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Synthetic Procedures

All procedures were performed under a nitrogen atmosphere. Acetonitrile was distilled over CaH_2, and toluene over Na. Acetone absolute and ethyl acetate absolute were from Fluka. All other commercially available reagents and solvents were used without further treatment.
$AlF_3 \cdot 3H_2O$, $GaF_3 \cdot 3H_2O$, $InF_3 \cdot 3H_2O$, $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$, $CoCl_2 \cdot 4\ H_2O$, $Co(O_2CCH_3)_2 \cdot 4H_2O$, $In(O_2CCH_3)_3$, di-propylamine and pivalic acid were from Aldrich; $[Co_2\ (OH_2)(O_2CMe_3)_4(HO_2CMe_3)_4]$ was obtained by the method given in:
G. Aromi, A. S. Batsanov, P. Christian, M. Helliwell, A. Parkin, S. Parsons, A. A. Smith, G. A. Timco, and R. E. P. Winpenny Chem. Eur. J. 2003, **9**, 5142 . 5161.

Compound 2 $[(C_3H_7)_2NH_2][Ga_7NiF_8(O_2CCMe_3)_{16}]$ Variant A.
A mixture of gallium fluoride trihydrate $GaF_3 \cdot 3H_2O$ (2,0 g, 11.1 moles), pivalic acid (20.0 g, 195.8 mmol), dipropylamine (1.0 g, 9.9 mmol) and basic nickel(II) carbonate hydroxide tetrahydrate, $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ (0.31 g, 0.527 mmol) were stirred with heating at 160^{o}C for 55 hours in a slow flow of N_2 allowing the gaseous products from the reaction to leave the flask. On cooling to 80^{o}C, MeCN (50 cm^3) was added and the mixture was vigorously stirred for 15 minutes. This was then cooled to room temperature and after 1h the microcrystalline product was filtered, washed with acetonitrile (3 x 25 cm^3), then with acetone (3 x 5 cm^3) and dried in a flow of N_2 at r.t. The product was then dissolved in pentane (50 ml) and filtered prior to evaporating the solvent to dryness under a N_2 flow. This gave light green crystalline product. Yield: 2.42g, 72%. Elemental analysis calculated for $Ga_7NiC_{86}H_{160}O_{32}NF_8$: Ga, 20.18; Ni, 2.43; C, 42.70; H, 6.67; N, 0.58; F, 6.28. Found: Ga, 20.01; Ni, 2.35; C 43.99; H 6.98; N, 0.51; F, 6.31. Electrospray mass-spectra ES MS (sample dissolved in toluene, run in MeOH) *m/z*: - 2315 $[M - (C_3H_7)_2NH_2]^-$, + 2440 $[M+Na]^+$; + 2316 $[M- (O_2CCMe_3)]^+$

Compound 2 $[(C_3H_7)_2NH_2][Ga_7NiF_8(O_2CCMe_3)_{16}]$ Variant B.
The same procedure as variant A with the exception that heating at 160 ^{o}C was for 10 hours and the product was not washed additionally with acetone. Yield: 3.15 g, 93.7% calculated from $GaF_3 \cdot 3H_2O$. Elemental analysis calculated for $Ga_7NiC_{86}H_{160}O_{32}NF_8$: Ga, 20.18; Ni, 2.43; C, 42.70; H, 6.67; N, 0.58; Found: Ga, 19.76; Ni, 2.43; C 43.32; H 6.97; N, 0.51. Crystals suitable for X- ray studies were obtained by recrystallisation of **2** from ethylacetate, toluene or these solvents diluted with MeCN. *Here we report the full crystal structure of **2** from toluene.*

Crystallization of 2 from ethyl acetate : $[(C_3H_7)_2NH_2][Ga_7NiF_8(O_2CCMe_3)_{16}]$ **(**1.15 g) was dissolved in boiling ethyl acetate (15 ml), then the light green solution was slowly cooled to r.t. and left in a very slow flow of N_2 . Well shaped X-ray quality crystals, were collected after one day, washed with a small amount of acetone and dried in N_2. Yield: 1.0 g, 87%. Elemental analysis calculated for $Ga_7NiC_{86}H_{160}O_{32}NF_8$: Ga, 20.18; Ni, 2.43; C, 42.70; H, 6.67; N, 0.58; F, 6.28; Found: Ga, 19.91; Ni, 2.43; C 42.75; H 6.86; N, 0.55; F, 6.16.

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*Crystals of **2** from ethyl acetate are isostructural with compound **1** crystallised from ethyl acetate.*

Compound 1 $[(C_3H_7)_2NH_2][Ga_7CoF_8(O_2CCMe_3)_{16}]$ was obtained by a procedure identical to variant **2A** using $CoCl_2 \cdot 4H_2O$ instead of $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$. Yield: 63%. Elemental analysis calculated for $Ga_7CoC_{86}H_{160}O_{32}NF_8$: Ga, 20.17; Co, 2.44; C, 42.70; H, 6.67; N, 0.58; F, 6.28. Found: Ga, 20.17; Co, 2.46; C 42.68; H 6.72; N, 0.53; F, 6.70. ES MS (sample dissolved in toluene, run in MeOH) *m/z*: + 2317 $[M- (O_2CCMe_3)]^+$ Crystals suitable for X- ray studies were obtained by recrystallisation of **1** from ethylacetate.

Compound 3 $[(C_3H_7)_2NH_2][In_7NiF_8(O_2CCMe_3)_{16}]$ Variant A.
The same procedure as in variant **2A** using 2.5 g (11.1) mmoles) of indium fluoride trihydrate $InF_3 \cdot 3H_2O$ instead of $GaF_3 \cdot 3H_2O$ heating at 160 ^oC for only 7 hours and. The product was not washed with acetone. Yield: 1.89 g, 43.7 % calculated from $InF_3 \cdot 3H_2O$. Elemental analysis calculated for $In_7NiC_{86}H_{160}O_{32}NF_8$: In, 29.39; Ni, 2.15; C, 37.77; H, 5.90; N, 0.51. Found: In, 29.43; Ni, 2.13; C 38.24; H 5.85; N, 0.40.

Crystallization of 3 from ethyl acetate/ acetonitrile:
$[(C_3H_7)_2NH_2][In_7NiF_8(O_2CCMe_3)_{16}]$ (1.4 g) was dissolved in boiling ethyl acetate (8 ml), then the light green solution was filtered and diluted by slow addition of 2ml of acetonitrile, then slowly cooled to r.t. and left in a very slow flow of N_2. Large, light green well shaped crystals were collected the next day, washed with a small amount of solution of ethyl acetate : acetonitrile (2:1) and dried in a N_2 flow. Yield: 1.0 g, 71.4%. Elemental analysis calculated for $In_7NiC_{86}H_{160}O_{32}NF_8$: In, 29.39; Ni, 2.15; C, 37.77; H, 5.90; N, 0.51; F, 5.56. Found: In, 28.65; Ni, 2.09; C 38.10; H 5.81; N, 0.43; F, 5.53.

Compound 3 $[(C_3H_7)_2NH_2][In_7NiF_8(O_2CCMe_3)_{16}]$ Variant B.
The same procedure as in variant 3**2A** with the exception that 0.2 g (0.34 mmol) of $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ were used and that the heating time at 160 ^oC was 5h. Yield: 2.7 g, 62.4 % calculated from $InF_3 \cdot 3H_2O$. Elemental analysis calculated for $In_7NiC_{86}H_{160}O_{32}NF_8$: In, 29.39; Ni, 2.15; C, 37.77; H, 5.90; N, 0.51. Found: In, 28.98; Ni, 2.11; C 37.97; H 6.04; N, 0.48.

Crystallization of 3 from ethyl acetate/ acetonitrile as above.
Elemental analysis calculated for $In_7NiC_{86}H_{160}O_{32}NF_8$: In, 29.39; Ni, 2.15; C, 37.77; H, 5.90; N, 0.51; F, 5.56. Found: In, 28.93; Ni, 2.06; C 37.97; H 5.93; N, 0.42; F, 5.37.

Compound 3 $[(C_3H_7)_2NH_2][In_7NiF_8(O_2CCMe_3)_{16}]$; Variant C.
The same procedure as in variant **2B** using $InF_3 \cdot 3 H_2O$ instead of $GaF_3 \cdot 3H_2O$. Yield: 0.46g, 10.7 % Elemental analysis calculated for $In_7NiC_{86}H_{160}O_{32}NF_8$: In, 29.39; Ni, 2.15; C, 37.77; H, 5.90; N, 0.51. Found: In, 29.36; Ni, 2.13; C 37.98; H 6.05; N, 0.46.

Compound 4 $[(C_3H_7)_2NH_2][In_7CoF_8(O_2CCMe_3)_{16}]$
The same procedure as in variant **3A** using $[Co_2(OH_2)(O_2CMe_3)_4(HO_2CMe_3)_4]$ 1.27 g (1.34 mmol) instead $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$. Yield: 2.34 g, 54.1 % calculated from

$InF_3 \cdot 3H_2O$. Elemental analysis calculated for $In_7CoC_{86}H_{160}O_{32}NF_8$: In, 29.39; Co, 2.15; C, 37.77; H, 5.90; N, 0.51. Found: In, 28.71; Co, 2.22; C 38.48; H 6.11; N, 0.46.

Crystallization of 4 from ethyl acetate/ acetonitrile was similar to **3**. The obtained light pink crystals have the same cell parameters as **3**. Elemental analysis calculated for $In_7CoC_{86}H_{160}O_{32}NF_8$: In, 29.39; Co, 2.15; C, 37.77; H, 5.90; N, 0.51; F, 5.56 Found: In, 28.50; Co, 2.22; C 37.87; H 5.99; N, 0.47; F, 5.64.

Compound 5 $[(C_3H_7)_2NH_2][Al_7NiF_8(O_2CCMe_3)_{16}]$ Variant A.
The same procedure as in variant **2A** using aluminium fluoride trihydrate, $AlF_3 \cdot 3H_20$ (1.53 g, 11.1 mmol) instead of $GaF_3 \cdot 3H_2O$ and a heating time at 160 ^oC was of 12h. The pentane extract was evaporated to dryness to give a light green product (0.4g) that was dissolved in boiling ethyl acetate (5 ml) and left in N_2 for slow cooling. Light green crystals including suitable for X-ray structural characterization were filtered the next day, and washed with a small amount of acetone and dried in N_2. Yield: 0.34 g, 10.1 % calculated from $AlF_3 \cdot 3H2O$. Elemental analysis calculated for $Al_7NiC_{86}H_{160}O_{32}NF_8$: Al, 8.91; Ni, 2.77; C, 48.73; H, 7.61; N, 0.66; F, 7.17. Found: Al, 8.51; Ni, 2.69; C 48.38; H 7.74; N, 0.62; F, 6.69. ES MS (sample dissolved in toluene, run in MeOH: + 2140 [$M+Na]^+$; + 2219 [$M+ (C_3H_7)_2NH_2]^+$.

Compound 5 $[(C_3H_7)_2NH_2][Al_7NiF_8(O_2CCMe_3)_{16}]$ Variant B.
The same procedure as in variant **5A** with the exception that the heating time at 160 ^oC was 7h and the crystals were not washed with acetone. Yield: 0.28 g, 8.3 % calculated from $AlF_3 \cdot 3H_2O$. Elemental analysis calculated for $Al_7NiC_{86}H_{160}O_{32}NF_8$: Al, 8.91; Ni, 2.77; C, 48.73; H, 7.61; N, 0.66. Found: Al, 9.98; Ni, 2.60; C 48.62; H 7.65; N, 0.50. ES MS (sample dissolved in toluene, run in MeOH: + 2140 [$M+Na]^+$; + 2219 [$M+ (C_3H_7)_2NH_2]^+$.

Compound 5 $[(C_3H_7)_2NH_2][Al_7NiF_8(O_2CCMe_3)_{16}]$ Variant C.
The same procedure as in variant **2B** using $AlF_3 \cdot 3 H_2O$ instead of $GaF_3 \cdot 3H_2O$. The pentane extract was evaporated to dryness giving 0.28 g of light green powder. Yield: 5.1%. Elemental analysis calculated for $Al_7NiC_{86}H_{160}O_{32}NF_8$: Al, 8.91; Ni, 2.77; C, 48.73; H, 7.61; N, 0.66. Found: Al, 8.20; Ni, 3.20; C 48.86; H 8.04; N, 0.95. ES MS (sample dissolved in toluene, run in MeOH) *m/z*: -2015 [$M - (C_3H_7)_2NH_2]^-$, + 2140 [$M+Na]^+$; + 2016 [$M- (O_2CCMe_3)]^+$.

Isolation of 6-9 from aluminium and indium fluoride reactions

From the acetonitrile filtrate of the synthesis of **3** variant **C** a small number of green crystals grew in the fridge at 4° C in 5 days. These crystals were identified by X-Ray crystallography as the new complex **$[In_2NiO(O_2CCMe_3)_7(HO_2CCMe_3)]$ (6).** The crystals were filtered and washed with acetonitrile. The MeCN washings were left at r .t. for one day which gave light green crystals which were identified by X-ray structural characterization as a solid state mixture $[In_2Ni_2(OH)_2(C_5H_9O_2)_8(C_5H_9O_2H)_2] \cdot [In_2Ni_2(OH)_2(C_5H_9O_2)_8(MeCN)_2]$ (**7**·**8**).

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Using $InF_3 \cdot 3\,H_2O$ instead $GaF_3 \cdot 3H_2O$ and the same procedure as for compound **1,** $[In_2Co_2(OH)_2(O_2CCMe_3)_8(MeCN)_2]$ (**9**) was isolated as pink crystals from the acetonitrile filtrate that was kept in the fridge at 4°C for 3 months.

The highly moisture sensitive compound **$[(C_3H_7)_2NH_2]_2[Al_4F_{12}(O_2CCMe_3)_2]$** (**10)** was isolated after evaporation of acetonitrile filtrate of compound **5** (variant C). First the acetonitrile was removed by distillation, and the liquid residuum was diluted with hexane. Initially a cloudy solution was obtained, from which a small amount of white crystals suitable for X-ray crystallography grew in 3 months at r.t.

Syntheses of 6-8 and 10 using indium(III) acetate

Compound 6 $[In_2NiO(O_2CCMe_3)_7(HO_2CCMe_3)]$
A mixture of indium(III) acetate $In(O_2CCH_3)_3$ (2.0 g, 6.9 mmol), pivalic acid (20.0 g 196 mmol) and $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ (0.4g, 0.7 mmol) were refluxed in toluene (25 ml) with stirring for 3h, then toluene was distilled and the resulting mixture was heated at 160°C for 5h in a slow flow of N_2. On cooling to 80°C, acetonitrile (30 cm^3) was added and the solution was slowly cooled to room temperature. The light green crystalline product, including X-ray quality crystals, was filtered next day, washed with a small amount of cold acetonitrile and dried in a flow of N_2 at r.t. Yield: 1.5 g, 39.3% calculated from $In(O_2CCH_3)_3$. Elemental analysis calculated for $In_2NiC_{40}H_{74}O_{17}$: In, 20.59; Ni, 5.26; C, 43.07; H, 6.69; N, 0.00. Found: In, 17.14; Ni, 4.13; C 44.22; H 7.28; N, 0.00.

Compound 7 $[In_2Ni_2(OH)_2(O_2CCMe_3)_8(HO_2CCMe_3)_2]$
A mixture of Indium(III) acetate $In(O_2CCH_3)_3$ (1.0 g, 3.42 mmol), pivalic acid (10.0 g, 98 mmol) and $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ (0.4g, 0.7 mmol) were refluxed in toluene (25 ml) with stirring for 3h , then toluene was distilled and resulting mixture was heated at 160 °C for 5h in a slow flow of N_2. On cooling to 80°C, acetonitrile (10 cm^3) was added and the obtained solution was slowly cooled to room temperature. The light green crystalline product including X-ray quality crystals was collected by filtration next day, washed with a small amount of cold acetonitrile and dried in a flow of N_2 at r.t. Yield: 1.2 g, 42.8% calculated from $In(O_2CCH_3)_3$. Elemental analysis calculated for $In_2Ni_2C_{50}H_{94}O_{12}$: In, 16.47; Ni, 8.42; C, 43.07; H, 6.80; N, 0.00. Found: In, 13.45; Ni, 7.0; C 44.55; H 7.00; N, 0.00.

Compound 8. $[In_2Ni_2(OH)_2(O_2CCMe_3)_8(MeCN)_2]$ variant A.
Compound **7** $[In_2Ni_2(OH)_2(O_2CCMe_3)_8(HO_2CCMe_3)_2]$, 1.0g (0.717 mmol) was stirred for 1h under N_2 in acetonitrile (20 cm^3). Light green microcrystalline product was collected by filtration after one day, washed with acetonitrile and dried in a flow of N_2 at r.t. Yield: 0.72 g 78.9%. Elemental analysis calculated for $In_2Ni_2C_{44}H_{80}N_2O_{18}$: In, 18.05; Ni, 9.23; C, 41.54; H, 6.34; N, 2.20. Found: In, 18.20; Ni, 9.44; C 41.55; H 6.60; N, 2.39.

9. **$[In_2Co_2(OH)_2(O_2CCMe_3)_8(MeCN)_2]$**
A mixture of indium(III) acetate, $In(O_2CCH_3)_3$ (1.0 g, 3.4 mmol), pivalic acid (10.0 g, 98 mmol) and cobalt acetate tetrahydrate, $Co(O_2CCH_3)_2\,4H_2O$ (0.85g, 3.41 mmol) were refluxed in toluene (25 ml) with stirring for 3h, then toluene was distilled and the

resulting mixture was heated at 160 ^{o}C for 5h in a slow flow of N_2. On cooling to 80° C, acetonitrile (10 cm^3) was added and the solution cooled to room temperature. The pink crystalline product was collected by filtration the next day, dissolved in diethyl ether (30 cm^3) then diluted with acetonitrile (15 cm^3) and the solution concentrated by evaporation under a N_2 stream at r.t. to 10 cm^3 volume. The light pink crystals, including crystals suitable for X-ray study were collected by filtration after 3 days, washed with acetonitrile and dried in a flow of N_2 at r.t. Yield: 1.15 g 52.7%. Elemental analysis calculated for $In_2Co_2C_{44}H_{80}N_2O_{18}$: In, 18.04; Co, 9.26; C, 41.53; H, 6.34; N, 2.20. Found: In, 17.88; Co, 8.82; C 41.68; H 6.58; N, 2.16.