N 0.54; found: Cr 16.48, Ni 2.25, C 45.04, H 7.12, N 0.48.

ES-MS (sample dissolved in THF, run in MeOH )  $m/z$ : - 2465  $[\text{M} - \text{H}_2^t\text{BuN}^{\text{is}}\text{Pr}]^-$  ; + 2581  $[\text{M}]^+$  ; + 2604  $[\text{M}+\text{Na}]^+$  .

6. The portion of the crude microcrystalline material that was insoluble in ethylacetate (0.085 g) was dissolved in hot THF (45 ml). After cooling the solution to room temperature square blocks began to grow that were collected by filtration after one week. Yield 0.05g (0.7%, calculated from  $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ )

#### Variant C.

$\text{CrF}_3 \cdot 4\text{H}_2\text{O}$  (5.0 g, 28 mmol),  $^t\text{BuNH}^{\text{is}}\text{Pr}$  (0.35 g, 3.0 mmol), and  $\text{Me}_3\text{CCO}_2\text{H}$  (50.0 g, 490 mmol) were heated while stirring at  $140^\circ\text{C}$  for 1.5 h before the addition of  $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  (0.3 g, 0.5 mmol). The temperature was then increased to  $160^\circ\text{C}$  and the flask heated for a further 52 hours. The flask was cooled to room temperature and 50 ml of acetone was added and stirred for 30 min. The **microcrystalline** product was collected by filtration, washed with a large quantity of acetone, dried in air and then several extractions with THF were made. The first extraction was with THF (150 ml) at room temperature, and the extract was filtered and the filtrate (N1) evaporated to dryness. The second extraction was with hot THF (4 x 100 ml), and the extracts were filtered, combined and the filtrate (N2) evaporated to dryness.

Toluene (50 ml) was added to the solid obtained from filtrate N1, stirred for 1h and the microcrystalline product was separated by filtration, washed with toluene and dried in air. The product was then dissolved in hot ethylacetate (35 ml) filtered, and to the hot filtrate acetonitrile (5 ml) was added. This led to crystallisation of hexagonal prisms of **5** in 3 days. Yield 0.95g (14 %, calculated from  $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ )

Elemental analysis (%): calcd for  $\text{C}_{97}\text{H}_{180}\text{Cr}_8\text{F}_9\text{N}_1\text{NiO}_{36}$ : Cr 16.11, Ni 2.27, C 45.12, H 7.03, N 0.54; found: Cr 16.44, Ni 2.19, C 44.84, H 7.09, N 0.47.

ES-MS (sample dissolved in THF, run in MeOH)  $m/z$ : - 2465  $[\text{M} - \text{H}_2^t\text{BuN}^{\text{is}}\text{Pr}]^-$ ; + 2581  $[\text{M}]^+$ ; + 2604  $[\text{M} + \text{Na}]^+$ .

6. Toluene (50 ml) was added to the solid obtained from filtrate N2, stirred for 1h and the microcrystalline product was separated by filtration, washed with a large quantity of toluene, dried in air and recrystallized from hot THF. After cooling the solution to room temperature the square blocks began to grow that were filtered after one week. Yield 0.45g (6.0%, calculated from  $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ).

Elemental analysis(%): calcd for  $\text{C}_{107}\text{H}_{198}\text{Cr}_9\text{F}_{10}\text{N}_1\text{Ni}_1\text{O}_{40}$ :

Cr 16.39, Ni 2.06, C 45.01, H 6.99, N 0.49; found: Cr 16.52, Ni 1.96, C 44.89, H 7.19, N 0.43.

ES-MS (sample dissolved in THF, run in MeOH)  $m/z$ : +2753  $[\text{M} - \text{O}_2\text{CCMe}_3]^+$ ; + 2877  $[\text{M} + \text{Na}]^+$

Compound **[Himid]<sub>2</sub>[Cr<sub>6</sub>Ni<sub>2</sub>F<sub>8</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>16</sub>] 7** and compound **[Himid]<sub>2</sub>[Cr<sub>8</sub>NiF<sub>11</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>17</sub>] 8** are products of one synthesis.

**[Himid]<sub>2</sub>[Cr<sub>6</sub>Ni<sub>2</sub>F<sub>8</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>16</sub>] 7.** CrF<sub>3</sub>·4H<sub>2</sub>O (3.0 g, 17 mmol), imidazole (imid) (0.7 g, 10 mmol), 2NiCO<sub>3</sub>·3Ni(OH)<sub>2</sub>·4(H<sub>2</sub>O) (0.3 g, 0.5 mmol) and Me<sub>3</sub>CCO<sub>2</sub>H (12.0 g, 118 mmol) were heated while stirring at 140°C for 24 h. The flask was cooled to room temperature and acetone (30 ml) was added and stirred for 1h. The product was filtered, washed with acetone, dried in air and then extracted into hexane (3 x 50 ml) and the extract was filtered. The solvent was removed by evaporation and the green solid was crystallized from ethylacetate, giving X-ray quality crystals in two days. Yield 1.0 g (34 %, calculated from 2NiCO<sub>3</sub>·3Ni(OH)<sub>2</sub>·4H<sub>2</sub>O).

Elemental analysis (%): calcd for C<sub>86</sub>H<sub>154</sub>Cr<sub>6</sub>F<sub>8</sub>N<sub>4</sub>Ni<sub>2</sub>O<sub>32</sub>: Cr 13.35, Ni 5.02, C 44.19, H 6.64, N 2.40; found: Cr 13.85, Ni 4.61, C 43.91, H 6.74, N 2.25.

**[Himid]<sub>2</sub>[Cr<sub>8</sub>NiF<sub>11</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>17</sub>] 8.**

The portion of the crude product from synthesis **7** that did not dissolve in hexane was extracted with hot THF (70 ml) and filtered. Slow cooling and evaporation of the filtrate gave a green crystalline product suitable for X-ray analysis. The product was collected by filtration, washed with hexane and dried in air at room temperature. The compound can be recrystallised from ethylacetate or THF/MeCN. The paper includes details for crystals grown from THF/ MeCN. Yield 1.4g (27%, calculated from CrF<sub>3</sub>·4H<sub>2</sub>O).

Elemental analysis(%): calcd for C<sub>91</sub>H<sub>163</sub>Cr<sub>8</sub>F<sub>11</sub>N<sub>4</sub>NiO<sub>34</sub>: Cr 16.37, Ni 2.30, C 43.01, H 6.47, N 2.20. found: Cr 16.39, Ni 2.43, C 43.41, H 6.75, N 2.20.

**[HMeimid]<sub>2</sub>[Cr<sub>8</sub>Ni<sub>2</sub>F<sub>12</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>18</sub>] 9.**

CrF<sub>3</sub>·4H<sub>2</sub>O (3.0 g, 17 mmol), 1-methylimidazole (Meimid) (0.9g, 11 mmol), 2NiCO<sub>3</sub>·3Ni(OH)<sub>2</sub>·4H<sub>2</sub>O (0.35 g, 0.6 mmol) and Me<sub>3</sub>CCO<sub>2</sub>H (12.0 g, 118 mmol) were heated while stirring at 140°C for 5.0 h. The flask was cooled to room temperature and acetone (30 ml) was added and stirred for 30 min. The product was filtered, washed with a large quantity of acetone, dried in air and was extracted with hexane (3 x 50 ml) at room temperature. Concentration of the hexane solution by slow evaporation gave in two days 0.35g of crystalline product including suitable crystals for X- ray analysis. The crude product was also extracted with THF (50 ml). This extract was concentrated by evaporation and gave 0.65g of crystalline product in two days, including X- ray quality crystals. X- ray analyses for both crystals showed the same molecular structure, but with different solvent molecules in the crystal lattice. The paper includes details for crystals grown from hexane. Yield 1.0g (24 % calculated from CrF<sub>3</sub>·4H<sub>2</sub>O).

Elemental analysis(%): calcd for  $C_9H_{17}Cr_8F_{12}N_4Ni_2O_{36}$ :

Cr 15.14, Ni 4.27, C 42.84, H 6.46, N 2.04. found: Cr 14.86, Ni 3.99, C 42.85, H 6.72, N 1.99.

**[HBuimid]<sub>2</sub>[Cr<sub>8</sub>Ni<sub>2</sub>F<sub>12</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>18</sub>] 10.**

CrF<sub>3</sub>·4H<sub>2</sub>O (3.0 g, 17 mmol), 1-Buthylimidazole (Buimid) (1.0 g, 8.1 mmol), 2NiCO<sub>3</sub> · 3Ni(OH)<sub>2</sub> · 4H<sub>2</sub>O (0.55 g, 0.94 mmol) and Me<sub>3</sub>CCO<sub>2</sub>H (12.0 g, 118 mmol) were heated while stirring at 140°C for 12.0 h. The flask was cooled to room temperature and acetone (30 ml) was added and stirred for 30 min. The product was filtered, washed with a large quantity of acetone, dried in air and then extracted with hot hexane (3 x 50 ml). Slow cooling and concentration of the hexane solution by evaporation in two days gave crystalline product including suitable crystals for X ray synchrotron diffraction structure analyses. Yield 0.75g (13 %, calculated from CrF<sub>3</sub>·4H<sub>2</sub>O).

Elemental analysis(%): calcd for  $C_{104}H_{188}Cr_8F_{12}N_4Ni_2O_{36}$ :

Cr 14.69, Ni 4.15, C 44.11, H 6.69, N 1.98. found: Cr 14.72, Ni 4.19, C 43.78, H 6.64, N 1.91.