Synthetic Procedures

All procedures were performed under a nitrogen atmosphere. Acetonitrile was distilled over CaH₂, 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.

AlF₃·3H₂O, GaF₃·3H₂O, InF₃·3H₂O, 2NiCO₃·3Ni(OH)₂·4H₂O, CoCl₂·4H₂O, Co(O₂CCH₃)₂·4H₂O, In(O₂CCH₃)₃, di-propylamine and pivalic acid were from Aldrich; [Co₂(OH₂)(O₂CMe₃)₄(HO₂CMe₃)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. Timeo, and R. E. P. Winpenny Chem. Eur. J. 2003, 9, 5142 - 5161.

**Compound 2 [(C₃H₇)₂NH₂][Ga₇NiF₈(O₂CCMe₃)₁₆]** Variant A.
A mixture of gallium fluoride trihydrate GaF₃·3H₂O (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, 2NiCO₃·3Ni(OH)₂·4H₂O (0.31 g, 0.527 mmol) were stirred with heating at 160°C for 55 hours in a slow flow of N₂ allowing the gaseous products from the reaction to leave the flask. On cooling to 80°C, MeCN (50 cm³) 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 cm³), then with acetone (3 x 5 cm³) and dried in a flow of N₂ at r.t. The product was then dissolved in pentane (50 ml) and filtered prior to evaporating the solvent to dryness under a N₂ flow. This gave light green crystalline product. Yield: 2.42g, 72%. Elemental analysis calculated for Ga₇NiC₈₆H₁₆O₃₂NF₈: 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–(C₃H₇)₂NH₂]-, + 2440 [M+Na]+; + 2316 [M- (O₂CCMe₃)]+

**Compound 2 [(C₃H₇)₂NH₂][Ga₇NiF₈(O₂CCMe₃)₁₆]** Variant B.
The same procedure as variant A with the exception that heating at 160°C was for 10 hours and the product was not washed additionally with acetone. Yield: 3.15 g, 93.7% calculated from GaF₃·3H₂O. Elemental analysis calculated for Ga₇NiC₈₆H₁₆O₃₂NF₈: 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 :** [(C₃H₇)₂NH₂][Ga₇NiF₈(O₂CCMe₃)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 N₂. Well shaped X-ray quality crystals, were collected after one day, washed with a small amount of acetone and dried in N₂. Yield: 1.0 g, 87%. Elemental analysis calculated for Ga₇NiC₈₆H₁₆O₃₂NF₈: 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.
Crystals of 2 from ethyl acetate are isostructural with compound 1 crystallised from ethyl acetate.

Compound 1 [(C3H7)2NH2][Ga7CoF8(O2CCMe3)16] was obtained by a procedure identical to variant 2A using CoCl2 · 4H2O instead of 2NiCO3 · 3Ni(OH)2 · 4H2O. Yield: 63%. Elemental analysis calculated for Ga7CoC86H160O32NF8: 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- (O2CCMe3)]+

Crystals suitable for X-ray studies were obtained by recrystallisation of 1 from ethylacetate.

Compound 3 [(C3H7)2NH2][In7NiF8(O2CCMe3)16] Variant A.
The same procedure as in variant 2A using 2.5 g (11.1 mmoles) of indium fluoride trihydrate InF3 · 3H2O instead of GaF3 · 3H2O heating at 160 °C for only 7 hours and. The product was not washed with acetone. Yield: 1.89 g, 43.7 % calculated from InF3 · 3H2O. Elemental analysis calculated for In7NiC86H160O32NF8: 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:
[(C3H7)2NH2][In7NiF8(O2CCMe3)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 N2. 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 N2 flow. Yield: 1.0 g, 71.4%.

Compound 3 [(C3H7)2NH2][In7NiF8(O2CCMe3)16] Variant B.
The same procedure as in variant 2B with the exception that 0.2 g (0.34 mmol) of 2NiCO3 · 3Ni(OH)2 · 4H2O were used and that the heating time at 160 °C was 5h. Yield: 2.7 g, 62.4 % calculated from InF3 · 3H2O. Elemental analysis calculated for In7NiC86H160O32NF8: 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 4 [(C3H7)2NH2][In7CoF8(O2CCMe3)16]
The same procedure as in variant 3A using [Co2(OH2)(O2CMe3)4(HO2CMe3)4] · 1.27 g (1.34 mmol) instead 2NiCO3 · 3Ni(OH)2 · 4H2O. Yield: 2.34 g, 54.1 % calculated from
InF$_3$·3H$_2$O. Elemental analysis calculated for In$_7$CoC$_8$H$_{16}$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$_7$CoC$_8$H$_{16}$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$_3$·3H$_2$O (1.53 g, 11.1 mmol) instead of GaF$_3$·3H$_2$O and a heating time at 160 °C 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$_3$·3H$_2$O. Elemental analysis calculated for Al$_7$NiC$_{86}$H$_{16}$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$_3$H$_7$)$_2$NH$_2$]$^+$.

**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 °C was 7h and the crystals were not washed with acetone. Yield: 0.28 g, 8.3 % calculated from AlF$_3$·3H$_2$O. Elemental analysis calculated for Al$_7$NiC$_{86}$H$_{16}$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$_3$H$_7$)$_2$NH$_2$]$^+$.

**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$_3$·3H$_2$O instead of GaF$_3$·3H$_2$O. The pentane extract was evaporated to dryness giving 0.28 g of light green powder. Yield: 5.1%. Elemental analysis calculated for Al$_7$NiC$_{86}$H$_{16}$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$_3$H$_7$)$_2$NH$_2$]$^+$, + 2140 [M+Na]$^+$; + 2016 [M- (O$_2$CCMe$_3$)]$^+$.

**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 $[\text{In}_2\text{NiO(O}_2\text{CCMe}_3)_2(\text{HO}_2\text{CCMe}_3)]$ (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 $[\text{In}_2\text{Ni}_2(\text{OH})_2(C_3\text{H}_7\text{O}_2)_3(C_3\text{H}_6\text{O}_2\text{H})_2]$ $[\text{In}_2\text{Ni}_2(\text{OH})_2(C_3\text{H}_7\text{O}_2)_3(\text{MeCN})_2]$ (7).
Using InF$_3$ 3 H$_2$O instead GaF$_3$ 3H$_2$O and the same procedure as for compound 1, [In$_2$Co$_2$(OH)$_2$(O$_2$CMe$_3$)$_8$(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$_3$H$_7$)$_2$NH]$_2$[Al$_4$F$_{12}$(O$_2$CMe$_3$)$_2$] (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$_2$NiO(O$_2$CMe$_3$)$_7$(HO$_2$CMe$_3$)]

A mixture of indium(III) acetate In(O$_2$CCH$_3$)$_3$ (2.0 g, 6.9 mmol), pivalic acid (20.0 g, 196 mmol) and 2NiCO$_3$·3Ni(OH)$_2$·4H$_2$O (0.4 g, 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$_2$CCH$_3$)$_3$. Elemental analysis calculated for In$_2$NiC$_40$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$_2$Ni$_2$(OH)$_2$(O$_2$CMe$_3$)$_8$(HO$_2$CMe$_3$)$_2$]

A mixture of indium(III) acetate In(O$_2$CCH$_3$)$_3$ (1.0 g, 3.42 mmol), pivalic acid (10.0 g, 98 mmol) and 2NiCO$_3$·3Ni(OH)$_2$·4H$_2$O (0.4 g, 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$_2$CCH$_3$)$_3$. Elemental analysis calculated for In$_2$NiC$_{50}$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 44.45; H 7.10; N, 0.00.

**Compound 8** [In$_2$Ni$_2$(OH)$_2$(O$_2$CMe$_3$)$_8$(MeCN)$_2$] variant A.

Compound 7 [In$_2$Ni$_2$(OH)$_2$(O$_2$CMe$_3$)$_8$(HO$_2$CMe$_3$)$_2$] variant A. Compound 7 [In$_2$Ni$_2$(OH)$_2$(O$_2$CMe$_3$)$_8$(HO$_2$CMe$_3$)$_2$], 1.0 g (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$_2$NiC$_{44}$H$_{80}$N$_2$O$_{18}$: 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$_2$Co$_2$(OH)$_2$(O$_2$CMe$_3$)$_8$(MeCN)$_2$]

A mixture of indium(III) acetate, In(O$_2$CCH$_3$)$_3$ (1.0 g, 3.4 mmol), pivalic acid (10.0 g, 98 mmol) and cobalt acetate tetrahydrate, Co(O$_2$CCH$_3$)$_2$·4H$_2$O (0.85 g, 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 °C for 5h in a slow flow of N₂. On cooling to 80° C, acetonitrile (10 cm³) 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 cm³) then diluted with acetonitrile (15 cm³) and the solution concentrated by evaporation under a N₂ stream at r.t. to 10 cm³ 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 N₂ at r.t. Yield: 1.15 g 52.7%. Elemental analysis calculated for In₂Co₂C₄₄H₃₈N₂O₁₈: 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.